HERBICIDE BEHAVIOUR IN A BOREAL FOREST PODZOL

CENTRE FOR NEWFOUNDLAND STUDIES

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SHELDON HELBERT

HERBICIDE BEHAVIOUR IN A BOREAL FOREST PODZOL

BY

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A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of Master of Science

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Abstract

Herbicide Behaviour In A Boreal Forest Podzol

Keywords: *Herbicide, Distribution, Persistence, Leaching, Forest, Podzol, Soil, 2,4-D, Dicamba, Hexazinone, Tebuthiuron, Picloram.*

There is inadequate information concerning herbicide persistence in soils of the boreal forest. A field study of herbicide behaviour in an Orthic Humo-Ferric Podzol began in the spring of 1983 in northeast central Newfoundland on a south-facing slope near Gambo Pond. 2,4-D, dicamba, hexazinone, tebuthiuron and picloram were applied on 5 test plots within a clear-cut site. Under stringent controls the LF, Ae, Bf, BC and C soil horizons were sampled up to 486 days after application. Residue analyses of samples from the soil horizons show the distribution of herbicides through the profile over time, and indicate each herbicide's propensity to leach and persist. Results show that all herbicides leach to all depths sampled indicating that there is the potential for contamination of lower levels including groundwater. The amounts detected in the lowermost horizon range from 0.9 mg a.i. per m^2 for picloram to 74.5 mg a.i. per m^2 for hexazinone (mg active ingredient values are adjusted for recovery, soil moisture, bulk density and horizon thickness). Initial application rates varied between herbicides and are reflected in the residue concentrations detected. With the exception of tebuthiuron, 90 % of the herbicides disappeared from the soil 5 months after application. With the exception of picloram the herbicides persisted within the range of time intervals suggested by other authorities. Each ecosystem has particular sensitivities which must be buffered by environmental parameters (*e.g.*, bulk density, clay and organic matter content, soil moisture and ambient temperature) limiting the movement and distribution of herbicides in the soil. Thus, herbicide use must be carefully managed to safeguard the natural environment.

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Chapter 1
OBJECTIVES AND INTRODUCTION

1.1. Introduction

At a time when the use of herbicides in the natural environment is of growing importance in silviculture, agriculture and maintenance of rights-of- ways, scientists and the general public are becoming increasingly concerned with their effects on environmental quality. Two major problems concern the potential for groundwater contamination and the persistence of toxic chemicals in the soil. This study is concerned with two aspects of herbicide behaviour in a boreal forest podzol which primarily relate to the second problem. The first is the mean distribution of residues down through the soil profile to the lower limit of sampling and the second is their measured quantities as distributed over time. These aspects respectively address the degree of leaching which occurs during sample intervals and the quantities of herbicides which remain unaltered and biologically active in the soil.

The study area is near Gambo Pond, Newfoundland. Five herbicides (2,4-D, dicamba, hexazinone, tebuthiuron and picloram)[1] were applied to five field plots of 11 m x 20 m and sampled at intervals up to 16 months later to a maximum depth of 1 m (see appendix A, page 116, for schematic diagrams of the 5 sample plots). Thus, leaching below the upper part of the C horizon, loss through volatilization and photodegradation at the soil surface and plant intake are not accounted for. A further constraint placed on the study is the inability of the analytical techniques to extract and detect a percentage of the residues bound to soil organometallic complexes (Khan, 1982). Notwithstanding these constraints the experiment was designed in conditions broadly typical of much of Canada's boreal forest environment. The results should aid industry and government in regulating the uses of these herbicides to minimize toxic accumulation of residues in the soil. This is of special concern where reapplications for silviculture may be necessary, and to reduce the potential of groundwater contamination.

---

[1] The chemicals 2,4-D and picloram are products of Dow Chemical and are marketed under the trade names of "Esteron 600" and "Tordon 101", respectively. The dicamba is marketed under the trade name of "DyCleer 24" by Velsicol Chemicals. The hexazinone is sold by DuPont of Canada under the name of "VelparL" and Elanco produces the tebuthiuron under the name of "Spike 80W".

In modern forestry practices herbicide use is a tool that forest management considers essential to remain competitive in the marketplace. Yet there is concern that the use of herbicides may result in long-term deterioration of the forest environment. This is an issue of overwhelming importance for Canada and therefore will receive some attention in Chapter 5, Section 5.3, page 100, regarding the relationship between herbicide use and forest management.

1.2. Objectives

1. To determine the distribution and persistence of herbicides in the profile of a boreal forest podzol; that is, to ascertain in quantitative terms, the mean concentration of 2,4-D "(2,4-dichlorophenoxy) acetic acid", dicamba "3,6-dichloro-*o*-anisic acid", hexazinone "3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4 (1H,3H)-dione", tebuthiuron "N-[5-(1, 1-dimethylethyl)-1, 3, 4-thiadizol-2-yl]N, N,-dimethylurea" and picloram "4-amino-3,5,6-trichloropicolinic acid" herbicides in space (soil horizon) and time (herbicide persistence).
2. To characterize the soil (its physical and chemical properties) and selected climatic variables with the aim of understanding the herbicides' persistence and location in the soil profile through time.

The first objective is accomplished by spraying, sampling, and analyzing contaminated soil samples for residues of the parent compound. The analyses were done by private and commercial chemical laboratories. In general the analysis of the soils for herbicide residues requires an extraction and cleanup process which yields a sample that can be run through a gas liquid chromatograph, a high pressure liquid chromatograph or a similar chromatographic device. At the appropriate time a sample is siphoned from the column which is then placed in a mass spectrometer for specification. The mass spectrometer provides a graph of the compounds in the sample within a specified frequency range. A knowledge of which peak(s) on the graph represent the compound(s) in question is determined by calibration: A clinically pure sample is provided by the manufacturer with which a mass spectrometer analysis will identify the compound's peak(s), without the noise caused by other compounds in the the test sample, and thus is used as a standard for identification. Once the compound's peak(s) is identified the area under the curve on the graph is calculated giving a semi-quantitative result.

The second objective is to describe the distribution and persistence of the selected herbicides with respect to soil properties (organic matter content, particle size, bulk density, field moisture content, horizon thickness and, soil temperature) and selected climatic variables (precipitation, air temperature and potential evapotranspiration). The information comes from a variety of sources and though it does not permit an exhaustive statistical analysis it lends itself to general interpretation. As herbicides are organic compounds they are expected to behave in a somewhat similar fashion to those organic compounds naturally found in the soil. Therefore, an understanding of those patterns and processes (*eg.* insolation, moisture regime, temperature

regime, evapotranspiration, mass flow, diffusion, leaching and microbial degradation) operating in and on the soil will allow for an interpretation of the herbicides' distribution and persistence in the soil profile through time. Statistical analysis is limited to a descriptive regression equation of the persistence curves where the herbicide residue data are time dependent. Thus, to accomplish the second objective, pertinent literature on the subject, the residue analysis data, the physical and chemical soil data generated from analysis and collected from other sources, and the meteorological records observed on site are required. These sources collectively encourage a synthesis of the whole describing the pattern and process of herbicide distribution and persistence in a boreal forest podzol.

1.3. Herbicide Classification

For this experiment the following table 1-1, page 4, presents the common name, chemical name, commercial product formulation name, molecular formula and molecular weight for the five selected herbicides. Classification of these herbicides by primary mode of action puts them into two groups: 1) Growth regulators for 2,4-D, dicamba and picloram; 2) Photosynthetic inhibitors for hexazinone and tebuthiuron (Warren, 1976, pp.1-4). According to Warren (*ibid.*) some characteristics of these two groups of herbicides follow:

Growth Regulators

1. All affect plant growth in a similar way and appear to act at the same site as the natural plant auxin or indole-acetic acid. However, all are much more active than the natural auxin.
2. Their effect on the plant is systemic rather than contact, thus they are effective when only part of the plant is treated.
3. As a result of systemic effect, low pressure and low volume sprays can be used.
4. The dose response curve may be quite flat. That is, effects on plant growth may be seen at doses far below the lethal dose. This creates a potential problem with spray drift to non target species.
5. They are quite mobile in soil.
6. With the exception of dicamba and picloram, they do not persist long in the soil.
7. They all have low mammalian toxicity.

Photosynthetic Inhibitors

1. Photosynthesis is stopped rapidly in susceptible plants. In resistant plants the effect on photosynthesis is much less and is temporary.
2. All can be absorbed by the roots and most are absorbed by leaves, but leaf absorption varies greatly between compounds.
3. In general, these compounds are moderately to highly resistant to movement in the soil, but this varies with the compound, soil, and rainfall.
4. Persistence in the soil varies from a few weeks to more than 2 years, depending upon the herbicide, amount applied, climate and soil.
5. All have very low mammalian toxicity.

(source: *ibid.*)

Table 1-1: Herbicide names, molecular formula and molecular weight

Common name	Chemical name	Product name	Molecular formula	Molecular weight
2,4-D	Butoxyethanol ester of (2,4-dichlorophenoxy) acetic acid	Esteron 600	$C_{14}H_{18}Cl_2O_4$	321.2
Dicamba	3,6-dichloro-*o*-anisic acid	DyCleer 24	$C_8H_6Cl_2O_3$	221.0
Hexazinone	3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine 2,4 (1H,3H)-dione	VelparL	$C_{12}H_{20}N_4O_2$	252.3
Tebuthiuron	N-[5-(1, 1-dimethylethyl) -1, 3, 4-thiadizol-2-yl] N, N,-dimethylurea	Spike 80W	$C_9H_{16}N_4OS$	228.3
Picloram	4-amino-3,5,6-trichloropicolinic acid	Tordon 101	$C_6H_3Cl_3N_2O_2$	241.5

1.4. Location

A site near Gambo, Newfoundland, located in the area covered by the Glovertown map sheet (cartographic series: 2D/9, RF=1:50,000), grid reference 008997, was chosen for the experiment primarily because this area is representative of the boreal forest environment (see Figure 1-1). In addition, this research is facilitated because of soil surveys already conducted in the Gambo area (Wells and Heringa, 1972; Hender, in preparation). The choice of location is augmented by the reasons given in the site selection subsection 3.1, page 38. The following map and inset show the location of the site in two different scales (see map figure 1-2, page 6).

1.5. Geology

The soils in the area are derived from tills which are predominantly composed of Devonian granites and include some Ordovician shales, slates and graywackes (Jenness, 1963, p.28). The granitic rocks are generally pink to red, coarse-grained biotite granites, with large euhedral phenocrysts or porphyroblasts of potash feldspar (*ibid.*). According to Jenness (1960; 1963), Lundqvist (1965, cited in Tucker and McCann, 1980, p.1477) and, Tucker and McCann (1980) the site was glaciated during the Late Wisconsin. The experimental site occurs in the area which Jenness termed the "inner drift zone". This zone is characterized by glacio-fluvial deposits which formed behind the end moraine constituting the boundary between the inner and outer drift zones (Figure 1). Jenness estimated that 7000 to 8000 years have passed since deglaciation in the area, leaving a short time period for soil development.

Figure 1-1: Photograph showing the boreal forest in the top of the picture with Gambo Pond in the background. In the foreground of this south-facing view is the meteorological station showing the continuous recording rain gauge, Stevenson Screen and two white, cumulative, cylindrical rain gauges diagonally opposite of each other. The station is just below the top of the ridge. Behind the meteorological station is the picloram plot where, in the lower end, the field assistant is clearing away slash.

1.6. Relief and Drainage

The area consists of rolling hills with steep slopes and the relief is generally less than 100 m. The flat hill tops, low relief, high precipitation and variable spread of glacial sediments have resulted in much ponding and a deranged drainage pattern. The extensive areas of poor drainage on slopes and hill tops support spruce and peat bogs. The field site is well drained and occupies the upper portion of a south-facing slope with an overall grade of 23 %. Groundwater and runoff in the experimental area flows south for approximately 500 m before entering Gambo Pond, which drains into Freshwater Bay and the North Atlantic Ocean.

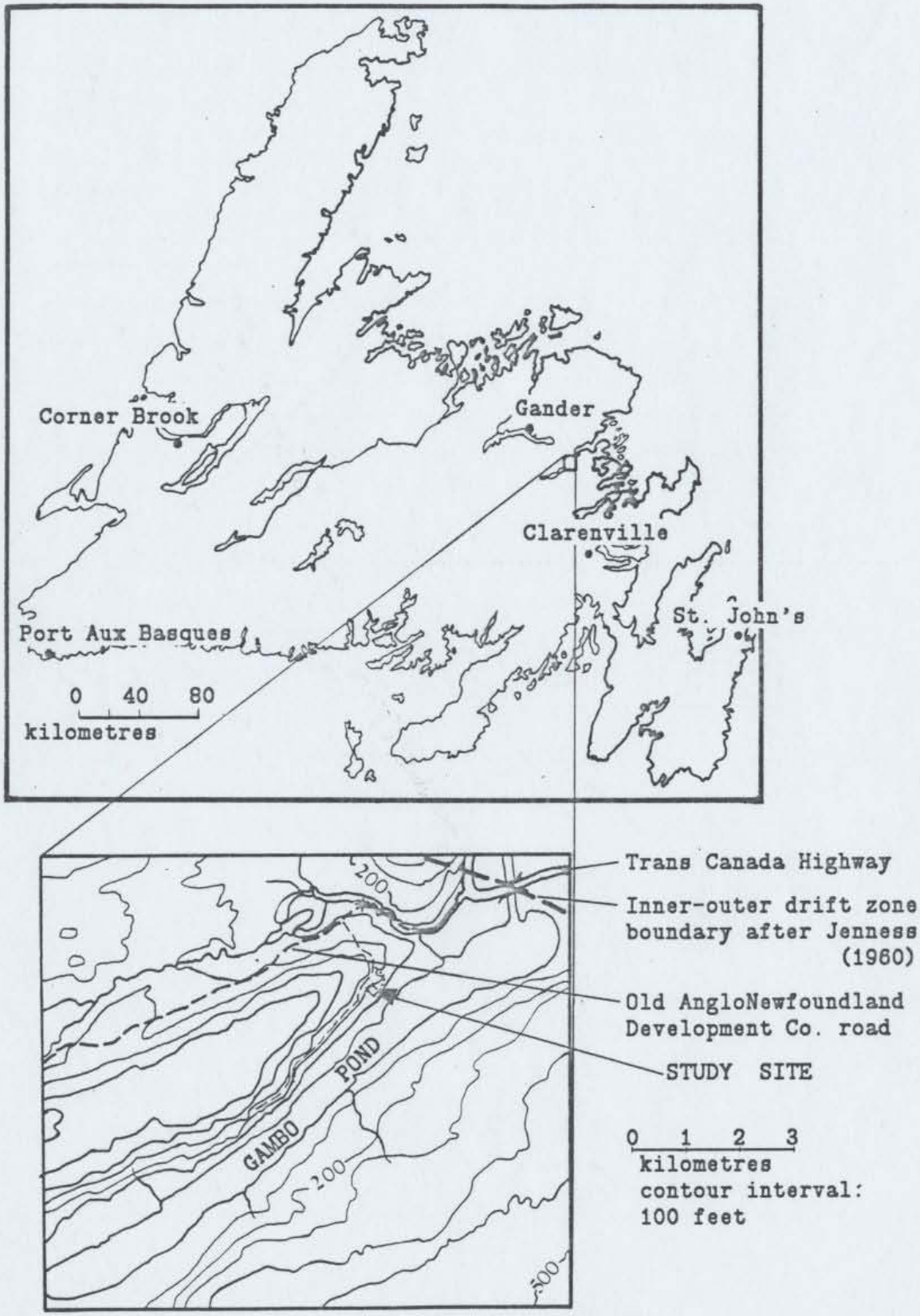

Figure 1-2: Location of Newfoundland herbicide study, 1983 - 1984

1.7. Climate

The region exhibits a continental type climate moderately to strongly influenced by marine conditions. This is termed a "modified continental" climate (Banfield, 1981, p.127). Banfield's climatic zones of Newfoundland describe the area as:

> "3. East coast and hinterlands. ...(1100 - 1500 mm of precipitation per year). Occasional heavy precipitation with north-easterly or northerly airflow, especially in Gander area. Winters cold with 50 - 70 % precipitation falling as snow; snow cover normally continuous at least throughout February (longer to the northwest). Cool, late springs with sea ice persisting until mid-May. Summers generally warm and fairly sunny." (*ibid.*, p.129)

The area's frost-free season has a mean duration of 120 - 140 days (Banfield, 1983, p.69) and the number of degree-days above 5 ° C annually averages approximately 120 degree-days (*ibid.*, p.73). The growing season, defined as the frost-free period, generally extends from the beginning of June to the beginning of October. There is a 50 % chance that the mean annual potential evapotranspiration is 350 - 400 mm (*ibid.*, p.96); however, most of this occurs during the short growing season when there is an equal chance that 75 to 100 % of this moisture is lost through evapotranspiration (*ibid.*, p.97). The closest class A evaporation pan is located 34 km away at Gander International Airport (elevation, 151 m) where for the months of June, July, August and September, 1983, Environment Canada recorded the following values (mm), respectively: 148.9#, 147.2#, 113.2 and 78.2#[2]. These pan values are significantly higher than the evaporation values for a lake[3] surface which are calculated from the daily net pan loss values and a mathematical model designed for lakes. The calculated lake values for the same period are as follows: 113.8e, Missing, 85.3 and 56.5e[4]. A comparison of these values with the 5 year means (1980 - 1984, inclusive) for the same months show: for June both pan and lake values are greater than one standard deviation from the mean; for July and August both pan and lake values are within one standard deviation of the mean (except for July lake record which is missing); finally, for September both pan and lake values are less than one standard deviation from the mean. The following table, 1-2, (page, 8) lists class "A" pan evaporation, calculated lake evaporation and statistics for 1980 through to 1984.

---

[2] source: Atmospheric Environment Service, Monthly Record, Meteorological Observations in Eastern Canada. # = data missing for one or more days.

[3] This hypothetical lake is defined as a small natural open water body with negligible heat storage (personnal communication: Mr. Miller, Atmospheric Environment Service, Environment Canada, Pleasantville, St. John's, Newfoundland).

[4] e = estimated value.

Table 1-2: Evaporation (*mm*) From A Pan Surface, Gander, Newfoundland, 1980 - 1984

	June		July		August		September	
Year	Pan	Lake	Pan	Lake	Pan	Lake	Pan	Lake
1980	138.8E	96.8E	118.8	79.7	104.4	73.1	101.6	71.1
1981	121.6	85.2	176.5	123.8	127.3	89.1	102.8	72.0
1982	119.8	82.6	133.7	93.8	140.8	98.6	92.6θ	64.8E
1983	148.9	113.8E	147.2θ	Missing	113.2	85.3	78.2θ	56.5E
1984	89.1	70.5	173.4	128.6	135.8	99.1	82.0θ	60.0E
Total:	627.2	457.9	744.6	425.5	621.5	445.2	457.2	324.4
Mean:	125.4	91.6	148.9	106.3	124.3	89.0	91.4	64.9
Stand. Dev.:	19.24	14.04	26.59	23.56	15.27	10.73	11.16	6.77

E = estimated value.
θ = data for one or more days missing.
Pan = recorded class "A".
Lake = calculated from pan values and a mathematical model where lake is defined by Atmospheric Environment Service as a small natural water body with negligible heat storage.

1.7.1. Water Balance

At the experimental site, 20 to 27 % of the above mentioned annual precipitation of 1100 to 1500 mm was recorded between June 24 and October 27, 1983 (126 days). If 50 to 70 % of the precipitation falls as snow, then the approximate accumulation of 300 mm of rain for the 126 day period represents the 29 to 55 % range of annual rainfall. Because much of the rainfall occurs in the spring and fall, coinciding with the change in seasons, the actual amount of precipitation that fell is likely to be closer to 29 %. A cumulative rainfall graph for the above period show variations in accumulated rainfall from a number of sites in the region (see Figure 1-3, page 10). The graph depicts recorded values (mm) for: one automatic continuous recording gauge on site for 50 days; the mean of two manual cylindrical white plastic gauges on site in proximity to the continuous gauge; one similar cylindrical gauge at the Gambo Forestry Station, approximately 10 km from the site along Freshwater Bay; and two primary stations at the Terra Nova National Park headquarters and at Gander International Airport, both approximately equidistant from the site at about 40 km.

The soil water deficit during the growing season is estimated as 100 - 150 mm at the 50 % occurrence level, and 150 - 200 mm at the 10 % occurrence level (Banfield, 1983, p.98). Using Thornthwaite's method for calculating the water balance (Thornthwaite and Mather, 1957), for both 150 and 200 mm soil moisture storage capacities, there are respectively 17 and 38 mm soil

moisture deficit-days out of 76 possible days[5] for the period of July 17 through to September 30, 1983. For the same period there are fifteen 1 mm moisture deficit-days and one 2 mm moisture deficit-day for the 150 mm storage capacity and, twenty-six 1 mm moisture deficit-days and six 2 mm moisture-deficit days for the 200 mm storage capacity. Thus, there are a few days each summer when the soil moisture deficit approaches a critical point subjecting the plants to physiological stress and minimizing herbicide movement in the liquid phase. This point has important implications concerning herbicide application and effectiveness which is discussed later in Chapter 5, page 100.

1.8. Vegetation

The area is the most distinctly boreal part of the island (Damman, 1983, p.173). Damman (*ibid.*, p.199) compares his "Central Newfoundland Ecoregion" to the "Middle-Boreal Zone" of Ahti *et al.*, (1968); the "Main-Boreal Zone" of Sjors, (1963); the "Boreal Zone" of Ducruc *et al.*, (1976); and to the "Predominantly Forest Zone" of Rowe's "Boreal Forest Region", (1972).

The vegetation found in the area is associated with black spruce stands (*Picea mariana*) which dominate much of the area because of the high frequency of fires (Damman, 1983, p.174). There is pedogenic evidence of at least one fire as many soil profiles exhibit a very thin charcoal layer (see Figure 1-4). More recently people have influenced the floral community by clear-cutting the forest in 1981. The majority of plants which presently occupy the site and the surrounding south-facing slope are black spruce (*P. mariana*), balsam fir (*Abies balsamea*), white birch (*Betula papyrifera*) and trembling aspen (*Populus tremuloides*). Some of the shrub species found in the area are red maple (*Acer rubrum*), american mountain ash (*Sorbus americana*), choke cherry (*Prunus virginiana*), a willow (*Salix sp.*), partridge berry (*Vaccinium vitis-idaea*), blueberry (*V. angustifolium*) and highbush cranberry (*Viburnum trilobum*). Sheep laurel (*Kalmia angustifolia*) dominates the ground cover of the experimental site as well as many local sites which have also been disturbed by recent forest harvesting operations. In addition, there are three different lichens, four mosses (*Musci*), one liverwort (*Hepaticae*), one fern (*Pterophyta*), bunchberry (*Cornus canadiensis*), corn lily (*Clintonia borealis*), creeping snowberry (*Gaultheria hispidula*) and star flower (*Trientalis borealis*).

[5] where: soil moisture deficit-days = the sum of all daily soil moisture deficit values $\geq$ 1 mm per day for a specified number of days in months.

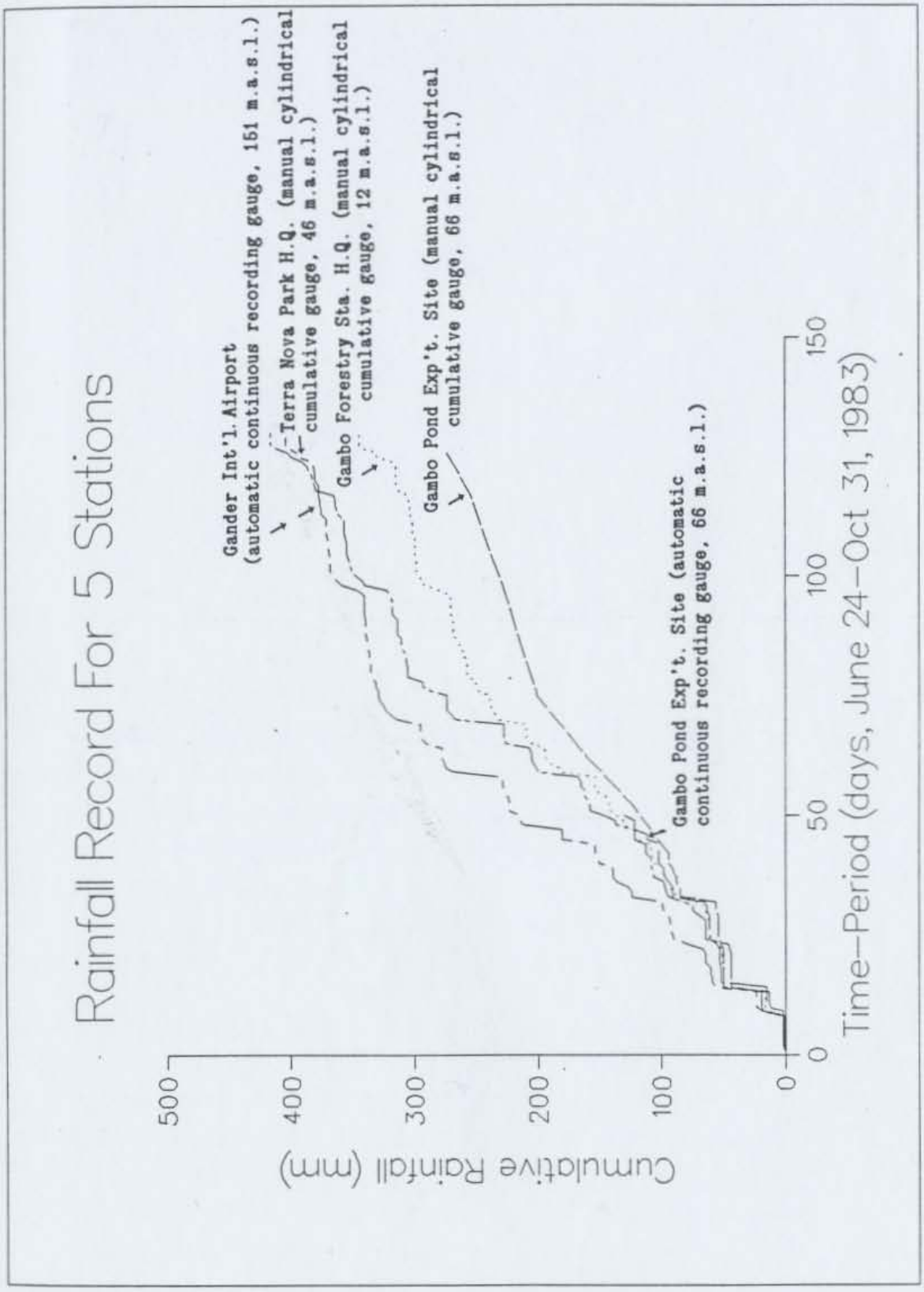

Figure 1-3: Cumulative rainfall graph, June 24 - October 27, 1983

Figure 1-4: Photograph of the thin black charcoal layer (2 - 5 mm thick) between the LF and the Ae horizons, taken from the dicamba plot, pit 1, October, 1983.

1.9. Soil

The podzolic order is the soil subject of this study because it is a dominant order in the boreal ecosystem; 128,008 hectares of podzols are 61.57 % of the soil survey of the Gander-Gambo area, (Wells and Heringa, 1972, pp.17-18). Podzols occur with more than 50 % frequency province-wide (Roberts, 1983, p.121), and constitute 15.6 % of soils and rockland in Canada (Foth and Schafer, 1980, p.265).

1.9.1. Classification

Podzols have **B** horizons in which amorphous humic substances and mobile Fe and Al accumulate in various amounts (Canadian Soil Survey Committee, 1978, p.93). Podzols typically occur in coarse to medium textured, acid parent materials, under forest or heath vegetation in cool to very cool humid to perhumid climates (*ibid.*). Under the Canadian System of Soil Classification the soil being studied is defined as an **Orthic Humo-Ferric Podzol**, Gambo series (*ibid.*, p.98; Wells and Heringa, 1972). Its nearest U.S. and F.A.O. equivalents can be made from the great group *Humo-Ferric Podzol* and they are *Cryorthod* or *Haplorthod* and *Orthic Podzol*, respectively (Canadian Soil Survey Committee, 1978, p.133). The soil is well drained, of sandy loam texture, low base status, granular in structure, and with a pH range of 3.2 - 5.5 ($CaCl_2$).

The common horizon sequence of an Orthic Humo-Ferric Podzol is: LFH, Ae, Bf, BC and C. These soils are identified by the following properties:

1. They have a podzolic B horizon at least 10 cm thick (Bf or thin Bhf and Bf).
2. They do not have a Bh, Bhf or an Ah horizon more than 10 cm thick, an ortstein horizon more than 3 cm thick, a placic horizon, a duric horizon, a fragipan, a Bt horizon, nor evidence of gleying in the form of distinct or prominent mottles within one metre of the surface.(Canadian Soil Survey Committee, 1978, p.101)

Usually Orthic Humo-Ferric Podzols have L,F, and H or O horizons and an Ae horizon. Parts of the Bf may be cemented; but they do not meet the requirements of an ortstein horizon (*ibid.*).

On site soil samples from an 8 m long x 1 m wide x 2 m deep control section, analyzed by Agriculture Canada, corroborate previous evidence which describes the soil as an Orthic Humo-Ferric Podzol. The following excerpts are from a Soil Survey Report which is being prepared for publication (Hender, 1985, in preparation)[6].

Gambo Soils

> The Gambo Soils have been classified as Orthic Humo-Ferric Podzols, Gleyed Humo-Ferric Podzols and Orthic Gleysols. The parent material is glacial till composed of roughly equal parts of granite and of metamorphosed fine-grained sedimentary rocks. ... They are moderately well to poorly drained, exceedingly stony sandy loam soils. They usually occur on undulating topography. Silt cappings common on the stones in the C and BC horizons are probably caused by the downward movement of silt from the overlying B horizons.
>
> The Orthic Humo-Ferric Podzol soils usually occur on the top of well-drained slopes. ...

Figures 1-5 and 1-6 show two typical Orthic Humo-Ferric Podzol profiles.

Specific measurements of soil characteristics were made on site: permeability, bulk density, field moisture content and horizon thickness were those which were primarily thought to be significant with respect to herbicide movement.

1.9.2. Permeability

Hender (in preparation) states that Orthic Humo-Ferric Podzols occur on the top of well-drained slopes. It follows then, that as the site is on an upper slope and the soil is an Orthic Humo-Ferric Podzol, it is well-drained. To complement this, field permeability tests show that at the average flow rate of 0.04 l/min/cm^2, for the forest floor, the soil is well-drained. The permeability rate decreases to approximately 0.02 l/min/cm^2 on the compacted surface of skid tracks. The results of the permeability tests are tabled in appendix C, page 124.

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[6]Courtesy of Frank Hender, Atlantic Soil Survey, Agriculture Canada, Mt. Pearl, Newfoundland.

Figure 1-5: Photograph of an Orthic Humo-Ferric Podzol profile, tebuthiuron plot, pit 3, June, 1984.

1.9.3. Bulk Density

The bulk density of the soil averages 0.23, 1.34, 1.24, 1.41 and 1.50 g/cm^3 for the LF, Ae, Bf, BC and C horizons, respectively. In general, bulk density decreases with an increase in organic matter content. It tends to increase with an increase in gravel content (Ferman, 1967, p.2-3) and it increases with depth if there is a translocation of fine silt and clay particles. These characteristics easily explain the lowest value for the LF layer, the higher value for the Ae horizon which is a gravelly layer and, the increasingly greater values for the Bf, BC and C layers in which fine mineral particles have been translocated (see appendix D, page 126, for the field description of the soil profile). The results of the bulk density tests are tabled in appendix E, page 128.

Figure 1-6: Photograph of an Orthic Humo-Ferric Podzol profile, picloram plot, pit 1, November, 1984.

1.9.4. Field Moisture Content

The field moisture content is usually higher for the absorbent sponge-like organic LF horizon than for the mineral Ae - C horizons. LF moisture values range from 45 % through to 75 % (by weight) with a mode of 52 to 67 % whereas, the figures for the mineral layers range from approximately 8 % through to 32 % moisture with a mode of 11 to 22 % (see Appendix F, 131). Seasonal variations in soil moisture fluctuate with seasonal changes in weather. Soil moisture during the summer is at a low when precipitation is low and moisture demand is at a maximum. Soil moisture increases in the fall during the soil moisture recharge period and carries through the winter over into the spring when precipitation is high and the moisture demand is at a minimum. The mean values for all horizons clearly present this pattern for the following dates in 1984: May 28^{th}, 26 %; August 4^{th}, 22 %; November 17^{th} and 18^{th}, 27 %. The results of the field moisture determinations are tabled in Appendix F, 131.

1.9.5. Horizon Thickness

Soil sampling for residues was on an horizon basis, thus it is important to know how the horizon thicknesses vary from one another. The organic LF layer averages 12.2 cm thick, the Ae layer is the thinnest averaging 6.9 cm, the Bf layer is the thickest averaging 25.3 cm, the BC averages 14.7 cm and the upper limit of the C averages 9.8 cm. The mean horizon thicknesses, sample size and range are presented in Tables 4-6 through 4-9, pages 81-87 and supplementary statistics can be found in Appendix G, 133.

1.10. Principles

For the purpose of discussion, the dispersion of herbicides through the soil and their chemical and biological breakdown constitute their dissipation. Leaching and volatilization as dissipation mechanisms inherently involve movement which is discussed with emphasis on the leaching aspect in the Subsection 1.10.2. Following that, Subsection 1.10.3, deals with persistence, the balance of those herbicides which have not dissipated.

1.10.1. Dissipation

The three modes of herbicide dissipation in soils are leaching, degradation and volatilization. The factors governing these processes are: i) Chemical characteristics of the compound, ii) soil organic content, iii) clay content, iv) soil reaction (pH), v) soil temperature, vi) soil water content, vii) bulk density, viii) air temperature, ix) precipitation, x) insolation, xi) evapotranspiration, xii) soil and plant bioactivity, xiii) slope and microtopography, and xiv) land use. This list has been compiled from sources wherein some authorities only enumerate some of the factors and others categorize selected factors into defined groups (Association of Official Analytical Chemists, 1981; Goring and Hamaker, 1972; Guenzi, 1974; Hance, 1980; Khan, 1980; Morrill *et al.*, 1982; Truelove, 1977). Furthermore, these factors also influence the adsorption-desorption process (Calvet, 1980; Grover, 1975; Grover and Smith, 1974; Haque *et al.*, 1968; Khan, 1973a; McCall *et al.*, 1972; Nearpass, 1976; Terce and Calvet, 1978). The adsorption of herbicide molecules with mineral and organic soil particles does, at times, bind them such that the residues cannot be extracted by methods commonly used in residue analysis (Khan, 1982). Hence, the analytical methods which do not detect these types of residues, termed *bound residues*, underestimate the soil or plant burden of total pesticide residues (*ibid.*, p.2). Desorption releases herbicide molecules for transport in the liquid and vapour phases (leaching and volatilization respectively), for physical, chemical and microbiological breakdown (degradation) and finally, for plant uptake.

1.10.2. Movement

Herbicide movement in the soil involves both the gaseous and liquid phases. In the gaseous phase volatilization of the compound permits movement through soil pores and micropores. Theoretically, the compounds may condense and volatilize a number of times with a finite limitation imposed by the herbicide's eventual degradation. Regardless, the volatility of a compound depends on its vapour pressure, ambient temperature and soil porosity. In addition, the random motion of the chemical's molecules, diffusion, will aid in its movement. Diffusion is also operative in the liquid phase, though its importance as a transport mechanism is significantly less than that of mass flow. In the liquid phase herbicides can be transported in solution or as a colloid moving through the soil. Solute transport depends on the chemical's solubility at a specific temperature, the amount of chemical available for solution (*i.e.*, not bound to an adsorbent) and the antecedent saturation condition of the solute. Colloid transport requires a liquid medium and is further dependent on the quantity of available adsorption sites, the degree to which these adsorbents are mobile, and the strength of the bond between the adsorbate and the adsorbent. Of the initial herbicide application which enters the soil, the amount which is not quickly adsorbed (*i.e.*, the full utilization of all available adsorption sites or the adsorption site pool) is free or available (*i.e.*, the balance of herbicide after all adsorption sites are occupied) for degradation, leaching and volatilization. Once this free quantity of herbicide has moved through the soil and/or degraded, any further release of herbicide quantities is then dependent on their desorption from the adsorbing surfaces. Thus, there is an initial loss of free or available herbicide and then a slower loss determined by the desorbing surface.

1.10.3. Persistence

For the purpose of this study, persistence is the residence time of a pesticide in the soil environment (Khan, 1980, P.164). One unit of measure expressing a chemical's persistence which is widely used is that of *half-life*. In the strict physical sense the term *half-life* relates to first order kinetics, (*i.e.*, it is a rate constant). This use of the word represents the property that a constant percentage is lost per unit time and that the half-life is independant of the concentration (Goring and Hamaker, 1972, p.276). However, in this study where herbicide persistence is not in concordance with rate laws the terms, DT_{50} or DT_{90} (50 % or 90 % disappearance time), are more appropriate (*ibid.*, p.277). In this sense half-life loosely means the time required for one half of the pesticide to disappear (DT_{50}). These DT indices are useful to give an approximation of persistence at a given concentration, but as they depend on the initial concentration they are only relative points of measure on the disappearance curve (Khan, 1980, p.165). The persistence and other chemical characteristics of the selected herbicides are listed in Table 1.3 (page 17).

Table 1-3: Characteristics Of Selected Herbicides

Manufacturer	Names: trade & common	Chemical group	Active ingredients(%) and chemical formulations	Half-life
Dow	Tordon 101, Picloram and 2,4-D	Pyridine acid and Chloro-phenoxy	6% 4-amino-3,5,6-Trichloropicolinic acid and 24% 2,4-Dichlorophenoxy acetic acid, both present as Triiso-propanolamine salts.	> 12 mths[1] > 17 mths[2]
	Esteron 600, 2,4-D	Chloro-phenoxy	60% 2,4-Dichlorophenoxy acetic acid, present as a butoxyethyl ester (a low volatile form).	≤ 1 mth[3] 17 days[4] 28 days[5]
Dupont	Velpar L, Hexazinone	Symmetrical Triazine, (6-membered heterocyclic ring)	25% 3-Cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione, present as a water dispersible liquid.	3-15 mths[7]
Velsicol	DyCleer 24, Dicamba and 2,4-D	Dihalo-benzoic & Chloro-phenoxy	20% 3,6-Dichloro-O-anisic acid & 40% 2,4-D, both present as Dimethylamine salts.	3-12 mths[6] > 2 mths[2] 32±39 days[4] 30 & 27 days[5]
Elanco	Spike 80W, Tebuthiuron	Substituted Urea	80% N-(5-(1,1-dimethyl ethyl)-1,3,4-thiadiazol -2-yl)-N,N-dimethylurea, present as a wettable powder.	> 12 mths[1] ≥ 12-15 mths[8]

1: persistence of herbicide activity in temperate zone soils at the usual application rates for total vegetation control (Klingman & Ashton, 1975, p.76).
2: persistence of herbicides in soils: time taken for a compound applied to soil at the normal dosage to decrease by more than 75 % (Kearney *et al.*, 1969, pp.137-139).
3: same as 1 above but for temporary effects.
4: average 50 % disappearance time (Hamaker, 1972, p.331).
5: average 90 % disappearance time (Hamaker, 1972, p.331).
6: same as 1 above but for full season control.
7: same as 2 above but as a triazine related herbicide.
8: the minimum for areas receiving 40-60 inches annual rainfall (Elanco, p.3).

The following factors which affect the degradation of herbicides can be divided into two groups. The first set belong to the bio-chemical group:

1. Molecular configuration of the compound.
2. Organic matter content and composition of the soil.
3. Soil reaction (pH).
4. Clay content and mineralogy of the soil.
5. The presence of other compounds or ions.
6. The formulation of the herbicide compound.
7. The initial concentration of the herbicide application and that of any previous applications.

8. The chosen method and the depth of the herbicide application.

The second set belong to the environmental group:

1. Soil moisture.
2. Soil temperature.
3. Incoming solar radiation.
4. Air pressure.
5. Cloud cover.
6. Aerobic/anaerobic soil conditions.

The molecular configuration of a compound is important because it relates the herbicide to its mode of action. In addition, herbicide compounds can be catalyzed by enzymes through imitating substrates similar to many found naturally in the soil. Bailey and White (1970, p.43) describe four structural factors which determine the chemical character of a pesticide molecule and these are:

1. Nature of functional groups such as carboxyl, carbonyl, alcoholic hydroxyl and amino.
2. Nature of the substituting groups that may alter the behaviour of functional groups.
3. Position of substituting groups with respect to the functional groups that may enhance or hinder intramolecular bonding.
4. Presence and magnitude of unsaturation in the molecule that affects lyophilic-lyophobic balance.

They go on to discuss the basic principles behind these factors which facilitate their comprehension.

> The nature of the functional group determines: 1) Whether a compound is acidic, basic, or amphoteric in nature, 2) ability to undergo hydrogen bonding, and 3) ability to undergo coordinate covalent bonding (*i.e.*, to form a chelate structure with a transition metal ion). The nature of the substitution on the ring as well as the position of the substituting group enhances or lessens each of the above phenomena. ... The nature and position of the substituting group may affect the ability of the molecule to undergo intramolecular hydrogen bonding (*i.e.*, hydrogen bonding to the silicate surface) by promoting intramolecular hydrogen bonding... .
>
> The nature and position of the functional groups and the position and length of the alkyl portion of the molecule determines the lyphobic to lyophilic balance of the molecule. The exact nature of the balance will determine the relative affinity the molecules will have for polar and for nonpolar adsorbents.
>
> (*ibid.*, pp.43-44)

The importance of organic matter as a factor in herbicide degradation should not be underestimated. First, the soil micro-fauna and flora are instrumental in metabolizing and degrading herbicides. Second, quantification of the content (usually expressed as a percent of a measured unit) and identification of the composition (primarily the humin, humic acid and fulvic acid fractions) of soil organic matter provide knowledge of the availability of substrates with which the herbicides can complex and participate in soil chemical reactions. The interaction of pesticides and soil organic matter has been studied by a number of authorities (Grover, 1968;

1971; Grover and Smith, 1974; Khan, 1972; 1973a; 1973b; 1980; McCall *et al.*, 1972; Morrill *et al.*, 1982; Nearpass, 1976; Norris, 1970; Schnitzer and Khan, 1978).

Soil reaction (pH) may affect degradation directly if the compound's stability is pH dependant, and indirectly via its effects on adsorption or on the composition of the soil microbiota (Hance, 1980, p.89).

The clay - pesticide interactions that occur in the soil are similar to those of clay - soil organic substances. In a pure form the anionic nature of many clay minerals will form associations with cations whether they be soil nutrients (*eg.*, Ca^{++} or Mg^{++}) or pesticides. Of course the adsorptive capacity of the clay is first determined by its properties; abundance, surface area, lattice arrangement, interlamellar spacing and electrical charge. In the soil environment clay is not always in a pure form. Clay minerals that undergo isomorphous substitution are capable of adsorbing more elements than their crystalline forms (Green, 1974, pp.3-32).

The presence of other compounds or ions in the soil is thought on the one hand to enhance the pesticide's effectiveness (Bovey *et al.*, 1972; Hamill *et al.*, 1972), while on the other is thought to increase the chemical's rate of degradation (Bovey *et al.*, 1972; Morrill *et al.*, 1982, pp.174-176) and to be inconsequential (Bovey *et al.*, 1972; Hamill *et al.*, 1972).

The formulation of the herbicide relates, in many respects, to the presence of other compounds or ions in the soil. Some of the formulations available for the selected herbicides best exemplify this in Table 1-4.

Table 1-4: Some Conventional Formulations For The Five Selected Herbicides

Herbicide	Formulation
2,4-D	1) Liquid in the emulsifiable acid form and in the dimethylamine salt form.
	2) Sodium salt in the water soluble powder form.
	*3) Liquid esters in the oil soluble and emulsifiable with water forms.
Dicamba	*1) Liquid in the dimethylamine salt form.
	2) Granular form as the acid or amine salt.
Hexazinone	*1) Dispersable liquid ester emulsifiable with water.
	2) Pellet formulation.
Tebuthiuron	*1) Formulated as a wettable powder.
	2) Pellet formulation.
Picloram	1) Potassium salt formulated as a water soluble liquid, as a pellet and as a potassium salt-disodium tetraborate bead.
	2) Triisopropanolamine salt as a liquid formulation.
	*3) Isooctyl ester as a liquid formulation.

* = Formulations used in this experiment.

The initial concentration and repeated application of herbicides has been given attention by a number of authorities. However, the role that initial concentration plays in herbicide persistence is unclear as there are a number of conflicting studies. Grover (1967), Meikle (*et al.*, 1973) and

Lutz (*et al.*, 1973) take the position that herbicide degradation is independant of initial concentration, whereas Altom and Stritzke (1973) and, Hance and McKone (1971) are of the mind that the rate of degradation is dependant on initial concentration. Repeated applications create the possibility of toxic accumulation in the soil which depends upon the herbicide's half-life, availability of adsorption sites and the ability of soil microbiota to adapt to and utilize the herbicide molecule or some part of it for energy (Audus, 1960; Morrill *et al.*, 1982, p.187; House *et al.*, 1967).

The chosen method of application and the depth of the application are both related to the compound's formulation for the purpose of affecting the target species. Whether the herbicide works systemically or on contact, and whether it is applied on the surface or injected into the soil, if the chosen method of application does not reach the target species then there will be herbicide wasteage which will be available for photodecomposition, volatilization, leaching and degradation.

The environmental group of factors will be discussed together because they are inter-related. Insolation is the energy source which directly and indirectly controls air temperature and pressure, soil temperature and moisture and, the aerobic/anaerobic soil condition. Soil moisture is required for herbicide movement, soil and plant bioactivity and is the object of evapotranspiration. Thus, soil moisture can affect leaching and the effectiveness of microbial degradation. Soil temperature can be a limiting factor in the boreal forests as consistent daily temperatures below 0 °C will inhibit leaching and, soil and plant bioactivity, hence degradation. Air pressure directly affects winds, both of which, along with air temperature, directly affect humidity and rates of evapotranspiration, given that the antecedent soil moisture status is not a limiting factor. Thus, air pressure can affect the leaching and volatilization modes of herbicide dissipation. Cloud cover is the result of insolation affecting air pressure and air temperature which in turn determines the relative humidity which, at the appropriate altitude, will condense into clouds. The clouds further influence the insolation that actually reaches the ground surface, the air temperature, winds and rate of evapotranspiration. Air pressure and cloud cover will respectively influence the volatilization mode of dissipation and photodegradation. The aerobic/anaerobic soil condition is determined by the bulk pore space (often expressed in terms of bulk density) and by the soil moisture content. The aerobic/anaerobic soil condition is one determinant establishing whether degradation is primarily oxidative or non-oxidative.

Chapter 2
PREVIOUS RESEARCH

2.1. Introduction

Since 1960 (Audus, 1960), authorities in the field of pesticide[7] research have been very active in contributing to our knowledge of these substances.

In the United States and in Canada public concern over the adverse effects of some pesticides on nontarget biota and ecosystems has dictated the need for more and better information on environmental chemistry along with the necessary understanding for pesticide use in the regulatory decision making process. Canada has achieved this through the Pest Control Products (P.C.P.) Act and Regulations (Environmental Protection Service, 1985, p.1). In both Canada and the United States registration of pesticide for domestic, commercial or restricted use first requires that certain information be presented to the registration authorities for review.

In the United States some of the information required as it relates to this study is addressed by the following questions:

> 1) What is the rate of dissipation of the pesticide in soil? ... 3) Do the residues leach through the soil? ... 5) Is the pesticide found in soils?
>
> (Kovacs, 1983, p.5)

In Canada similar information is requested in the P.C.P. Act and the P.C.P. Act Regulations; "scientific information sufficient to facilitate evaluation of the product with respect to merit and safety (section 4(1) P.C.P. Act and section 9(1) P.C.P. Act Regulations)." (Environmental Protection Service, 1985, p.6). "Merit" is its effectiveness and "safety" is for humanity and the environment.

In short, these registration prerequisites and the multitude of information that the necessary studies have generated have answered many of the questions pertaining to pesticide efficacy, toxicity, bioaccumulation, hazard assesment, mobility, spray drift, persistence and degradation.

The many studies found in the literature concerning herbicides in the soil are of a diverse

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[7] pesticide is the umbrella term for all biocides: herbicides, fungicides, rodenticides, nematicides, insecticides, algacides, germicides, etc..

and very complex nature. They can be based on different principles and their methods can lead to divergent interpretations. Rather than indicating opposing views these conflicting conclusions may only mirror the complexities of soil-herbicide interactions. In addition, those studies described in the literature which are very complex or very specific often lack some detail of information critical to an objective review. Instead of being able to reach conclusions the reader finds that only more questions arise.

2.2. Herbicide Behaviour

A myriad of studies concerning herbicide persistence has been undertaken, including studies pertaining to the degradation and mobility aspects of herbicide persistence. However, the conclusions drawn from many of the persistence studies are difficult to generalize because of the variety of conditions under which the tests have been conducted. Test conditions range from uncontrolled field environments to partial control in greenhouses through to the almost completely controlled experiments in laboratories.

Baur *et al.* (1972) studied the concentration of picloram in a soil profile over a 2 year period down to a depth of 2.4 metres in an Axtell fine sandy loam near Carlos, Texas. In addition, they concurrently compared conventional formulations (spray and granular potassium salt) with polymerized ones (spray and granular) in a Lakeland sand (an alluvial soil in the bottomlands of the Navasota river) and an Irving clay loam near the Carlos site (*ibid.*, p.306). Conventional formulations are the standard manufactured form of the herbicide and may be applied as a granular pellet or a wettable powder or in a liquid carrier as an emulsifable concentrate, soluble solution concentrate or soluble salt (Ross, 1976, pp.10-12). Polymer formulations require the addition of a carboxylic acid and a metal ion in the presence of an aldehyde catalyst (Bovey *et al.*, 1972, p.332). Heating during the preparation of these formulations increases the length of the polymer, its molecular weight, and hardness (*ibid.*). The heating decreases the rate of degradation of the polymer or release of the herbicide. Thus, polymerized formulations should extend the biological activity of the compound and reduce leachability (*ibid.*). Bovey *et al.* (*ibid.*) suggest that picloram leachability is decreased by some polymer formulations studied in soil columns under simulated rainfall but that after six months under field conditions there was no significant difference between polymerized and conventional picloram. Furthermore, their investigation shows (*ibid.*, p.333) that there is no significant difference in canopy reduction of honey mesquite (*Prosopis juliflora* var. *glandulosa*), huisache (*Acacia farnesiana*), Macartney rose (*Rosa bracteata*), live oak (*Quercus virginiana*), white brush (*Aloysia lyciodes*), and winged elm (*Ulmus alata*) between conventional picloram and polymerized picloram. Similar results are given for 2,4-D and dicamba (*ibid.*). It becomes apparent that the production of these polymer

formulations does not merit the extra cost. On soils in Texas, Baur *et al.* (1972) found that residues one year after application of 3.36 kg/ha of picloram, either as polymerized spray or granule or as conventional spray or granule, were sufficiently reduced to allow growth of most herbaceous species (*ibid.*, p.303). In addition they concluded that in sandy soil picloram tended to leach throughout the sampled depths (0 to 244 cm) with slightly higher concentrations between 137 and 183 cm (*ibid.*). It may be that these values detected for the six month sample period are representative of the pulse of herbicide which has moved down to the 137 through to the 183 cm interval with diffusion, gravity and 39.1 cm (*ibid.*) of rain acting as the pulsing mechanism. In the clay-loam soil, leaching was considerably less as indicated by high levels near the top which diminished with progressively deeper sampling (*ibid.*). The high clay content of the clay-loam soil, range of 17.5 to 41.7 % (*ibid.*, p.307), between the surface and 61 cm sample depths, would provide a substantial pool of adsorption sites, thus minimizing leaching to lower depths. The only questionable step they took was in the use of a power auger as a sampling tool. The use of an auger is most often responsible for contamination of lower sampling depths by loosened soil particles from the upper levels.

Lutz *et al.* (1973) studied the persistence and movement (vertical and lateral) of picloram and 2,4,5-T in a Fannin clay-loam (Typic Hapludult), a Chandler fine sandy loam (Dystrochrept) and a Chester loam (Typic Hapludult) in North Carolina. They found that there was a tendency for both herbicides to disappear most rapidly from the Fannin and least rapidly from the Chandler soil (ibid.,488). They attributed this to the low hydraulic conductivity of the Chandler soil which is only one-tenth that of the Fannin and Chester soils (ibid.). In addition, they noted that the critical inflection points on the degradation curves occurred at 15 days postspray for 2,4,5-T and at the 50 and 100 day postspray periods for picloram (ibid.). This study is most complete in the sampling design (Latin Squares) and questionable in one or two of the concluding statements. In the concluding paragraph of this article they state:

> The data presented suggest that losses of the two herbicides by surface and subsurface runoff will not be a problem on these soils, even with steep slopes, when the herbicides are applied at recommended rates. Other data suggest that the relatively high organic matter content and cation exchange capacity (compared to other non mountainous southern soils) undoubtedly were important in limiting herbicide movement.
>
> (*ibid.*)

With reference to the first quoted sentence there are two points to consider. First, most operative conditions under which herbicides are used do not include seeding the ground with orchard grass (*Dactylis glomeratus*) the year prior to the spray application. This condition limits the exposure of the mineral soil to rain splash erosion, sheet wash, overland flow and therefore losses of herbicide by runoff. In addition, grass roots generally have a much greater surface area, m^2 per m^2, than trees and shrubs. This factor determines the amount of surface area available for

herbicide absorption as well as having the property of holding the soil together and in place; thus minimizing erosion. Second, the experiment was conducted over the summer period (June through September) when soil moisture demand is at its annual peak and runoff is generally low. However, if they were to carry the experiment over into the fall (October through December) when soil moisture demand declines, and precipitation and runoff increase, they may have found greater movement of both picloram and 2,4,5-T. With reference to the second quoted sentence, the high cation exchange capacity of these soils (range: 11.8 - 17.8 *meq*/100 *gm*) may be a more important factor in limiting herbicide movement than they suggest. Many authorities have shown the significance of soil ions, anions as well as cations, as sites for herbicide adsorption (Haque *et al.*, 1968; Mortland, 1968; Grover, 1971; Bovey *et al.*, 1972; Grover and Smith, 1974; Nearpass, 1976; Terce and Calvet, 1978; Morill *et al.*, 1982, pp.174-176).

The radioactivity of a compound (usually carbon-14) can be determined by direct counting using a nuclear scintillation spectrometer. Given the level of a radioactively labelled herbicide is known, it is possible to follow the radio-tagged portions of the compound through its metabolic pathways even though they may occur as trace amounts. Thus, the use of radio-tagged compounds has increased our knowledge of herbicide behaviour in soils (Norris, 1966; Smith, 1973; 1974; Van Genuchten *et al.*, 1974; Rhodes, 1980; *et al.*, 1983; Harvey, 1983). Norris (1966) sampled the forest floor litter in an attempt to identify the potential for surface runoff contamination of streams. The experiment did not examine the possibility of stream contamination by subsurface runoff. In addition, the experiment of Norris (*ibid.*), as well as those of Smith (1973; 1974), were conducted not in the field but under laboratory conditions. On the other hand, Rhodes (1980) studied the degradation of ^{14}C-labeled hexazinone under field, greenhouse and laboratory conditions, thus enabling comparisons to be drawn. According to the mobility classification scheme of Helling and Turner (1968; Helling, 1971c, 1971d), the mobility of hexazinone in the field corresponded to thin layer chromatography results, "Class 4, Mobile" (*ibid.*, p.314). In addition, field loss of radioactivity correlated with the production of $^{14}CO_2$ in biometer flasks (Rhodes, 1980, p.314). Rhodes (*ibid.*) found that degradation patterns were similar under both conditions of field and greenhouse. Furthermore, the two soils used for the greenhouse experiment, Fallsington sandy loam and Flanagan silt loam, exhibited a similar 50 % disappearance time of less than 4 months (*ibid.*). For the soils under field conditions he found that the time for 50 % loss of ^{14}C residues was ca. 3-4 months in Delaware (Keyport silt loam), 6-7 months in Illinois (Flanagan silt loam), and 10-12 months in Mississippi (Dundee silt loam) (ibid.,313). He did not explain these differences, though his laboratory tests showed that hexazinone is degraded by microbial action (ibid.,314).

Altom and Stritzke (1973) studied the degradation of dicamba, picloram, 2,4-D and three other phenoxy herbicides in 3 soils prepared from under a thick stand of blackjack oak(*Quercus*

marilandica) and post oak (*Q. stellata*), from the nearby open grassy area and from a brushy oak area (ibid.,516). The undecomposed leaves and grass were removed, and the top 2.5 cm of soil along with the partially decomposed litter was sampled at each of the three areas. This experiment excluded the potentially important contribution of undecomposed organic matter as an absorbing matrix which inhibits herbicide movement. The undecomposed organic matter buffers the soil from rain splash erosion and sheet wash, and in conjunction with its high water holding capacity, slows down the movement of the water and therefore that of the herbicide as well. The experiment was conducted in a growth chamber under controlled environmental conditions using prepared soils. They found that for dicamba, picloram and 2,4-D the half-lives were 17-32 days, greater than 100 days, and 4-5 days respectively (ibid.,557-559). They concluded that the amount of herbicide degraded was generally directly proportional to the herbicide concentration and that type of vegetative cover or location of soil collection did have an influence on degradation of all the herbicides except 2,4-D (ibid.,559).

Suffling *et al.* (1974) studied the lateral loss of picloram and 2,4-D from a forest podzol during rainstorms in Delamere township, Ontario. After 13 months they measured a total loss in rapid runoff of 0.22 % of the applied picloram and 8.19×10^{-4} % of the applied 2,4-D (ibid.,303). Though these losses are negligible they are greater than those observed by other workers cited in the article (*ibid.*, p.304). However, the low values detected could be the result of dilution. This is possible when one considers that the experimental plot is 625 m^2 and the catchment area from which the water samples were collected is a minimum of 1200 m^2. This means that the water samples taken for residue analysis were diluted by an approximate factor of two. Davis, Ingebo and Pase (1968, cited in Lutz, *et al.*, 1973, p.485) state the percentage of watershed treated and the residue (ppm) concentration in the water from the total watershed; a very small but critical piece of information. Furthermore, because Suffling did not fully characterize the soil, interpretations relating to cation exchange capacity and available adsorption sites supplied by hydrated iron oxides (mobile iron) (*ibid.*, p.304) could be misleading. It is important to note that the workers did not measure the level of residues found in the soil. This study could have achieved a greater level of utility by taking a mass balance approach through analyzing soil samples. This approach would have given the inputs, throughputs and outputs (except losses due to gaseous phase mechanisms) necessary to balance the residue-soil-water system. The additional cost to analyze soil samples should have been minimal because Suffling apparently did the work himself and hence, the benefit would have been maximized.

Siron, Frank and Dell (1977, pp.526-533) conducted a persistence and movement study of picloram applied to the median and the shoulders of highway "401" between Windsor and Kingston, Ontario. They found that under climatic conditions of south western Ontario the picloram was substantially dispersed and after 30 months only trace amounts were detected. In

addition, they noted that lateral movement was not observed. Finally, they concluded that picloram applied at rates up to 350 grams active ingredient per hectare every three years does not build-up in the top 50 cm of soil (*ibid.*, p.526). In their sampling design they used line transects at eight stations over a distance of 580 km for sampling the ground. Unfortunately there does not appear to be any statement as to what type of design it is nor any reason for the choice of the design (*ibid.*, pp.527-528). Furthermore, if they begin the sampling using a Shelby type corer for the period of 1969-72, then why for the period of 1973-75, do they finish the experiment using an auger? The Shelby corer is 45 cm long and the auger is 15 cm long. This means that they must take three 15 cm auger samples which is of course going to contaminate lower levels by soil particles being loosened in the subsequent 15 cm upper levels. In their discussion they state:

> On both sides of the median the middle portion retained the picloram for a longer period of time than the top or bottom. This indicates that the gravel drainage at the pavement edge as well as the ditch line created a water course which hastened the picloram washout. The fact that picloram did not accumulate at any particular location indicates that lateral movement of the herbicide is limited.
>
> (*ibid.*, p.530)

The location of this ditch is not indicated in any of their figures (*ibid.*, pp.528, 531) but should have been, because if the ditch line helped create a water course which hastened the picloram washout then does this not mean that the picloram must have first moved laterally before it could enter the water course? One aspect of the results which is consistent with other studies indicates that a lag occurs: 1.6 months postspray for the 15-30 cm depth, 11.6 months for the 30-45 cm depth and does not occur for the 0-15 cm depth. It is interesting to speculate that if there had been a more intensive sampling schedule early in the experiment (one more data point would have sufficed) then I suspect a lag would have been observed in the 0-15 cm depth some time between the first (day 6) and second sample points (day 19).

Chang and Stritzke (1977, pp.184-187) studied in the laboratory sorption, movement and dissipation of tebuthiuron in four soils only preparing, at most, the top 20 cm of one soil for two depths (0-10 and 10-20 cm for a Udic Argiustalls, Zaneis series, sandy loam) (*ibid.*, p.184). The other three soils used were only composed of the top 10 cm: Typic Palustall, Bethany silt loam; Lithic Dystrochrepts, Hector loam; Psammetic, Eufaula sand. This means that comparisons and contrasts are restricted to the top 10 cm of soil. Contrasting two of the texturally different soils gives a rather good example of tebuthiuron's sorption and mobility. The two soils have particle size distributions and organic matter content as follows: Eufaula; 95, 3, 2 and 0.3 % and, Hector; 49, 37, 14 and 4.8 % sand, silt, clay and organic matter, respectively (*ibid.*). They found that adsorption was greatest on soil with the highest organic matter and clay content. Hector loam adsorbed 71 % versus 11 % for the Eufaula sand (*ibid.*, p.186). In addition, desorption was inversely related to organic matter content with no mention of clay as a desorbant. All of the

tebuthiuron was desorbed after six successive water extractions from the Eufaula sand but only 60 % the herbicide was desorbed from the Hector loam (*ibid.*). As one might expect they found that movement was greatest in the Eufaula sand, where tebuthiuron moved with the water front. Movement was significantly less in the Hector loam and the Bethany silt loam (30.0, 52.2, 17.8 and 4.4 % sand, silt, clay and organic matter, respectively) which they felt may be related more to the sorbing surfaces than solubility in water (*ibid.*). In general, their dissipation discussion is too brief to properly deal with persistence and this is particularly true of one paragraph where the only indication of persistence was the statement that, "tebuthiuron was fairly persistent since there was still growth reduction of corn after incubation for 160 days." (*ibid.*, p.187). They made favourable comparisons with the results of other workers such as Bailey and White (1964), Grover (1975), Helling (1971d) and, Abernathy and Davidson (1971) whose studies were conducted with "other substituted urea herbicides" (Chang and Stritzke, 1977, p.186). This statement does not aim to undermine these comparisons and in fact assumes that they are valid. The point to establish here is that there is for some unknown reason a shortage of literature, relative to the other selected herbicides, on subjects dealing with tebuthiuron.

Sung (1982) examined hexazinone persistence in two thermic Typic Hapludults; a clayey, kaolinitic soil (sand 48 %, silt 13 % and clay 39 % by volume; organic matter, 2.21 % by volume; CEC, 7.98 meq/100 gm; pH, 5.0; bulk density, 1.40 gm/cm^3) and a fine, loamy, siliceous soil (sand 78 %, silt 10 % and clay 12 % by volume; organic matter, 0.81 % by volume; CEC, 3.33 meq/100 gm; pH, 5.8; bulk density, 1.66 gm/cm^3). The persistence aspect of the study was limited to the top 24 cm of an over grazed pasture near Opelika and abandoned crop land near Auburn, Alabama (*ibid.*, p.10). Sung found that for both soils at both a low and high rate of application (2 kg/ha a.i. *versus* 4 kg/ha a.i.) 50 % of the herbicide disappeared within 4 weeks (*ibid.*, p.21). Sung also found that in general every layer (0 - 8 cm, 8 - 16 cm and 16 - 24 cm) in the clay site had higher hexazinone concentrations than corresponding layers from the loamy sand soil except for week 0 (*ibid.*, p.27). She attributes this variation to the higher cation exchange capacity of the clay soil (8.0 meq/100 gm *versus* 3.3 meq/100 gm) and the lower rainfall of clay site to that of the sandy loam soil and site as likely explanations (13.0 cm *versus* 35.7 cm) (*ibid.*, p.64). It is likely that the 24 cm depth was of limited usefullness, since leaching or herbicide movement below that level may be important in the humid southeast of the U.S.A. and many of these Hapludults are old weathered soils easily 2 m thick.

Blume, Litz and Doring (1983) carried out different experiments in Germany aimed at finding simple methods for forecasting the behaviour of organic chemicals in soils. Though the article lacks information concerning the sample design and procedures the study is rather comprehensive as it includes laboratory as well as field trials. In the topsoil of a very acid Arenosol of a pine forest with 19 % organic matter and a mean temperature of 14 °C, more than

50 % of the 2,4,5-T was recovered after four weeks in June 1980 (*ibid.*, p.211). They were surprised to find that there was almost no translocation of 2,4,5-T because the tritium-labeled water had moved downward more than 30 cm during this four week period (*ibid.*). In a similar trial in December 1980, little movement of 2,4,5-T was again detected in the humus rich topsoil of the Arenosol. In addition, only 15 % of the 2,4,5-T was decomposed in the acidic Arenosol (*ibid.*) during the first two weeks. During the subsequent 3 weeks with a soil temperature range of 1.3 to 1.8 degrees celsius, no 2,4,5-T was degraded in the forest soil. The low soil temperature minimized the decomposition and increased the risk of outwashing down to the groundwater (*ibid.*, p.212). The results indicated the influence of very low pH in the forest soil because high soil acidity favours the adsorption of anions, and consequently also 2,4,5-T. Their evaluation of adsorption experiments with an additional 28 different soil samples verified the high adsorption by high content of organic matter and under conditions of a low pH range of 3 to 4 (*ibid.*, p.213).

Norris (1970) collected and prepared forest floor material (L and F horizons; see soil section page 11 for explanation of horizon terminology) from beneath red alders (*Alnus rubra*) in Oregon in order to determine the effect of different rates of application of selected insecticide residues and herbicide combinations on degradation of 4 herbicides (2,4-D, 2,4,5-T, picloram, and amitrole) (ibid.,403). He reported that 56 % and 65 % of the 2,4-D applied at 2.24 kg/ha and 4.48 kg/ha respectively, were recovered from the forest floor material 10 days after treatment(ibid.,406). Picloram is considerably more resistant to degradation than the other 3 herbicides (ibid., 410) as Norris reports a 65 and 59 % recovery of the picloram applied at 0.56 kg/ha and at 0.56 kg/ha with 2.24 kg/ha of 2,4-D respectively, 180 days after treatment (ibid.,408). Again the problem arises that the experiment is limited to soil surface organic material which undergoes experimental pretreatment prior to herbicide application.

These studies are important to industry, government and society, but with every step or phase which removes the experiment from field conditions, the relevance of the results to real world situations diminish.

2.2.1. Models

Ideally, a model describing the environmental chemistry and behaviour of pesticides would provide the method for estimating environmental exposure levels (Yu *et al.*, 1975; Mackay, 1979; Eschenroeder *et al.*, 1980; Mackay and Paterson, 1981; McCall *et al.*, 1983; Yoshida *et al.*, 1983; Environmental Protection Service, 1985, p.25), for assessing hazards to people (Moghissi *et al.*, 1980; Blau and Neely, 1983; Nigg *et al.*, 1983), and for quantitative descriptions of the fate or transport of chemicals in terrestrial environments (Van Genuchten *et al.*, 1974; Eschenroeder *et al.*, 1983).

Mackay (1979) and MacKay and Paterson (1981) are avid proponents of the Fugacity approach which they present as an evaluative model for estimating the likely behaviour of toxic chemicals in the environment. In essence, the environment is compartmentalized into phases (*i.e.*, atmosphere, soil, water, aquatic biota and suspended solids, and sediment) which tend to equilibrate through transfer mechanisms when a toxic substance is injected into this "hypothetical but typical environment" (Mackay, 1979, p.1218). The author does not define this "hypothetical but typical environment" but rather refers the reader to other sources for relevant information. Mackay regards fugacity as the "escaping mechanism of a chemical substance from a phase." and makes the analogy that "Fugacity is to mass diffusion as temperature is to heat diffusion. Mass (or heat) always diffuses from high to low fugacity (or temperature)." (*ibid.*, p.1219). Fugacity depends on the kinetic and equilibrium data of the toxic substance and the physio-chemical compartment properties of the environmental parameters. This approach has the advantage of simplifying the complexities of the environment because it purports a very general model solely dependant on physical laws. In addition, a comparison of fugacity between compartments can provide insight into pesticide sources, sinks and transportation routes (*ibid.*, p.1219). Though the fugacity approach differs from the approach of this thesis, the forthcoming chapters will also add insight into these same aspects of herbicide behaviour. Validation of the model may only be possible through making general comparisons with numerous other studies of observed residue concentrations with the fugacity predicted values (*ibid.*, p.1223). This Newfoundland herbicide study does little to validate the fugacity approach. However, it is of greater utility than fugacity with respect to the soil compartment because of the enormous areal extent of boreal forest podzols in circumpolar countries. The fugacity approach promises to be very useful for preliminary evaluation of a product before it enters the commercial market; though this approach is not without its limitations. An example of one fundamental problem is the choice of compartment volumes where organic carbon contents are 2 and 4 % for soil and sediment, respectively (Mackay and Paterson, 1981, p.1010). It is obvious that these values are inadequate for environments in which organic carbon tends to accumulate in the upper soil horizons instead of being assimilated by the biomass. Another problem is the assumption of first-order processes which they prescribe to in order to avoid the complexities of higher order processes. This problem will appear again during the reviews of Yoshida *et al.*'s (1983) and Van Genuchten *et al.*'s (1974) articles (see page, 30 for discussion). Nevertheless, the Fugacity model used along with more detailed studies could provide for a comprehensive and integrative approach to pesticide regulation and management.

Yoshida, Shigeoka and Yamauchi (1983) propose a nonsteady-state equilibrium model conceptually similar to that of Mackay (*ibid.*, 1979. p.1223) which makes use of a series of differential equations. The rate of disappearance of a chemical in the environment is given by the following differential equation: $-d\,M_T/d\,t = \sum_i^n k_i\,M_i$

Where:

M_T = the total mass of the chemical in the environment,

i = the compartment composing the environment to the n^{th} compartment, *e.g.*, air, water, soil, aquatic biota, etc.,

M_i = the mass of the chemical in compartment i,

k_i = the sum of first-order rate constants of transformation and advection processes in compartment i.

This model, like that of Mackay's, depends on first-order rate constants (k_i) which raises a critical point for discussion (see page 30). Yoshida *et al.*'s model (*ibid.*) is a fugacity model which estimates time-concentrations for only the biota (fish), water and sediment environment compartments. They found that for the concentration-time profile in water and biota, the results were consistent with the monitored concentrations of Neely's pond experiment (*ibid.*, p.185). Furthermore, they compared their predicted results with the monitored results of the Japanese Environment Agency for 12 substances and they found that 10 of the 12 substances fell within acceptable ranges (*ibid.*, p.187). However, the "acceptable range" is set as one-tenth to tenfold the concentration ratio predicted by their model (*ibid.*). They defend this large acceptance interval by stating that it is a "hypothetical closed system", thus there are no inputs or outputs (*ibid.*). An improvement to this static or "hypothetical closed system" model would incorporate the inputs and outputs resulting in a dynamic model. It should not be too difficult to model an open system on a computer as hydrologists do for watersheds, both real and hypothetical (Chow, 1964; Sopper and Lull, 1967; Benson, 1968; Riggs, 1968; Shelton, 1974, 1981; Chapman and Dunin, 1975; Tajchman, 1981). Monitoring or estimating precipitation, solar radiation and toxic substances as the inputs to the environment, modifying these equilibrium and kinetic models to accomodate changes in volume and accessible compartments could yield the outputs of water and toxicants, as well as the mass or concentration distribution fraction, mean residence time, and concentration-time profile for the chemical.

Van Genuchten, Davidson and Wierenga (1974) evaluate kinetic and equilibrium equations for the prediction of picloram movement through porous media. Though this article predates the previous two articles it has withstood the test of time. Of their conclusions relevant to this study, two stand out: For the soil tested (Norge loam: pH, 6.6; cation exchange capacity, 9.2 meq/100 gm; organic matter, 1.7 %; sand 46 %, silt 38 % and clay 16 %), adsorption-desorption cannot be described by one equation (*ibid.*, p.31), and that first-order kinetic rate equations are inadequate for predicting picloram movement at high pore-water velocities, *i.e.*, 132 and 145 cm/day (*ibid.*, p.33). The fact that adsorption-desorption cannot be described by one equation is not new in hydrology. Ward (1975, pp.138-142, 151-160, 171-177) discusses theories and principles, and reviews the work of soil moisture authorities. A problem faced by hydrologists is that for any

particular soil textural type (*e.g.*, sandy, sandy loam, loam, clay-loam or clay) the wetting front will be described by a different equation than the drying front of the soil. The relationship for the wetting and drying of the soil depends on the pore size distribution and the suction at the air-water interface. As the suction changes, with either a wetting or drying soil, the volumetric moisture content also changes, until very high suctions are reached and pore spaces are mostly filled with air. At which point the moisture content is increasingly due to adsorption. This relationship is further complicated because even if the suction is held constant, the soil moisture content will vary depending on whether the soil is being wetted or dried. This phenomenon which describes the difference between the soil moisture content of a wetting versus that of a drying soil is referred to as *Hysteresis*. It may be that a comparison for elucidating the problems of finding a single equation for the adsorption-desorption of pesticides in the soil can be made with hysteresis. This is especially true when one considers the importance of soil water not just as a transportation medium but as the medium (solute) with which pesticides interact and which further facilitates their adsorption with soil particles. The conclusion that first-order kinetic rate equations are inadequate to predict picloram movement at high pore-water velocities is related to the problem of finding one equation which describes the adsorption-desorption of a pesticide in the soil. In order to understand this relation it is necessary to go back to the soil characteristics unique to the Norge Loam studied by Van Genuchten *et al.* (1974). This soil with a high content of fine particles (54 % silt + clay), and a corresponding mean bulk density of 1.54 gm/cm^3 will not have large pores in a packed column 30 cm long and a cross-sectional area of 45 cm^2 (*ibid.*, p.31); but they will have many small pores. The pore-water velocity of a packed soil column is not just dependent on the suction and distribution of pores but their size as well. The high pore-water velocities of 132 and 145 cm/day, may as the authors suggest, result in a residence time of the herbicide in the soil that is too short to allow diffusion to all adsorbing sites (*ibid.*, p.34). This would prevent the diffusion of picloram solution from larger pores to smaller pores, micropores and voids; hence the diffusion of solution would be redirected away from the inner surfaces of soil aggregates to the interface of the soil column and the glass cylinder. At lower pore-water velocities this is not a problem, nor would it be a problem at high pore-water velocities if the pores were of a larger size. Thus, as pore size distribution and suction affects adsorption-desorption of pesticides in soil so do they affect the movement of picloram in the soil. A higher order kinetic rate equation, which incorporates pore size, pore-water velocity, particle density or some related physical characteristic of soil volume, is necessary to accurately predict picloram movement at any suction for any soil. Another problem which can adversely affect their experiment and the testing of these equations is that the picloram solution will probably flow along the inside wall of the glass cylinders at the high pore-water velocities given. This would be a boundary flow problem and the effect of the flow along the soil column edge and over a smooth

glass surface would reduce the amount of picloram solution in contact with soil particle surfaces. This problem is compounded by the ratio of the surface area of the pore volume (0.41) per column and the surface area of the cylinder. Given the above cylinder dimensions, the surface area of pore volume per column is roughly 13800 cm^3 (assuming clay is kaolin with a surface area of 30 m^2/gm) and the surface area of the cylinder is approximately 800 cm^2. This gives a pore:cylinder surface area ratio of approximately 17:1 which means that the large surface area of these cylinders contributes a major surface area exposed to the overall picloram solution. This is an often overlooked scaling problem in this type of experiment which should be given much greater attention in the early stages of design. Van Genuchten's work has shown that first-order kinetics are inadequate to describe picloram movement in soil. This problem of choosing the lowest degree of an equation which best describes a particular aspect of pesticide behaviour has carried over into the selection of first-order kinetics to describe the disappearance of pesticides from the soil.

The idea that first-order kinetics can describe herbicide disappearance in soil is simple enough but studies have conflicted as to the degree the equation should take. Hance (1967, p.546; 1969, p.144) found that the decomposition curves for picloram and five other herbicides indicated that the reactions obeyed first-order kinetics. In a later study, Hance and McKone (1971) concluded with the opposing statement that:

> The rates of decomposition of atrazine, linuron and picloram cannot adequately be described in terms of either zero-order, half-order, first-order or Michaelis-Menten kinetics. There may be some theoretical justification, however, to attempt to use a fractional order equation of the Michaelis-Menten type, although this particular expression does not appear to be adequate.
>
> (*ibid.*, p.34)

In 1973, Meikle *et al.* (p.551) found that a fractional-order of 0.8 best fit the data for picloram disappearance. However, they only worked with one soil, a clay soil from Texas (pH, 6.8; organic matter, 2.7 %; sand 13 %, silt 39 % and clay 48 %).

It is evident that many herbicide studies have been conducted but none have yet been found which are field studies on undisturbed forest soils of the boreal ecosystem involving excavation pits for the sampling of soil for herbicide residues.

2.3. Sampling Techniques

In contrast to the wealth of information on herbicide behaviour there is without a doubt a shortage of literature on the development of techniques for sampling and sample preservation. Although some suggested guidelines for field degradation studies can be found in the 1975 Pesticide Registration Guidelines (Environmental Protection Agency, 1975, pp.26886-26889), in an

Alberta Environmental Service manual (Pledger, n.d.[8]), in the proceedings of a symposium on Herbicides and the Soil (Hormann *et al.*, 1974), and in the proceedings of a seminar on soil and groundwater sampling (Mooij and Rovers, 1976), the general consensus is that little attention has been directed toward the establishment of effective techniques for sampling soil for pesticide residues (Chesters *et al.*, 1974, p.452; Liestra, 1980, p.47).

Many authorities point out the need for basic information on soil properties, climatic data as well as land use patterns (Mooij and Rovers, 1976, p.10; Weber, 1977, p.60; Hurle and Walker, 1980, p.112; Helling and Dragun, 1981, p.67; Laskowski, *et al.*, 1981). This information is fundamental not only to pesticide research, but also to practical pesticide use. In addition, regardless of the analytical precision, the results of the residue analysis are only valid if the soil samples are truly representative of the field. Therefore, it is important that the sampling technique, "...provide an uncontaminated sampling unit of uniform cross-section throughout the thickness of the horizon sampled." (Cline, 1945, p.3). Based on this premise authorities have found it very difficult to identify "the best" or "a standardized" method to sample soils. In fact, many authorities concur that there is "no known best method for collecting and storing soils" (Laskowski *et al.*, 1981, p.126), "confusion as to which techniques are best" (Mooij and Rovers, 1976, p.i), and "there is a wide variety of suggestions for optimum soil sampling" (Hormann *et al.*, 1973, p.130; Cline, 1945, p.3; Wilson and Lavy, 1975, p.1009; and Weber, 1977, p.60).

Pledger (n.d., p.9) states that soil augers, core and tube samplers are preferred for taking soil samples from cultivated soils but that when these are not available a blade or shovel can be used. He then goes on to outline how to extract the samples which includes digging down to a depth of 15 cm. He then states that in uncultivated soils (*i.e.*, forest), pesticide residues usually remain in the organic or top layer and therefore, deep sampling may be unnecessary (*ibid.*, p.11). It may be that core and tube samplers are preferred for taking soil samples from cultivated fields but these devices can be inadequate in many deep or stony forest soils or in soils where leaching through the profile is a question. The use of different devices for different conditions (cultivated *versus* uncultivated) makes statistical comparisons less reliable than if the same technique was employed. In addition, augers are never satisfactory for pesticide soil residue investigations because the sampling units are not uniform with depth, the samples are not reproducible, the auger contaminates subsoil samples with overlying material, and destroys soil structure (Cline, 1945, p.3). If however, a pit is dug to the required depth, then with respect to the horizons the exposed face of the profile can be sampled. The results of which, would reflect the influencing soil processes of that particular soil type on the pesticide, as indicated by the horizon-concentration distribution of residues. Furthermore, without sampling the lower layers one would never know if

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[8] n.d. — no date.

contamination has extended below the top layer. In fact, because this manual is designed for sampling after a pesticide mishap has occurred, it is even more important that the lower layers are sampled for the purpose of monitoring the movement of the mass of chemical in case any corrective measures need to be taken.

The study of Hormann *et al.* (1973) shows that for each of atrazine and metabolite G 30033, 15 and 17 soil cylinders (dimension, 30 cm long x 5 cm inside diameter) taken from bare ground in Switzerland, were composited to each make one gross sample for residue analysis (±15 % of the average at a 95 % probability level) (*ibid.*, p.134). The sampling was done using a "HUMAX" portable electric soil drill (*ibid.*, p.132) which could be inadequate for undisturbed forest soils. Though not explicity stated, it is likely that they would have needed a much more powerful motor to drive the cylinders deeper than 30 cm, especially if those soils are undisturbed (forest soils *versus* cultivated soils), and if they are stony as forest soils often tend to be. They could have answered a very important question pertaining to residue variance through the profile if they sampled greater depths.

Wilson and Lavy (1975) have designed an application and sampling device which injects a solution at a predetermined depth and allows the precise relocation of the point of injection for sampling. The technique is designed for ^{14}C-labeled herbicides and therefore only provides for 5 gm of soil for every 2.5 cm interval (*ibid.*, p.1011). This is an inadequate size for chromatographic analysis (*eg.*, G.L.C. or H.P.L.C.) but can be increased if a number of samples are composited; a point they fail to make. They state that it takes approximately 2 minutes to take the sample and prepare for the next sample (*ibid.*, p.1011). However, there is concern of contamination between successive 2.5 cm intervals as the extraction tool is a tube (1.59 cm inside diameter) driven down to the desired sampling depth in which an auger is then inserted and screwed down to the corresponding depth at which point it is pulled out bringing along with it the 2.5 cm sample (*ibid.*, p.1010). They either need to develop decontamination procedures for the auger and tube or they require a greater number of clean augers and tubes. Decontamination of the auger between successive 2.5 cm intervals is easy enough but not so for the tube which would require extracting it from the ground and cleaning it for every 2.5 cm interval which is certain to loosen soil particles and disturb the bore hole. Assuming that there is a plentiful supply of tubes and that only the auger requires cleaning between sample intervals, then the added cleaning time of approximately 1 minute yields an overall time of 3 minutes to sample, package, clean and prepare for the next sample. If the profile is sampled to the depth of 1 metre at 3 minutes per 2.5 cm interval then 2 hours are required to sample each bore hole and 10 hours would be necessary to provide a 200 gm sample (5 bore holes). Independant of assessment of horizon variation with depth and assuming that every 20 cm section is to be composited (40 gm of soil per 20 cm of depth), then a minimum of five bore holes would be needed for residue analysis (200 gm of soil per

five 20 cm sections). Thus, it would take 7.5 hours to collect five composite samples of 200 gm each [sampling(2 min/2.5 cm soil . 40 sections/100 cm) + cleaning(2 min/20 cm intervals x 5 sections/100 cm) x 5 bore holes = 450 min to sample, package and clean]. To compound matters, if the worker was to investigate the distribution of residues in the soil on a horizon basis, as one should to maximize the information, then it would easily take 8 to 10 hours to complete the sampling for one chemical on any given day. All this could be avoided by digging soil pits and extracting the required number of samples from a freshly cleaved face of the profile which takes all but 4 hours for one experimental plot. The 3 excavation pits dug per sample date for each herbicide used in this Newfoundland study took approximately 45 to 75 minutes each using pick, shovel and large buckets. After 4 hours, the pits had been filled in and for each of the 5 horizons sampled, a composite of 2 kg was provided.

Weber (1977) follows the principles of soil sampling as outlined by Cline (1945) but deviates from them by making the misleading statement that, "To obtain soil samples from different soil depths to be used for chemical or biological herbicide assays, the only satisfactory samplers are the tube-type." (Weber, 1977, p.60). This may be incorrect because compaction occurs and the separation of different depths (or horizons) becomes difficult; the degree of compaction will vary from sample to sample and therefore the quantity of soil sampled will vary, which leads to statistical problems associated with nonuniform cross-sections and the lack of reproducibility. However, he does introduce the idea of using separate compositing pails for each depth interval (*ibid.*, p.61) though he does not suggest lining the pails with plastic bags as an added measure to prevent crosscontamination between sample dates. He suggests 9 sampling units for each composite sample yielding about 405 gm of soil from a plot which is 16.7 m^2. Whereas, in this study in Newfoundland, 9 sampling units for each composite sample yields about 2 kg of soil from a sampling area which is 162 m^2.

Apperson *et al.* (1980) conducted a study which compared a small plug sampler (1 cm dia. x 5 cm long = 3.9 cm^3) against a larger sampler (43 cm dia. x 5 cm long = 7258 cm^3). The experimental design consisted of first broadcasting Mirex 10:5 granules, and replicating each treatment 5 times, then extracting 400, 800 and 1200 plug sampling units versus one large area sample unit (*ibid.*, p.56). The residue data were subjected to analysis of variance, the subsample measurements were averaged and the mean, standard deviation and coefficient of variation calculated for each treatment (*ibid.*, p.57). Results for the plug sampler showed that the coefficient of variation decreased as the number of sampling units increased and as the subsample size increased. Results for the large area sampler showed that the mean, standard deviation and coefficient of variation all decreased as the subsample size increased. There were no significant differences ($p = .05$) found between or among subsample measurements, which indicates that the plug and large area samples were equally reliable (*ibid.*). It would have been of interest to this

Newfoundland study to discover how the methods compared with depth of sampling, since the variation in results is expected to increase with an increase in depth from the point of application; unfortunately Apperson *et al.* (*ibid.*), only sampled the top 5 cm.

Sieczka *et al.* (1952) designed a sampling technique particularly well suited for sandy soils. It is essentially a PVC pipe 76 cm long and 3.8 cm in diameter which is hammered into the sandy soil using a sledge hammer and a block of wood to protect the upper end (*ibid.*, p.358). This technique must work very well in sandy soils such as on Long Island, New York; they apparently did not even have any difficulty withdrawing the cylinder from the ground. George Mills of the Canadian Forestry Research Centre, St. John's, Newfoundland (personal communication) used the same technique but with a pipe 60 cm long and 25 cm in diameter on a stony forest soil in western Newfoundland, and with a 3/4 inch steel plate to protect the upper end. Mills had 60 successful core extractions out of 90 trys; in most of the unsuccessful cases the PVC pipe would crack or split, in some cases they would loose the core when excavating to remove it, and in one case the steel plate buckled out of shape to the point of being useless. The procedure required hammerring the pipe into the ground as deep as it would go without damaging the pipe or steel plate, then excavating around it removing large stones, hammering some more, then excavating and repeating the cycle until a full core or most of a full core had been removed. In the case where large boulders halted the drive of the core another spot had to chosen and the task begun anew. In the case where a large boulder inhibited the drive, the stone was removed and a smaller stone with surface geometry matching that of the void, created by removing the stone, was put in place to fill the gap and allow the continued drive of the core; it should be noted that in these cases the fit had to be very good or they would have had to stop and begin on a new spot. Mills went to great effort and expense to remove these intact cores for greenhouse controlled experiments, not just for pesticide residue analysis of field soils. The 3.8 cm diameter PVC pipe that Sieczka (*ibid.*) used would have been subjected to a much higher failure rate than Mills in the generally stony soils found in Newfoundland and the boreal forest at large. Thus, this method is not likely to become a standard technique for sampling soils in the field. One final point to discuss is that Sieczka (*ibid.*) states that, "Sampling soil at varying depths by digging or use of an auger can result in contamination of deeper layers by pesticide-laden surface particles falling in.". This is true for an auger but not for dug pits where, if one who is sampling begins from the bottom of the excavation pit and carefully works their way up, section by section, contamination of lower layers by loose soil particles falling downward will be avoided.

Rother and Millbank (1983) studied the implication of core size on the acetylene-reduction assay as a measure of nitrogen-fixing potential on a brown earth soil in England. They found that for adequate results of an analytical procedure of the extremely variable soil property of nitrogen, soil cores must be no less than 150 mm in diameter and 150 mm in length (*ibid.*, p.379). If it is

accepted that the coefficient of variation is higher in residue-analysis (*ca.*, 30 %) than in the determination of physical properties or nutrient content of soils (Hormann *et al.*, 1973, p.131), then it is all the more important to avoid using tube-type samplers whenever possible. The simplest alternative that workers are left with is the excavation of soil pits using a pick and shovel.

Though Cline's article predates the other articles presented in this section it is most relevant to this study both directly and indirectly: "A 16-inch tilling spade (shovel) with a round point is better suited to dry, stony, or heavy-textured soils." (Cline, 1945). A shovel of this sort removes a large quantity of soil in one scoop and the digging of the pit is further facilitated if a heavy pick is at hand to loosen up the heavy and/or stony and/or compacted soil. Other devices are inadequate or too difficult to use on these types of soils. If the soils are light, stone free or loose, then a pick is most probably unnecessary for the excavation of a soil pit. This pick, shovel and bucket routine is a very simple standard to follow; where comprability is of use and benefit.

2.4. Conclusion

In order to satisfy society's concerns over pesticide related issues information is required from a broad spectrum of specialists: chemists, physicists, biochemists, soil scientists, plant physiologists, toxicologists, entymologists, climatologists, land use managers, agriculturalists, silviculturalists and others. It is only after they have provided answers to critically important natural, physical and environmental questions that decisions can be made. If the answers meet the stringent criteria set forth by government regulatory offices, then the products may be registered for their safe use.

Herbicide movement and dissipation in soil involves a very complex system of processes including climatic, edaphic and hydrologic systems which continually act upon the *dynamic* biogeochemical nature of pesticides. Thus, even though there are countless numbers of herbicide studies, still more are required. These studies should lead to the development of models which could more efficiently answer questions required of our government regulatory bodies.

Field work involved in the study of pesticides requires a sampling technique which is both simple to use and encourages comparative studies for scrutiny by peers. It has been shown that the simple and relatively inexpensive sampling technique provided by pick and shovel, powered by an acceptable level of manual labour can provide the basis for a much needed sampling standard which satisfies many prerequisites.

Chapter 3
METHODS AND PROCEDURES

3.1. Site Selection

To be suitable for the experiment, the test site had to meet with the following criteria:

1. In general the environment had to be representative of the boreal ecosystem.
2. The soil type had to be typical of soil types found in the boreal environment.
3. The soil unit had to be of a large enough area to accomodate five experimental plots of 11 x 20 m and a minimum buffer area between plots of 5 m.
4. The soil had to have recently been supporting a forest cover generally typical of the boreal environment.
5. The site had to be accessible by van and not so far from St. John's as to be beyond economic threshold.
6. The forest cover had to have been removed within the past two years prior to spray application so as to expose the ground surface (see Figure 3-1).
7. The soil density and rockiness should not prevent digging pits with a long-handled shovel and a heavy pick.

3.2. Site Preparation

Preparing the experimental site required:

1. Clearing away slash (see Figures 3-1 and 3-2).
2. Marking off five plots of 11 m x 20 m, one for each chemical selected.
3. Installing at each of six stations, two soil moisture and two soil temperature probes at two different depths, zones of eluviation and illuviation (see Figure 3-3).
4. Installing four wedge-type cumulative rain gauges at the first four stations (see Figure 3-3).
5. Setting up a meteorological station with a continuous recording rain gauge, two cylindrical cumulative rain gauges and a single-louvred stevenson screen housing a continuous recording thermohygrograph and a wet and dry bulb thermometer (see Figure 1-1, page 5).
6. Digging the control section (1 m wide x 2 m deep x 8 m long) for soil classification and for extracting samples for soil testing(pH, carbon loss-on-ignition, particle size, bulk density, moisture content, humic and fulvic acid content, and available phosphorus).

Once the plots were prepared for the spray applications, control samples were taken for residue analysis with the assumption that no herbicides have been sprayed there before. Then

Figure 3-1: Photograph of herbicide application to the dicamba plot using a 'SOLO' gas-generated mist blower. Spray swaths delimited with string at 1 m intervals. Competing ground vegetation is *Kalmia angustifolia*.

spray applications using a "Solo" backpack type gas-generated mist blower (see Figures 3-1 and 3-2) were made with the selected chemicals, on the following dates and with the quantities stipulated in table 3-1.

Figure 3-2: Photograph of herbicide application to the dicamba plot showing the throttle (at hand) and large nozzle (at end of apparatus) of the 'SOLO' gas-generated mist blower. Large quantities of slash which were removed from the plots can be seen in the foreground, in the midground acting as a buffer between the dicamba and 2,4-D plots, and in the background.

3.3. Sampling Design

Numerous authorities such as Ball and Williams (1977), Blyth and MaCleod (1978), Hammond *et al.* (1958), Ike and Clutter (1968), Kholopova (1977), Mader (1963), McFee and Stone (1965), Troedsson and Tamm (1969), and, Welch and Fritts (1956), have studied the problems of sampling design in relation to selected soil properties, but few workers have studied these problems in relation to organic pesticides as a soil characteristic. However, the knowledge gained from the above mentioned authorities, along with the information presented forthwith, has provided the formal basis for the sampling design and procedures.

For the purpose of providing the best possible precision at the lowest cost, the spatial distribution of sampling points was determined to be a composite sample using a two-stage systematic grid sample design with judgement. The statistical principles of this method have been discussed by Armson (1977, p.256) and Chesters *et al.* (1974, pp.451-453), and in detail by Cline (1944, pp.275-288) and Petersen and Calvin (1965, pp.54-72). Cline (1944, p.280) states that,

> Compositing is valid only if (*a*) the sampling volume represents a homogeneous population, (*b*) equal amounts of each sampling unit contribute to the subsample analized, (*c*) no interactions that would affect the results materially occur, and (*d*) an unbiased estimate of the mean is the only objective.

Figure 3-3: Photograph of the fourth pedo-meteorological station, tebuthiuron plot, showing the transparent cumulative wedge-type rain gauge and flag tape marking the apparent depth of the soil moisture and temperature probes.

The population is the Orthic Humo-Ferric Podzol which was divided into homogeneous subpopulations for sampling purposes. The five subpopulations sampled (LF, Ae, Bf, BC and C) were constructed on a horizon basis to meet Cline's criteria (*a*) above. The rectangularly sloped field plots from which the sample units were taken, were divided into thirds to minimize areal and gradational variation. From each third, a square metre area was systematically chosen for digging the pit so that the subpopulations sampled were representative of the field's subpopulations. The composite sample was a complex unit made from three samples per subpopulation per pit x three pits for a total of nine sample units per subpopulation (horizon) and 45 sample units for the whole population (Orthic Humo-Ferric Podzol). A trowel was used to

Table 3-1: Rates of Application for Selected Herbicides

Herbicide		Actual amt. applied to 0.022 ha in 80 l water (litres)	Per hectare equivalent in 3636 l water (litres)	Manufacturer's suggested rates of application	Ratio of per hectare equivalent to suggested rates
active ingredients	formulation				
	Esteron 600*	1.10	50	5.5 l/ha in 80 l spray mixture	9:1
2,4-D	600g ai/l				
	DyCleer 24*				
Dicamba	200g ai/l	0.80	36	10 l/1000 l water	1:1
2,4-D	400g ai/l				
	Velpar L*				
Hexazinone	25% by wt.	1.76	80	6.97 l/ha	11:1
	Spike 80W#				
Tebuthiuron	80% by wt.	1.36	62	11.0 Kg/ha =62 l/ha	1:1
	Tordon 101#				
Picloram	60g ai/l	0.768	35	35 l/ha in 200 l spray mixture	1:1
2,4-D	240g ai/l				

g ai/l = grams of active ingredient per litre.
l = litres.
l/ha = litres per hectare.
% by wt. = percent by weight.
* = spray application occurred on July 21, 1983.
# = spray application occurred on July 22, 1983.

collect these nine units, each of approximately equal size to comply with criteria (*b*) above. The negative interactions of criteria (*c*) above were prevented by following the stringent procedures outlined below in "3.4 Sampling Procedure" subsection, page 43. Sampling judgement was necessary when extracting the units from the face of the profile to ensure that they represented a fair cross-section of the horizon sampled.

The temporal distribution of sampling points was determined to be a product of persistence data found in literature surveys (see table 1-3, page 17) and, the frequency and intensity of precipitation events after herbicide application dates. Complimentary to this, the best indication of leaching has been shown to be represented by a short period of intensive sampling immediately after application, before other dissipative processes become dominant (i.e. a period of 1-2 weeks (Environmental Protection Agency, 1975, p.26886). The following Table 3-2 lists the sample dates in days postspray.

Table 3-2: Soil Sample Periods for Herbicide Residues

Herbicide	Control Prior to Spray	Spray @	DAYS (postspray) Sample Periods								
			t-1	t-2	t-3	t-4	t-5	t-6	t-7	t-8	t-9	t-10
2,4-D* & Dicamba$	-1	0	3	6	10	14	24	48	98	312	382	486
Hexazinone	-1	0	3	6	10	36	86	312	382	486		
Picloram & Tebuthiuron	-1	0	5	11	32	64	310	483				

@ = July 21, 1983 for 2,4-D, dicamba and hexazinone.
July 22, 1983 for tebuthiuron and picloram.
* = 2,4-D data for t-7 not received.
$ = t-8, t-9 & t-10 samples only for dicamba.

3.4. Sampling Procedure

The rectangular plots of 11 m x 20 m were subdivided into grid squares of one metre square. The first metre from the edge of the plots was excluded from any sampling to avoid the problems of boundary effects leaving a potential of 162 m^2 from which to sample. The remaining 18 rows of grid squares were divided into three sections, each section consisting of six rows of nine squares for a total of 54 grid squares. The long-axes of the plots were oriented downslope thus, the first section where the sampling began was the bottom third of the plot. The composite was made up of three samples from each section for a total of nine samples from three spatially contiguous sections; the weight of the composite sample was approximately 2 kg.. Hence, for each section a pit from a selected grid square (1 m x 1 m) was dug exposing the LF, Ae, Bf, BC and C horizons along the edges of the square. Once the digging of the three pits was complete then three samples representing the upper, middle and lower portions of the C horizon of the first section were composited in a bucket lined with a disposable plastic bag. Following this the 4^{th}, 5^{th} and 6^{th} samples from the second pit were composited with the first three samples and then the 7^{th}, 8^{th} and 9^{th} samples from the third pit were composited with the first six samples. This was done for each successive overlying horizon. In order to minimize crosscontamination each experimental plot had five permanently marked buckets, one for each horizon. The conically shaped trowels used for extracting samples were cleaned between sampling horizons. First, by lightly rubbing the metal surfaces clean of soil particles with a wire brush, followed by a water wash, a soap wash, a second water wash, a dry with a clean paper towel, then a wash with an organic solvent

(petroleum ether) and finally, a dry with a clean paper towel (see Appendix B, page 122, for the checklist of materials and supplies used in the field to sample the soil). The depths of each of the nine samples were recorded and the pits were filled in after the sampling was completed. In both digging and filling the pits care was taken not to drop soil particles on the ground surface of the plots, not to trample over the plots and to use the shortest route in getting on and off the plots. Appendix A, page 116 shows the location of the 1983 - 1984 sample pits for the five selected herbicides.

The first pit was located in that row which appeared to have the fewest obstacles to digging (tree stumps, rock outcrops, skid tracks, old logs) and would therefore yield the greatest number of pits. The second pit was located in the same row and 1 metre from the first pit and so on for all pits throughout the sampling period. When an obstacle was encountered the pit was moved to the next metre. When the end of the row was encountered, the next pit was moved to the second row up or down from the initial row and the procedure continued until the entire sampling period was over.

3.5. Laboratory Program

Fifty-five soil samples were analyzed for each of the following properties: pH($CaCl_2$), carbon (loss-on-ignition), field moisture content, hygroscopic water content, bulk density in the geomorphology laboratory and particle size analysis(hydrometer method) in a chemistry laboratory courtesy of the chemistry department. Methods followed those suggested by McKeague (1978) in the "Manual on Soil Sampling and Methods of Analysis". These results were used to help identify the soil type and can be found in appendix J, page 139.

The Federal Department of Agriculture (Ottawa) analyzed six soil samples taken from the control section for carbon content (loss-on-ignition), field moisture content, pH (H_2O and $CaCl_2$), organically-bound Fe and Al, CEC, base saturation, total N, P, K, and Ca content, and particle size analysis. The classification of this soil as an Orthic Humo-Ferric Podzol has been done with the aid of these results tabled in appendix K, page 143 and those in appendices J and D, pages 139 and 126.

During the week of January 9, 1984, the author analyzed the L and F organic surface horizons for humic acid (HA) and fulvic acid (FA) in the C.B.R.I. (Chemistry and Biology Research Institute, Ottawa) at the invitation of Dr. Shahamat U. Khan. These results best characterize the humic substance in the organic surface layer (see appendix L, page 145).

The Provincial Department of Agriculture (Mount Pearl, Newfoundland) analyzed 55 soil samples for available phosphorus. These results are tabled in appendix M, page 147 and were used to ensure that a composite sample of nine units was adequate.

3.5.1. Analytical Procedures

The residue analysis of the soil samples required expertise and equipment not available to me. Thus, Eco-Research Laboratories (Hymus Blvd., Pte. Claire, Quebec) was contracted to do the 2,4-D analysis. Unfortunately the results are unusable because they did not do any duplicates, give recovery rates nor properly document the results[9] (personal communications: Joseph Feng, Forest Pest Management Institute, Sault Ste. Marie, 1985; Dr. S.U. Khan, Chemistry and Biology Research Institute, Ottawa, 1984). The Ontario Research Foundation did the analysis of dicamba for Velsicol Chemicals of Canada, Ltd.. The Atlantic Pesticide Laboratory at the Kentville Agricultural Center (Nova Scotia) did the analysis of hexazinone for Dupont of Canada. Dow Chemicals of Canada (for picloram) and Elanco Chemicals (for tebuthiuron) did residue analyses in their own laboratories in Midland, Michigan and Indianapolis, Indiana, respectively. The results of the residue analysis for the five herbicides can be found in Chapter 4, Tables 4-5 through 4-9, pages 80 through 87. With the exception of tebuthiuron[10] a summary of analytical procedures for each herbicide, as excerpts from the laboratory reports, are presented as follows.

2,4-D

Project #83C105:

All analyses followed methods laid down in "Analytical Methods Manual, Environment Canada, October, 1980. Phenoxy acid herbicides in sediments." (personal communication: Dr. Ian Borthwick, Manager, O.D.C. Scientific Ltd., St. John's, Newfoundland, September 30, 1983)

Dicamba

ORF Report PS-8357:

Analytical Methodology

It was originally planned to use HPLC/UV technique for the dicamba analysis, but severe interferences were encountered mainly due to the very high organic matter content of many of the samples.

A gas chromatographic (GC) method coupled with an ether/acid extraction, was again found unsuitable because of gross interferences. We finally adopted a GC method involving an alkaline extraction.

Principle of Method Used

The sample was blender-extracted with KOH, centrifuged, washed with methylene chloride,

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[9] In addition, plotting the raw 2,4-D data, Figure 4-2, page 54, indicates unacceptably high variance eliminating any meaningful discussion and is henceforth excluded from the thesis (data for Figure 4-2 is presented in Table 4-5, page 80).

[10] The analytical procedures for tebuthiuron were requested on a few occasions but none have ever been received.

acidified, extracted with methylene chloride, methylated with diazomethane, cleaned-up on deactivated Florisil and analysed by packed column GC/EC.

GC Analytical Parameters

Tracor 560 with Ni^{63} ECD and linearizer; glass column 1.8 m x 6 mm (4 mm ID) packed with 3% SE-30/6% OV-215 on chromosorb W (HP), 80-100 mesh; temperature of column, injector and detector: 129°C, 225°C and 350°C respectively; carrier: 5% methane in Argon at 60 ml/min.

Hexazinone

Contract # X-19489-P:

Procedure:

The procedure adopted for the determination of Hexazinone and Metabolites in soil was a method by R.F. Holt of DuPont (1981).

Changes made at the Kentville laboratory for the determination of Hexazinone and Metabolites A and B were: The chloroform extracts were transferred to ethyl acetate solvent and then directly injected (without derivatization) on the gas chromatograph.

For the determination of metabolite C, the water layer remaining after chloroform extraction for hexazinone and metabolites A and B was used.

G.C. Conditions: Instrument: Varian 3700 GC with a nitrogen phosphorus detector (thermionic specific). Column: 2 ft. x 2 mm ID x 1/4 in. OD pyrex U tube packed with 10% SP225 0 on 100/120 Supelcoport. Injection temperature: 220°C. Detector temperature: 320°C (Hexazinone and Mets. A & B), 350°C (Met. C). Column Temp. program: (1) Hexazinone and Mets. A & B: 200° to 275° at 40°C/min. Hold at 275° for 8 minutes. (2) Met. C: 180°C for 5 minutes. 180°C to 325°C at 40°C/min. 325°C for 4 minutes (for run #1, 180 to 325° at 40°C/min., 325° for 4 minutes was used). Carrier flow: 40 cc/min of nitrogen. Detector hydrogen pressure: 20 psi. Detector air flow: 200 cc/min. Bead current: 500. Chart speed: 0.5 in/min. Attenuation: 32 x 10^{-12} for runs 1 and 2. 32, 64 and 128 x 10^{-12} for different metabolites in run 3.

Picloram

The methods followed were those of Dow's, ACR 73.3 developed by Bjerke (1973) and ACR 73.3 S.2, a supplement to Bjerke's method developed by Johnson (1977). The principle of Bjerke's method follows:

Principle

The soil, as received, was well mixed and a sub-sample extracted with potassium hydroxide - potassium chloride solvent. The extract solution was acidified, saturated with sodium chloride, and equilibrated with diethyl ether. The ether solution was cleaned up by a basic alumina column which retains picloram. Picloram was eluted with ammonia-methanol solution. After evaporation

of the methanol, the residue was taken up in water, acidified, and treated with potassium permanganate. Picloram was extracted into diethyl ether, and esterified with diazomethane reagent. The ether solution was passed through a column of basic alumina for additional cleanup. The methyl ester of picloram was quantitatively determined by gas chromatography using an electron capture detector.

Johnson's (1977) method follows that of Bjerke's but with several necessary modifications for picloram residue determinations by gas chromatography for green forage, grain and straw.

3.6. Computations And Statistical Analysis

The data on available phosphorus was used to determine if the composite sample size of pine was large enough to give an unbiased estimate of the mean for the residue analysis. One cannot assume that the variability of soil phosphorus was representative of the variability of the selected herbicides in a boreal forest Podzol. However, as very little evidence could be found in the literature in relation to soil herbicide variance (Hormann *et al.*, 1973; Apperson *et al.*, 1980), and none with relation to the herbicides selected for this study, phosphorus was chosen. Though it is a very rough variance indicator, phosphorus was appropriate because it is one of those more variable soil characteristics. It is common knowledge that nitrogen is the most variable of soil properties but due to the diverse natural forms in which it exists (NO_3^-; NO_2^-; [HNO]; N_2; $HONH_2$; NH_3), and the variety of analytical techniques used to detect these different forms, it was not selected as a variance indicator. The following equation (3.1) is used to determine the number of samples necessary provided that some estimate of the variance is available.

$$n = t^2 x S^2 / D^2 \qquad (3.1)$$

where:

n = the number of required sampling units being estimated.

t^2 = the student's t with (n-1) degrees of freedom at the α probability level (found in statistic tables).

S^2 = the variance of the mean

$= \sum_{i=1}^{n} (X_i - X)^2 \div n(n-1)$.

where: X = mean of sampling units.

X_i = the value observed for the i^{th} sampling unit.

n = the number of sampling units

in the sample.

(n-1) = sample size with (n-1) degrees of freedom.

D = specified limit set by estimator, measured in units defined by X_i.

The raw data (*ppm*) was first adjusted for moisture content, bulk density, horizon thickness and recovery rates before a log transformation was performed. This adjusted data (*mg*) was then used to construct distribution graphs (figures 4-7 through 4-10, pages 59 - 62), time-dependant persistence graphs (figures 4-15 through 4-18, pages 70 - 73) and, part of tables 4-6 through to 4-9, pages 81 - 87. The adjusted residue values were computed by incorporating the above factors into the following equation expressed in the general form as follows:

$$AY_i = [(Y_i \div MM_i) \times BD_i] \times (D_i \times 10) \times (100 \div Rec_j)$$

where :

AY_i = Adjusted residue values in *mg* per m^2 and D*cm* thick, where:
i = 1, 2, 3, 4, 5 for LF, Ae, Bf, BC and C horizons, respectively.
Y_i = Unadjusted residue values in *ppm*, where:
i = as above.
MM_i = Soil dryness expressed as a unit fraction, where:
i = as above.
BD_i = Bulk density in $gm \cdot cm^{-3}$, where:
i = as above.
D_i = Horizon thickness in *cm*, where:
i = as above.
10 = Unit to convert μg to *mg* amd(m^2 to cm^2.
$(100 \div Rec_j)$ = Factor for recovery rates, where:
j = 1, 2 for organic (LF) and mineral (Ae-C) horizons.

Preliminary graphical regressions of the transformed data were prepared using the computer statistical package, "SPSS-X" (1983). These graphs then indicated an approximate model for the herbicides' disappearance which was constructed using the statistical package, "BMDP" (Dixon, 1983). The graphical presentation of the persistence data in Figures 4-15 through to 4-18, pages 70 through to 73 suggests a negative linear least-squares model for hexazinone and tebuthiuron and, a negative exponential decay model for dicamba and picloram; these models in linear form are as follows:

1) $\log (Y_i) = \alpha + \beta X_i$ → for hexazinone and tebuthiuron.

2) $\log (Y_i) = \alpha + \beta \log (X_i)$ → for dicamba and picloram.

The prediction of the time (independent variable, days = X) for 50, 75, 90 and 95 % of the

herbicides to disappear from the soil required either an inversion technique such as, $Y_i - \alpha \div \beta$ (Zar, 1984, pp.276-277; Neter *et. al.*, 1983, pp.172-174) or the regression equation expressed in terms of Y, $X_i = \alpha + \beta Y_i$ (linear least-squares). The computer package "BMDP" (1983, program *P9R*, pp.264-277) performed the latter, thus facilitating predictions of *days* (X) for dicamba, hexazinone, tebuthiuron and picloram,

Missing data for horizon thicknesses occurred for the first two sample periods. This problem was handled by using the IMSL computer routine GGNML, "pseudo-random normal numbers" routine (International Mathematics and Statistics Library, 1982, p.GGNML-1). It is appropriate when n is large ($n > 500$)[11] and the corresponding mean and standard deviation for the population is given. The GGNML algorithm generates pseudo-random *normal*(0,1) deviates by transforming uniform deviates to normal deviates using an inverse normal probability distribution function. The routine requires setting a seed value greater than or equal to a six digit number and, the population mean and standard deviation for each horizon. The sample size is 839 for LF through Bf horizons, 734 for the BC layer and 69 for the C layer. Where the mean and standard deviations for each of the following LF, Ae, Bf, BC and C horizons respectively are: 12.2, 2.1; 6.9, 2.6; 25.3, 4.9; 14.7, 1.0; and 9.8+, 1.9+. The routine is executed in double precision. Scattergrams and statistics (mean, standard deviation, standard error of mean, skewness and kurtosis) of the whole population (horizon thickness for all cases) and subpopulations (horizon thickness by time, plot and, time and plot) indicated normal distributions. T-tests comparing recorded values with normal random generated numbers (horizon thickness: for all cases, by time, by plot and, by time and plot) indicated that the random numbers are a subpopulation of the recorded horizon thicknesses.

[11] With the exception of the C horizon where n = 69; the minimum chosen to maintain continuity for the tebuthiuron and picloram C layer in which no residues were detected during the first two sample periods.

Chapter 4
RESULTS AND INTERPRETATION

4.1. Introduction

One photograph indicative of vegetative conditions on all plots is presented in Figure 4-1. This photograph shows the product's effects as a distinct contrast of vegetation growth and development, on and off the plot.

Figure 4-1: Photograph of vegetation effected by picloram *versus* nonsprayed peripheral area, one year later (August 1984). A quadrat 1 m x 1 m is at the top end of the plot.

There are five main components to this chapter: 1) The results of the phosphorus data are used to determine if the nine sampling units used for the composite are of an adequate size. 2) Most important of all, the results of the herbicide analyses are presented to fulfill the objectives of this thesis. 3) Graphical regression equations are formulated to predict herbicide disappearance times. 4) The results of the spiked samples are used as a check on the integrity of the procedures

adopted by the analytical laboratories. 5) Finally, the data for horizon thicknesses, residue concentrations as received, corrected for distribution factors, relative quantities detected per sample period and, amount detected as a percent of that applied are tabled at the end of this chapter.

The size of the composite sample is accepted as valid based on certain given assumptions and the data as presented in Appendix M, page 147. The graphs and tables that follow present the results of the herbicide analysis as received residues and adjusted for selected distribution factors: recoveries, soil moisture, mean bulk densities, and mean horizon thicknesses. It must be noted that with the exception of Figure 4-2, "Unadjusted 2,4-D residues", 2,4-D is excluded from this point onwards because of the reasons mentioned in Chapter 3, Section 3.5, page 45. This information is presented in four sets of graphical figures for each of the four selected herbicides showing the distribution of residues for the five horizons sampled. The first set of graphical figures which includes 2,4-D, pages 54, 55, 56, 57 and 58, contains four graphs for each herbicide showing the raw data unadjusted for any distribution factors. The second set of figures, pages 59, 60, 61 and 62, contains two graphs for each herbicide showing the residue data adjusted for selected distribution factors. The third set of figures, pages 66, 67, 68 and 69 contains one graph for each herbicide showing the difference in the quantities of total residues detected between the organic LF horizon and the four mineral horizons (Ae, Bf, BC and C). The fourth set of figures, pages 70, 71, 72 and 73, contains one graph for each herbicide showing the total sum of adjusted residues in the profile giving a clearer picture as to the herbicide's persistence. These persistence curves are used for a graphical regression technique which yields regression equations which in turn permits the prediction of points within the range of given data. Following this, Section 4.6, page 77 raises questions on the variability of the analytical techniques employed in residue detection. Finally, Section 4.7, page 79 lists pertinent data used for the residue figures and regression equations.

4.2. Sample Size

The following results must be accepted with limited validity for the purpose of determining an appropriate sample size. If one is concerned with the necessary sample size for valid information on phosphorus, then these results are very important. However, it can be misleading to extrapolate these results for information on required sample sizes for herbicide analysis. If phosphorus variance is similar to or greater than the variability of herbicide distribution in a podzol, then these results are very important. On the other hand, if this assumption of phosphorus variance $\geq$ herbicide variance is false, then the sample size of nine units per horizon and 45 units per soil is insufficient to determine their distribution through the profile over time.

The tabled results indicate that the chosen size of nine units is acceptable within the limits of ±1 standard deviation of phosphorus (*Kg/ha*) for the horizon in question. The phosphorus data used to construct the following table 4-1, can be found in appendix M, page 147.

Table 4-1: Sample Size Determination: phosphorus in *Kg/ha*

Horizon	n	df	Mean	Variance	Standard Deviation	$t_{\alpha 95}$ = 2.005		$t_{\alpha 90}$ = 1.674	
						D	*nx*	*D*	*nx*
LF	11	10	142.3	496.8	22.29	20	4.9	20	3.5
Ae	11	10	127.3	968.8	31.41	25	6.3	25	4.4
Bf	11	10	220.9	2504.1	50.04	50	4.0	50	2.8
BC	11	10	423.2	16831.4	129.74	100	6.7	100	4.7
C	11	10	850.9	53509.1	231.32	200	5.4	200	3.8
total:	55	54	352.9	68247.9	297.07	200	8.9	200	6.2

n = given sample size.
df = degrees of freedom.
D = desired limits in ±Kg/ha which for stringent purposes are less than one standard deviation from the mean.
nx = required sample size for given variance and desired limits.

The results show that 5, 7, 4, 7 and 6 samples are the minimum required number of units necessary at the 95 % confidence level for the LF, Ae, Bf, BC and C horizons, respectively. Alternatively, nine sample units are required for the soil profile as a whole at the 95 % confidence level. Thus, based on the above mentioned assumption of similar variance, the chosen size of nine sample units is of adequate size for analysis of herbicides in a boreal forest podzol.

4.3. Unadjusted Residues

This section is primarily presented for the comparison of the unadjusted residue distribution curves (Figures 4-3, 4-4, 4-5 and 4-6) with the adjusted curves (Figures 4-7, 4-8, 4-9 and 4-10). The patterns that these curves present do not change from those of the adjusted curves. However, there are numerical changes incurred by transforming the raw data into values representative of actual field conditions. First, there is the positive increase of actual values by factors defined by the horizon thicknesses, recovery rates and the milligram conversion unit. Second, these same factors also have a positive multiplicative affect which increases the overall range of values and tends to increase the spread between their points. The adjustments for soil moisture and soil bulk density do not noticeably change the patterns that the curves present.

Figures 4-2, 4-3, 4-4, 4-5 and 4-6, (pages 54, 55, 56, 57 and 58) show the residues in the common logarithm of parts per million (ppm) unadjusted for any distribution factors. This first set of figures presents the raw data for each herbicide on four graphs: The first graph shows the

initial intensive sample period and the second graph shows the entire sample period. Clarity on the graphs for the first phase of sampling was improved by increasing the scale of the X-axis. Both these graphs of the first set indicate the compounds' persistence and propensity to leach. The third graph shows the difference between total residues detected in the organic horizon versus the total sum of residues detected in the 4 mineral horizons sampled (Ae, Bf, BC and C). Finally, the fourth graph shows the total sum of residues in the profile giving a clearer picture as to the herbicides' persistence independent of any between-horizon variation.

4.4. Adjusted Residues

Following the "Unadjusted Residue" graphs, Figures 4-7 through 4-18, (pages 50 through 73) present the results of the herbicide analysis as total residues adjusted for recoveries, soil moisture, mean bulk densities, and mean horizon thicknesses. The results are expressed in common logarithms of total mg of a.i. (milligrams of active ingredient) per volume of soil (mean thickness of each soil horizon for a 1 m^2 sample area). The adjusted residue distribution and persistence data is presented on three sets of graphical figures: Two graphs for Figures 4-7 through 4-10, and one graph for each of Figures 4-11 through 4-14 and 4-15 through 4-18, respectively. These graphs show the distribution of residues (mg of a.i.) for the five horizons sampled, similar in format to the figures of unadjusted residues as stated in the previous Section 4.3, but in an expanded form.

4.4.1. Vertical Distribution, Adjusted Residues By Horizon

The first graph of Figures 59 through 62, pages 59 - 62, shows the initial intensive sample period and the second graph of these figures shows the entire sample period, both for each of the five horizons. Clarity on the graphs for the first phase of sampling was improved by increasing the scale of the X-axis. Similar to the unadjusted graphs this set of figures indicate the compounds' persistence and propensity to leach. There is no noticeably great difference in the patterns presented when contrasting the unadjusted graphs with the graphs which have been corrected for the selected distribution factors.

The three patterns clearly shown on the following Figures 4-7 through 4-10 are:

1. The distinct separation of values of the organic LF horizon from the mineral Ae to C horizons.
2. The pattern which represents the displacement process, where values of the lower horizons (Bf, BC and C) increase as the values of the upper horizons (LF, Ae and Bf) decrease.
3. The tendency for the values of the Ae horizon to be less than those of the Bf horizon.

First, for all of the hexazinone (except day 382), tebuthiuron and picloram sample periods

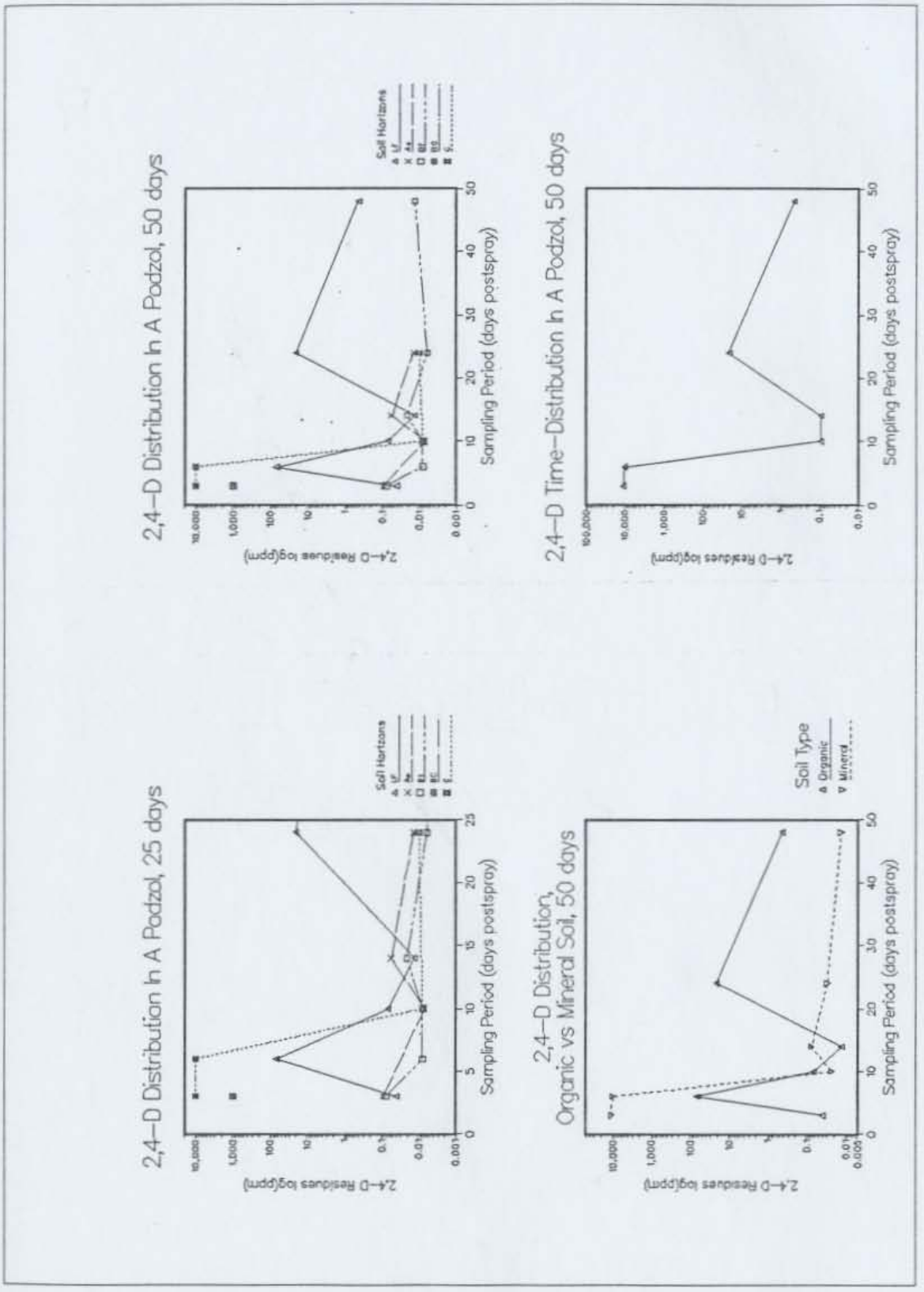

Figure 4-2: Unadjusted 2,4-D residues

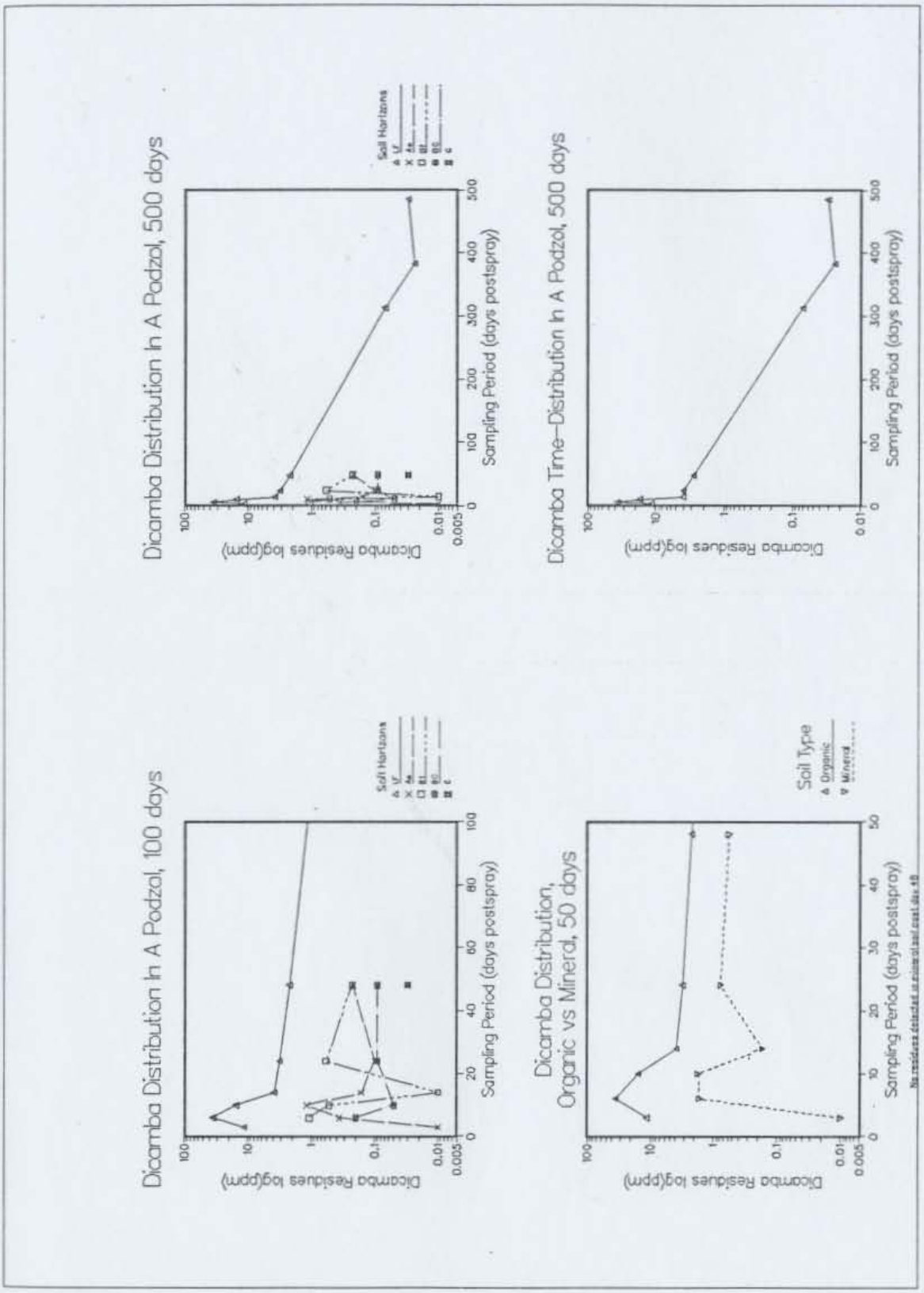

Figure 4-3: Unadjusted dicamba residues

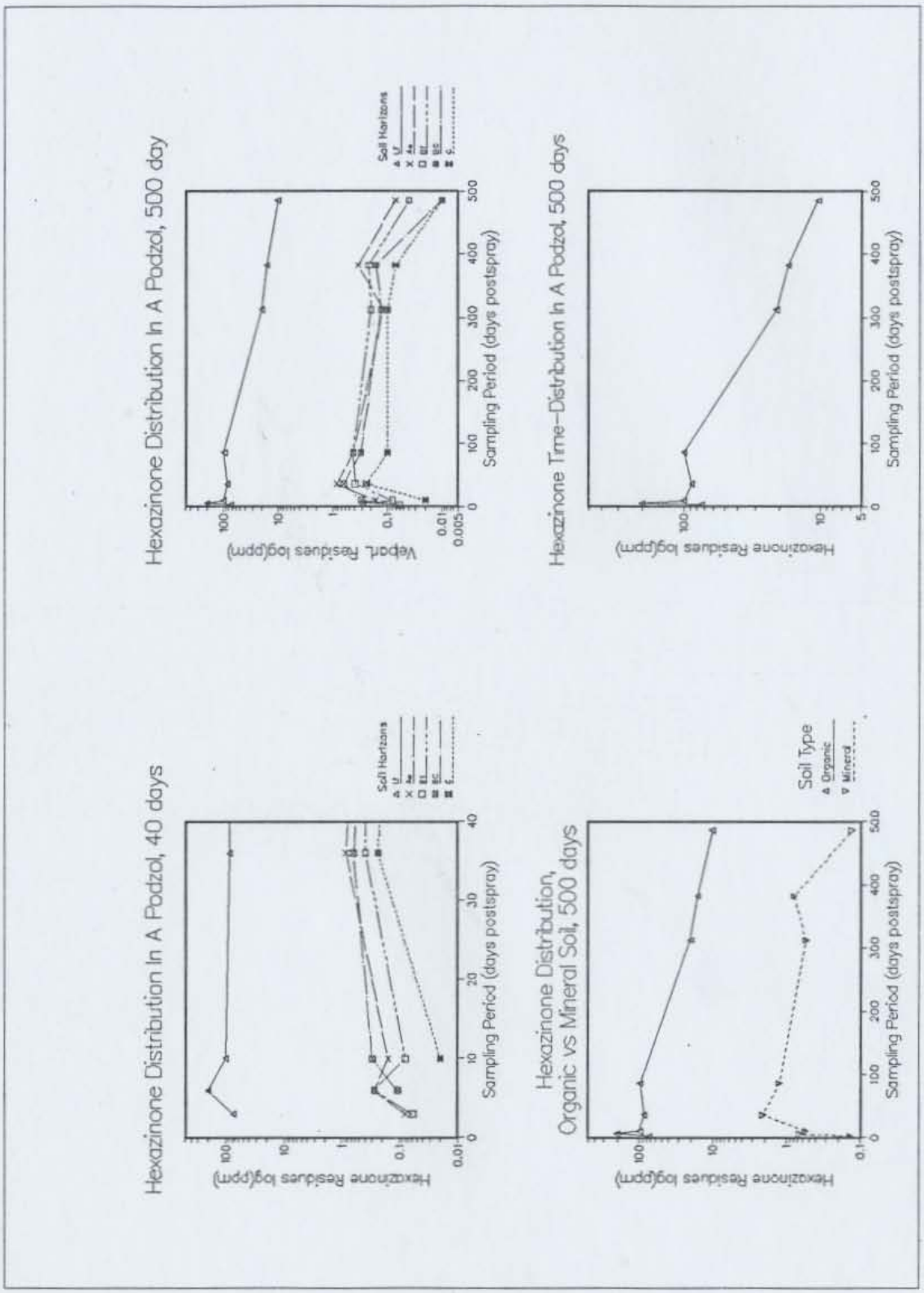

Figure 4-4: Unadjusted hexazinone residues

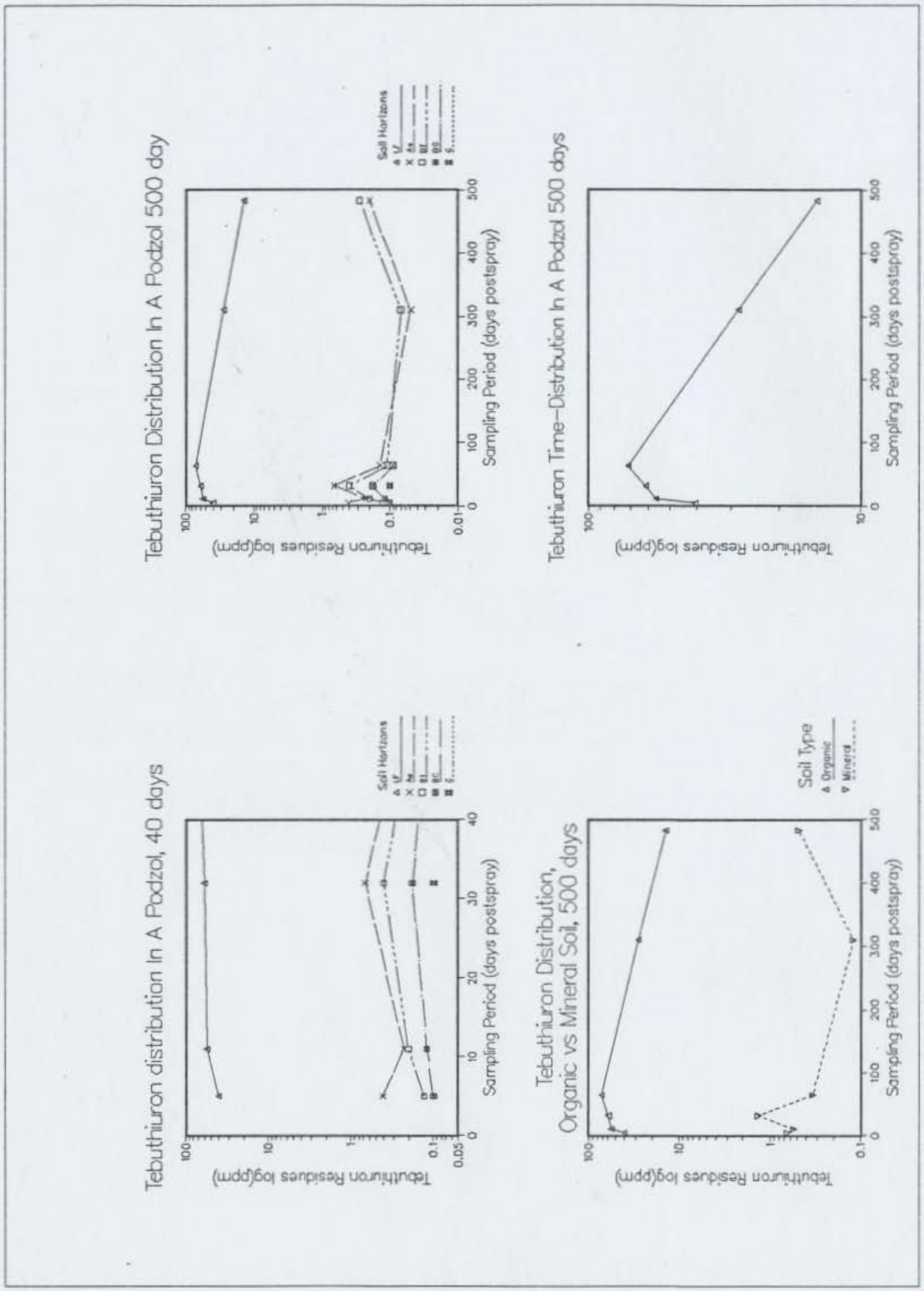

Figure 4-5: Unadjusted tebuthiuron residues

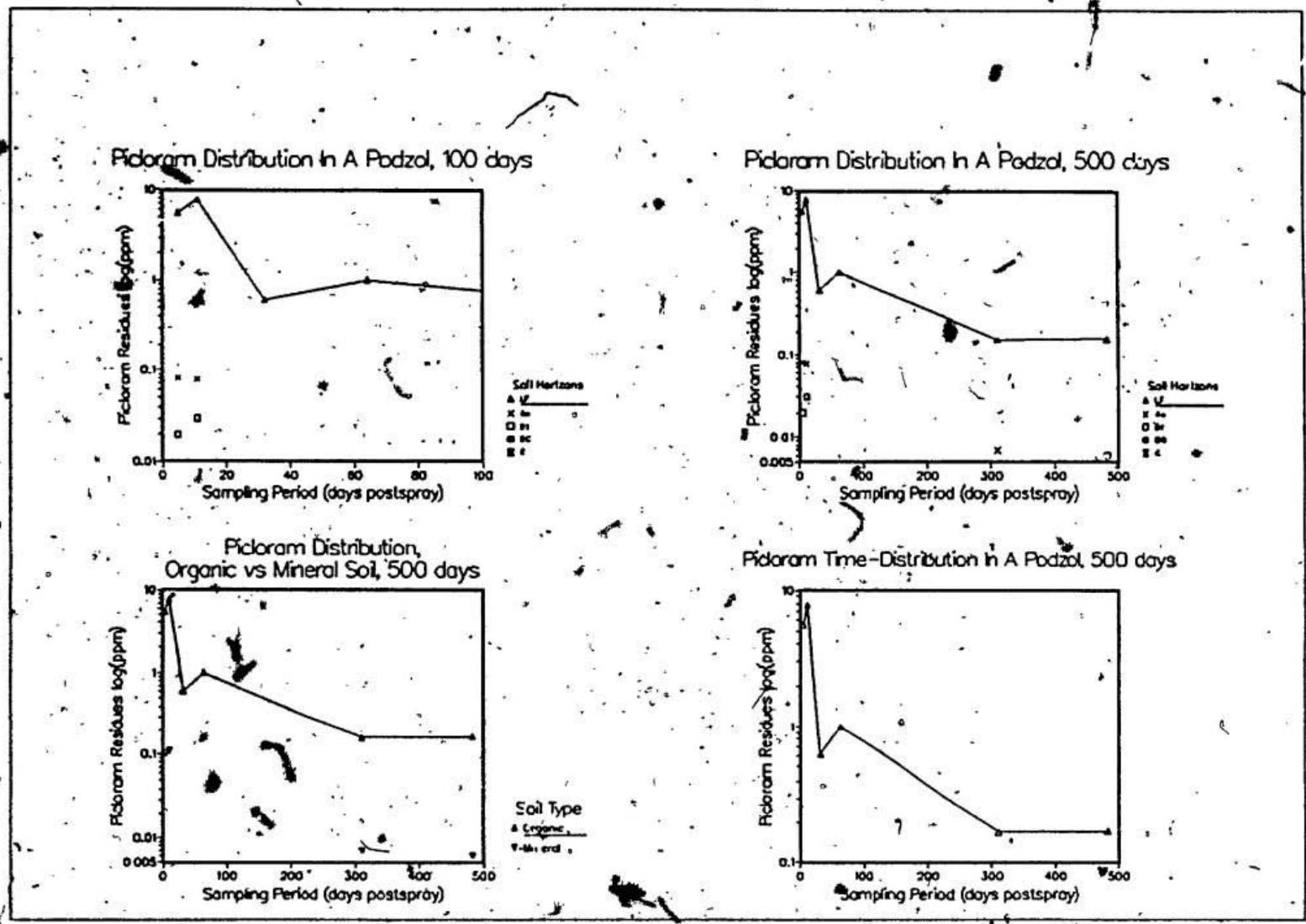

Figure 4-61 Unadjusted picloram residues

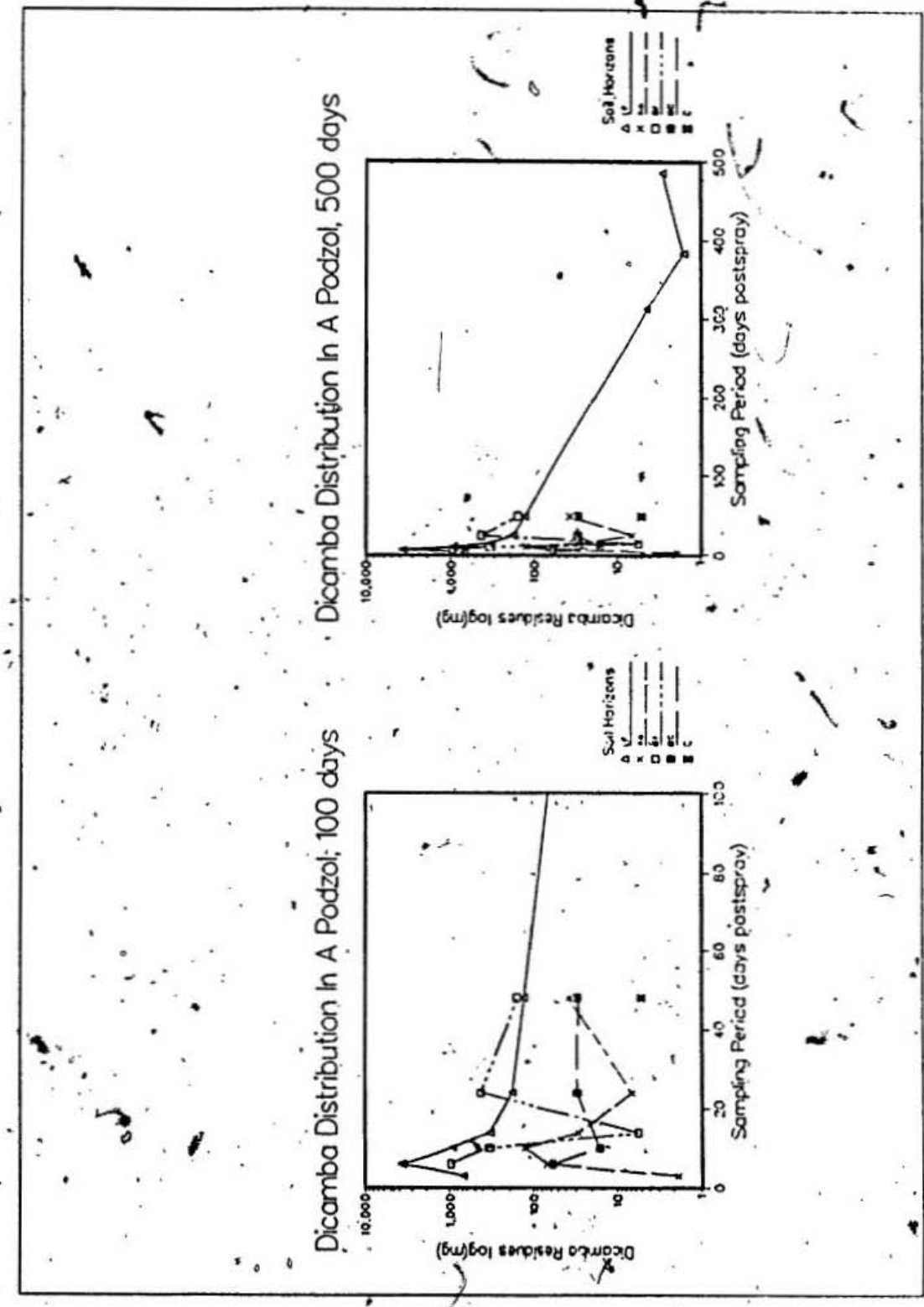

Figure 4-7: Adjusted dicamba residues

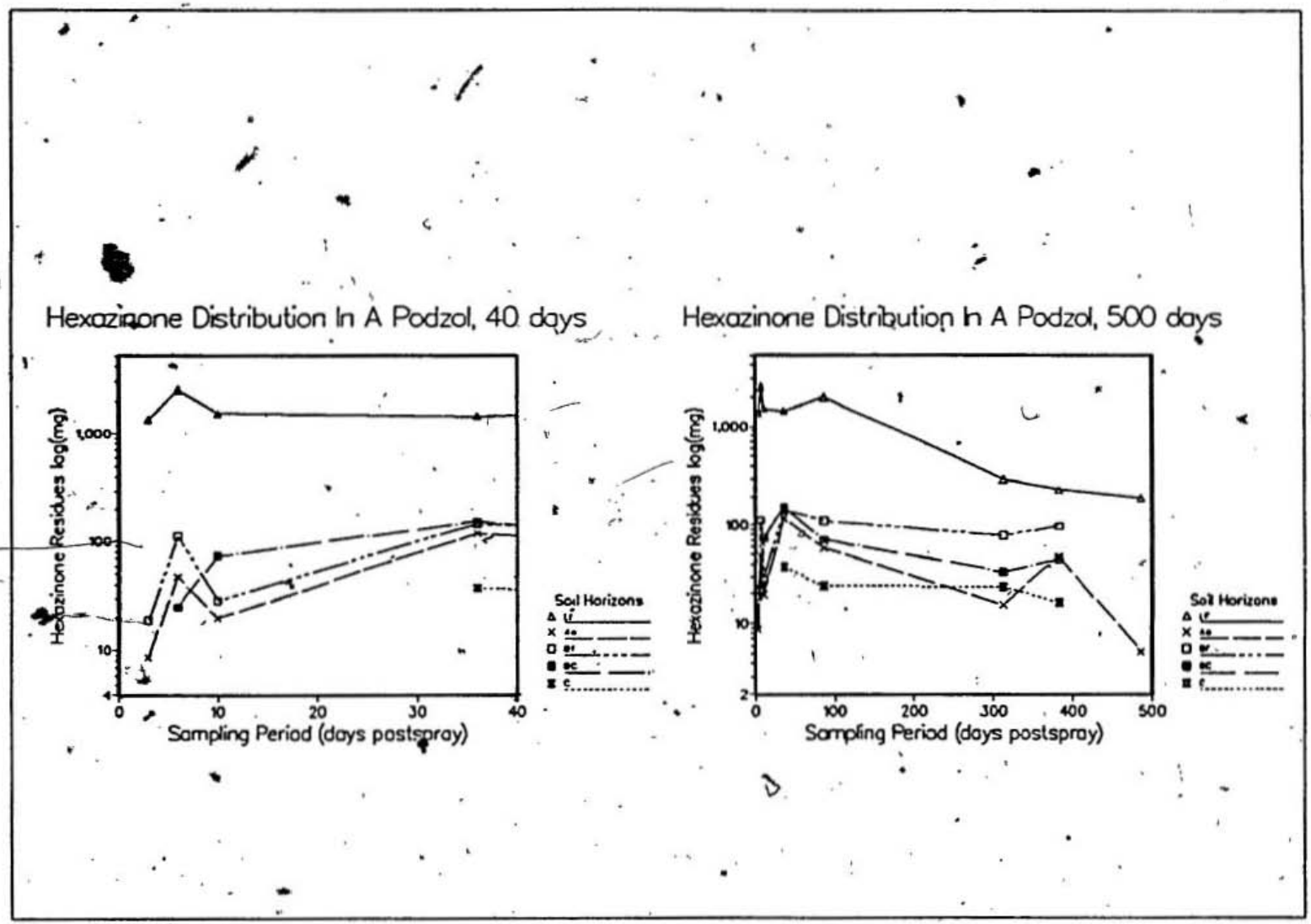

Figure 4-8: Adjusted hexazinone residues

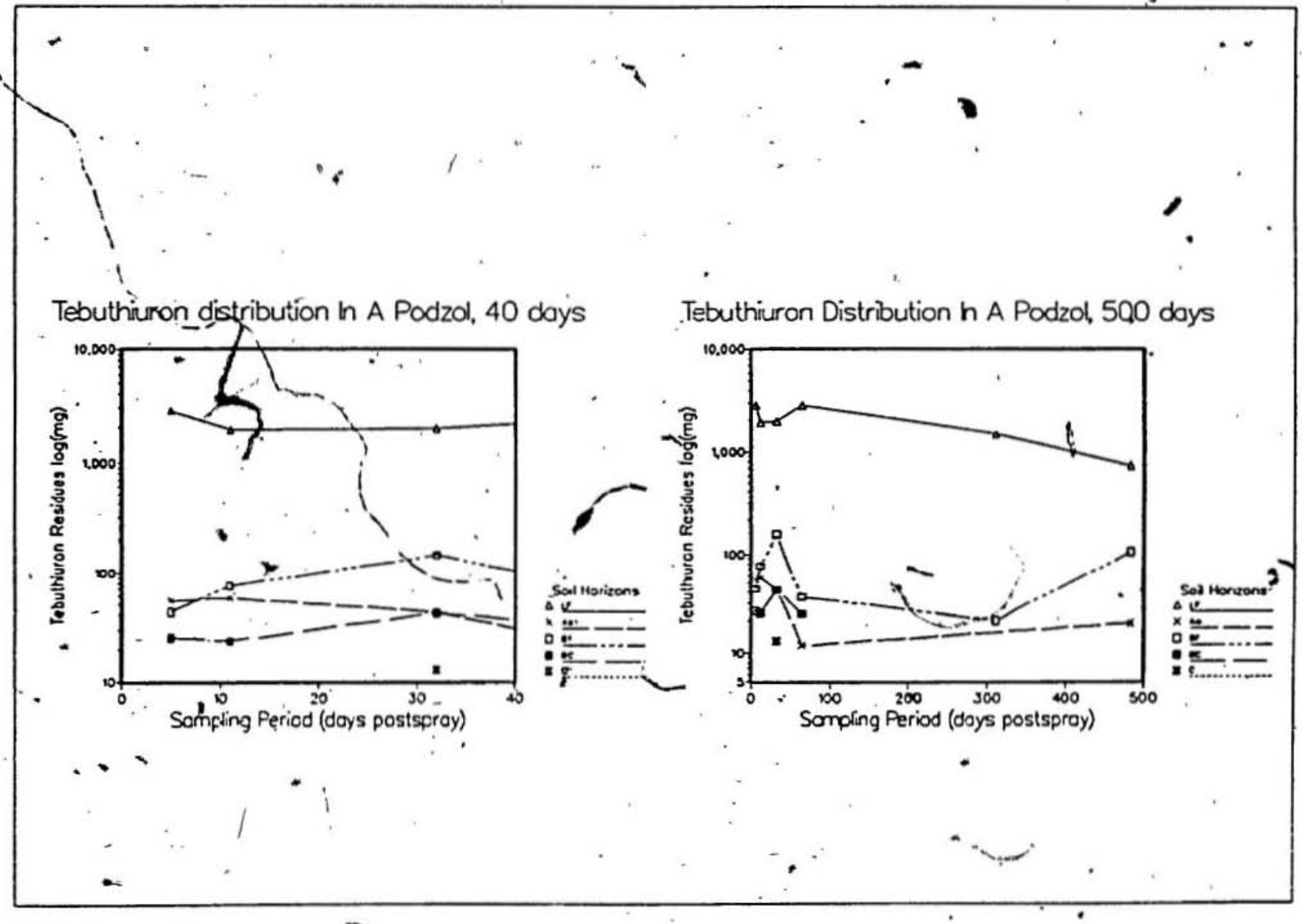

Figure 4-9: Adjusted tebuthiuron residues

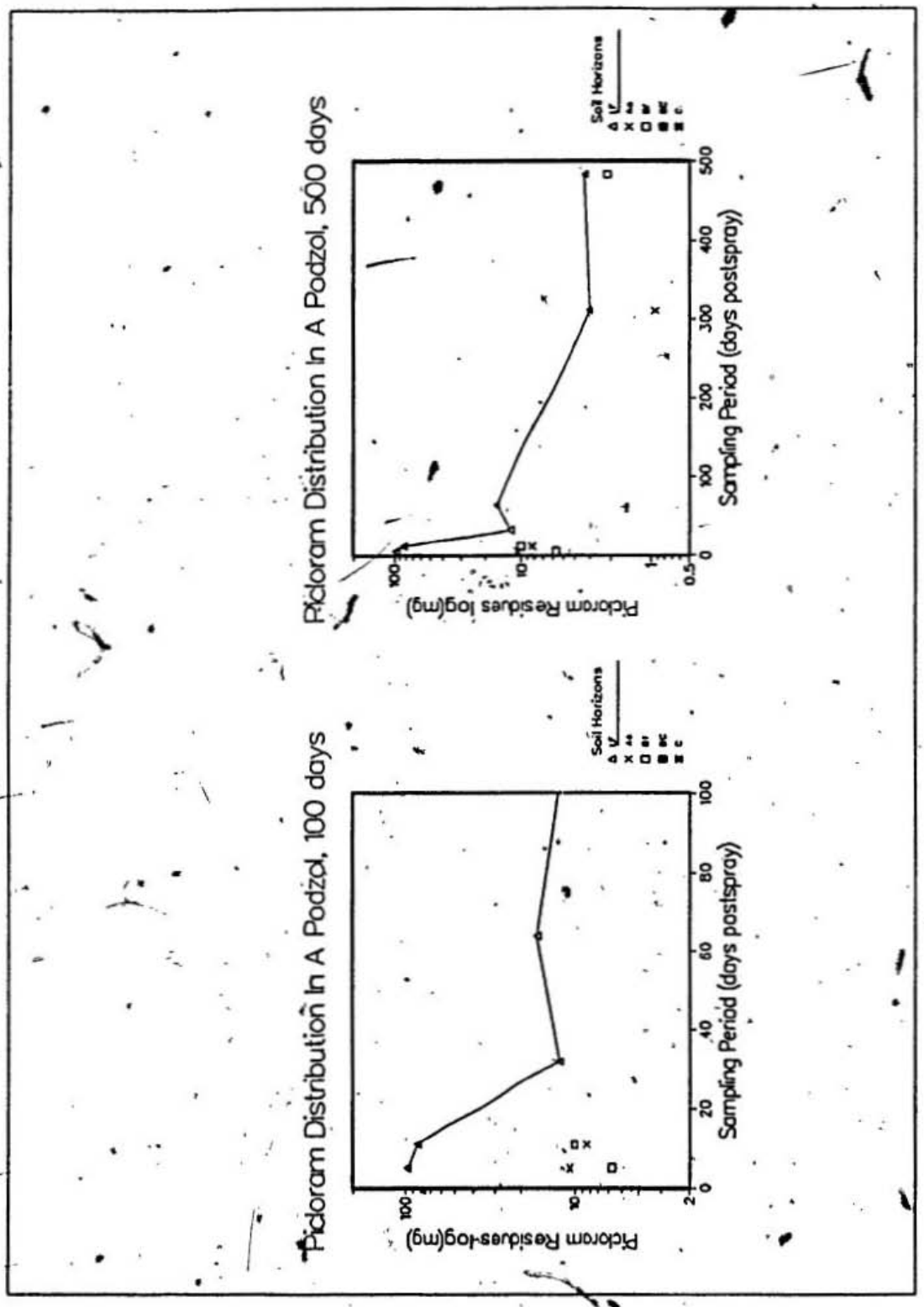

Figure 4-10: Adjusted picloram residues

the high LF values distinctly contrast with the low values of the four mineral layers, Ae through C. For dicamba this separation is distinct, though not as great as with the other compounds, and after day 14, the mineral soil residues increase to higher levels than those in the organic soil. This pattern ends after 34 days (post day 48), at which point mineral soil residues drop to below detectable levels making the separation extreme for the remainder of the sampling period. These high LF values (see Tables 4-6 through 4-9, pages 81 - 87 and Figures 4-11 through 4-14, pages 66 - 69) primarily occur because of the adsorptive characteristic of humic substances and other soil organo-metallic complexes (Grover, 1971, pp.417-418; Grover and Smith, 1974, pp.179-186; Khan, 1972, pp.1-12; Khan, 1980, pp.32-36; Morrill *et al.*, 1982, pp.170-172; Nearpass, 1976, pp.272-277; Weed and Weber, 1974, pp.39-65). The organic content of soils are most often represented by their organic carbon content which for this soil ranges as follows: LF 81.2-95.8, Ae 0.8-2.2, Bf 4.1-9.1, BC 1.3-2.8 and, C 0.8-7.7 %, respectively (see appendix H, page 135, for carbon content statistics). The contrast between the carbon content of the LF horizon, mean of 90.4 %, and the carbon content of the Ae through C horizons, mean of 2.72 %, is consistent with this pattern which continues throughout the entire experimental period of 486 days. It is unlikely that clay is more important than organic matter as a substrate for herbicide adsorption because of the small amounts found in this soil; 8.22, 8.81, 12.78 and 14.41 % clay in the Ae, Bf, BC and C horizons respectively (see appendix I, page 137 for results of particle size determinations). However, when one considers how very large clay's surface area to mass ratio can be its role in sorption may be significant. In addition, as the organic content decreases with depth the clay content increases, which may indicate that where organic matter contributes less and less adsorption sites with depth, clay is increasingly able to supply an alternative pool of adsorption sites.

Second, the pattern where residue values for the lower mineral layers (Bf, BC and C) increase over time can best be described as a displacement process. Initially, as the herbicides begin to move through, the soil the greatest quantities are detected in the LF layer (see Tables 4-6 through 4-9, pages 81 - 87). As time passes values for the LF layer begin to decline (post day 5 for picloram, day 6 for dicamba and hexazinone, and day 64 for tebuthiuron) and for relatively short periods, values for the Bf, BC and C horizons generally tend to increase (6 to 42 day range). This pattern continues for dicamba (day 14 to 20 for the Bf layer, day 10 to 48 for the BC layer and, day 48 for C layer), hexazinone (day 10 to 36 for the Ae, Bf, BC and C layers), tebuthiuron (day 5 to 32 for the Bf layer, day 11 to 32 for the BC layer and day 32 for the C layer), and picloram (day 5 to 11 for the Bf layer). These short periods indicate the movement of herbicide as a plug influenced by mass flow. When these periods end, there is a change away from this dominant plug pulsing pattern to patterns represented by other dissipation mechanisms. The actual shift away from the dominating process of mass flow is represented by the end points which terminate these intervals (days 48, 36, 32 and 11 for dicamba, hexazinone, tebuthiuron and

picloram, respectively). The evidence for the persistent nature of tebuthiuron is exhibited by the detection of residues in the Bf layer (day 310 and 483) and the Ae layer (day 483); and for picloram in the Ae layer (day 310) and the Bf layer (day 483). Whereas, for dicamba with a shorter half-life, no residues are detected in the mineral layers post day 48. The evidence for hexazinone, that residues are present in all horizons on day 312 and in the Ae layer on day 486, is more likely due to the high application rate than its kinetic half-life. Nonetheless, hexazinone residue levels decline for all horizons after the inflection point is reached (day 382). For the shorter lived dicamba, residue levels decline for all horizons post day 48. See table 1-3, page 17), for the compounds with the shorter half-lives. At this time the degradation factors begin to predominate over the distribution factors. That is, the displacement process has effectively ended, and any displacement of herbicide that may still be going on is being masked by the higher rate of degradation (dicamba and hexazinone). An anology to this displacement process, the notion of *translatory flow*, has been put forth by Hewlett and Hibbert (1967, pp.275-290). Translatory flow, as a component of interflow, is a process whereby soil water is displaced by the addition of new water to the soil, which under gravity and the physical property of water cohesion pushes the old water (antecedent soil moisture) down-slope. It can be described as a push-through process where momentum is generated by gravity and, where friction and evapotranspirational forces retard the push. According to Hewlett and Hibbert (*ibid.*, p.279), translatory flow predominates as a factor in the mid and lower portions of a slope but in the the upper slope areas it acts more as the pulse in soil moisture movement; the site lies on an upper slope with an overall grade of 23 %.

Third, the graphs generally exhibit very low values for the Ae layer, which by definition suggests that the leached "A" layer, or zone of eluviation, has a lower range of values than the "Bf" horizon, which as the illuviated layer is the zone of accumulation. As stated in the previous paragraph, residue values are initially the largest in the LF horizon and subsequently higher in the Ae horizon than in the adjacent Bf horizon. This pattern continues until the herbicide has pulsed through the profile and all available adsorption sites are occupied. After this has been achieved, herbicide movement begins to resemble the movement of amorphous humic substances and sesquioxides subject to the process of leaching. Henceforth, the pattern of lower values in the Ae than in the Bf horizon begin to materialize. This pattern of eluviation/illuviation occurs some time after day 3 and before day 6 and continues until day 48 for dicamba; after day 1 and continues until day 382 for hexazinone; after day 5 and before day 11 and continues until the last sample day (day 483) for tebuthiuron; and, after day 5 and before day 11 and continuing until before day 32, with some evidence that the process may continue up to day 483 for picloram. A characteristic of an eluviated "A" horizon is that it is deficient in substances such as organic carbon, nitrogen, mobile iron and aluminum, and clay. The tables presented in appendices J and

K (pages 140 and 144), show that for these substances their values are characteristically lower in the Ae than the Bf horizon. Thus, with respect to leaching, the selected herbicides appear to behave similarly to the previously mentioned amorphous substances.

4.4.2. Organic Versus Mineral Soil, Difference Of Adjusted Residues

The next set of figures (Figures 4-11 through 4-14, pages 66 - 69) portrays the difference between the total residue concentration detected (mg of a.i.) in the organic horizon (LF) and the total sum detected in the mineral horizons (Ae, Bf, BC and C). These figures facilitate an understanding of topics discussed in Subsections 4.4.1 and 4.4.3, pages 53 through 76. This graph exhibits the potential of the surface organic material as a buffer or primary sink limiting herbicide movement down through the soil. This potential becomes more evident when one examines the values presented in column six of Tables 4-6 through 4-9 which show that of residues detected a mean of approximately 84 % appear in the LF horizon.(n=29, LF values of column six).

4.4.3. Persistence, Sum Of Adjusted Residues

The final set of residue figures (Figures 4-15 through 4-18, pages 70 - 73) illustrate, for each herbicide, the sum of adjusted residues (common log of mg of a.i.) per profile as distributed over time. These graphs give a more comprehensive pattern of herbicide persistence independent of any between horizon variation. In general there are three trends to note on these graphs:

1. A lag period of 6 to 64 days from the time of application to the time of peak (the time of highest residue values detected); with the exception of picloram which does not display this pattern.
2. A relatively quick decline of residue values in 4 to 64 days following the time to peak (except for tebuthiuron).
3. A slower decline of residue values over the balance of the sample period (more than 400 days) as indicated by the minor decrease in slope.

These graphs are then described by regression equations (see Table 4-2, page 77) which allow interpolated predictions of either X or Y (days postspray or mg of adjusted residues, respectively). These equations are then used to compute the 50, 75, 90 and 95 % disappearance times (referred to as DT_{50}, DT_{75}, etc.) which are listed in Table 4-3, page 78.

The first phase of the distribution shows the lag where for dicamba and hexazinone there is a six day period to peak. The period to peak takes longer for tebuthiuron (64 days) and is not apparent for picloram unless it occurs before day 5. This initial phase may best be described as the equilibration period and can be interpreted as errors caused by one or both of the following two courses of events.

First, the herbicides were applied on two calm dry days in July 1983 (21st and 22nd) and the

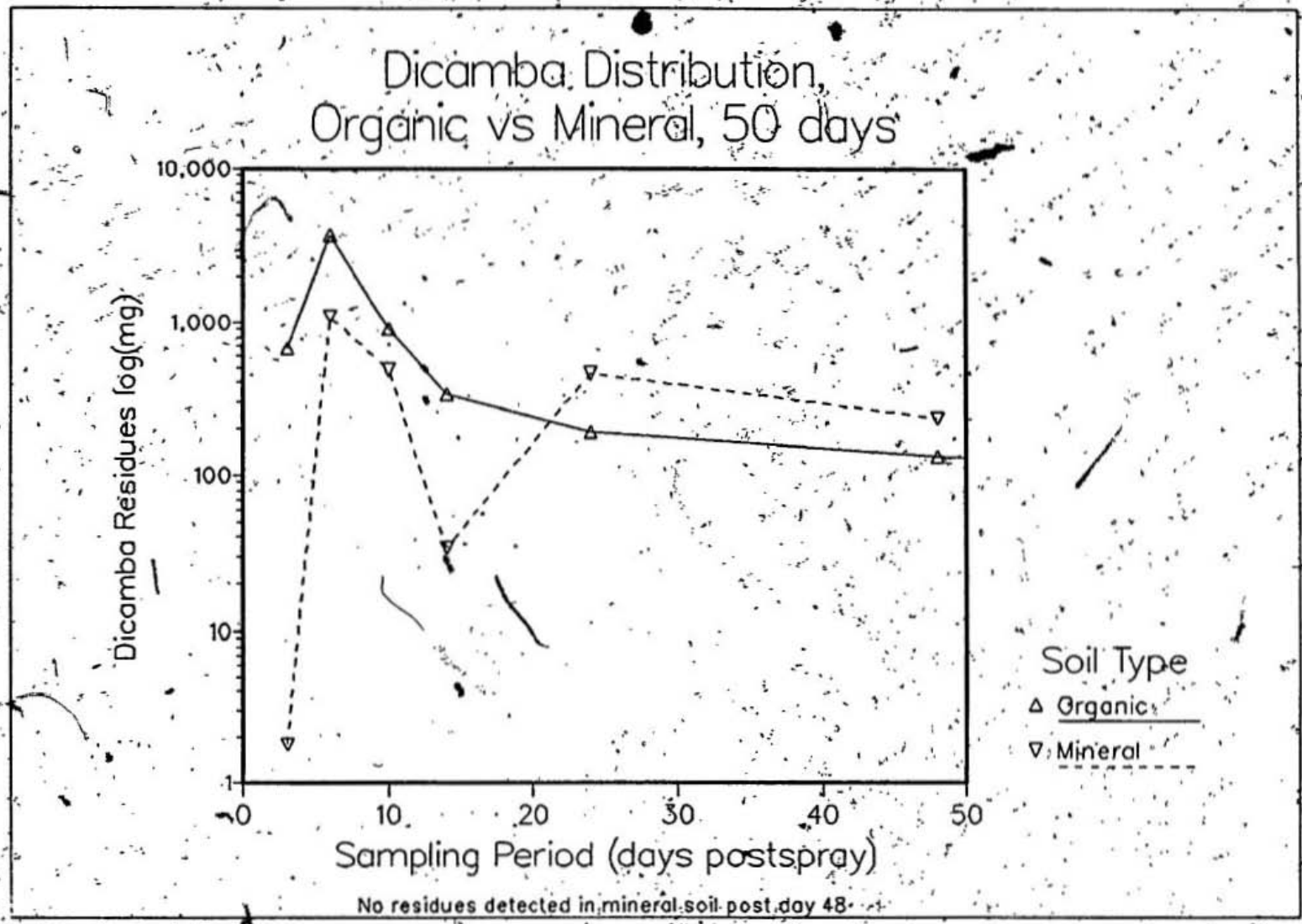

Figure 4-11: Organic versus mineral dicamba distributions

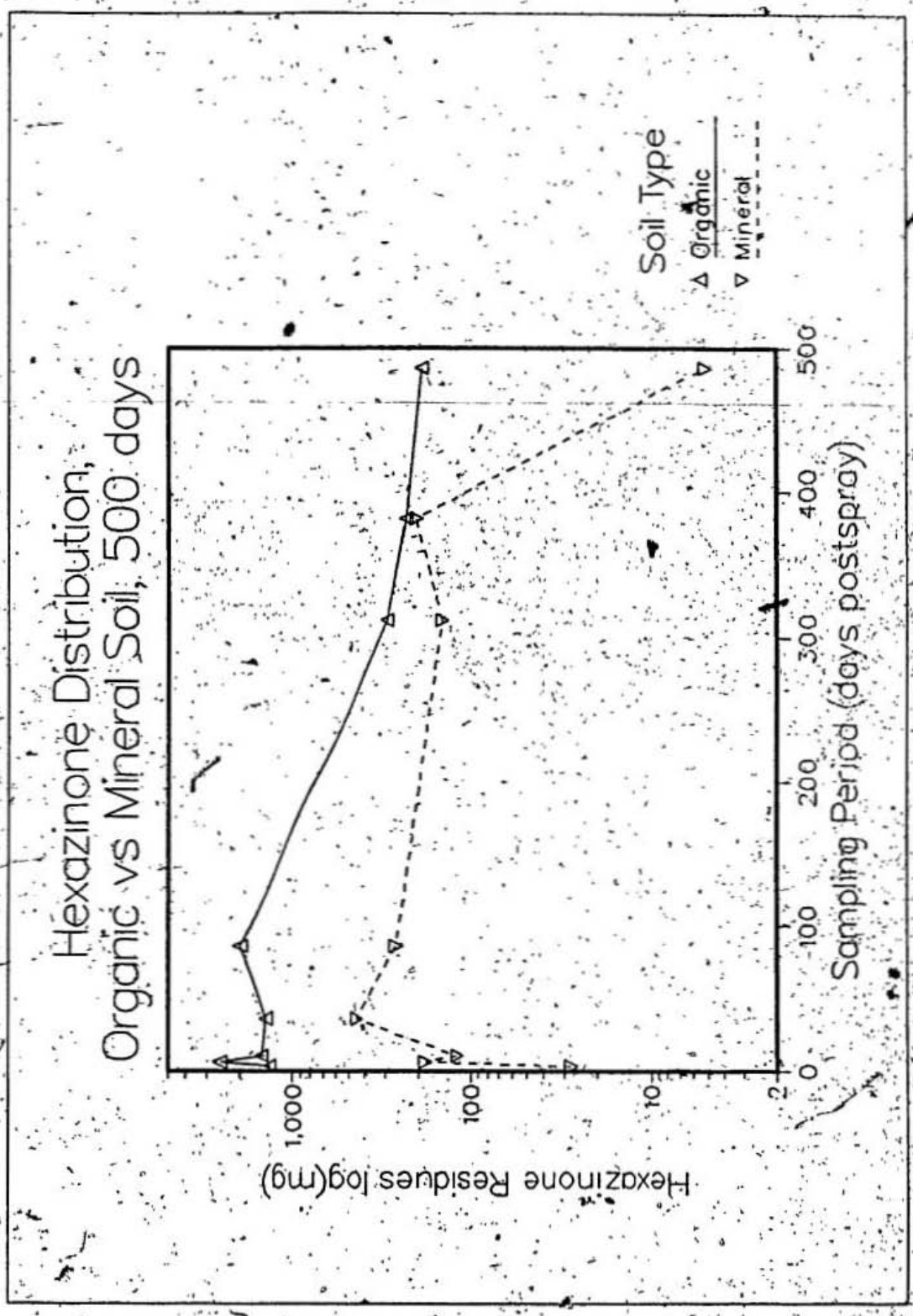

Figure 4-12: Organic versus mineral hexazinone distributions

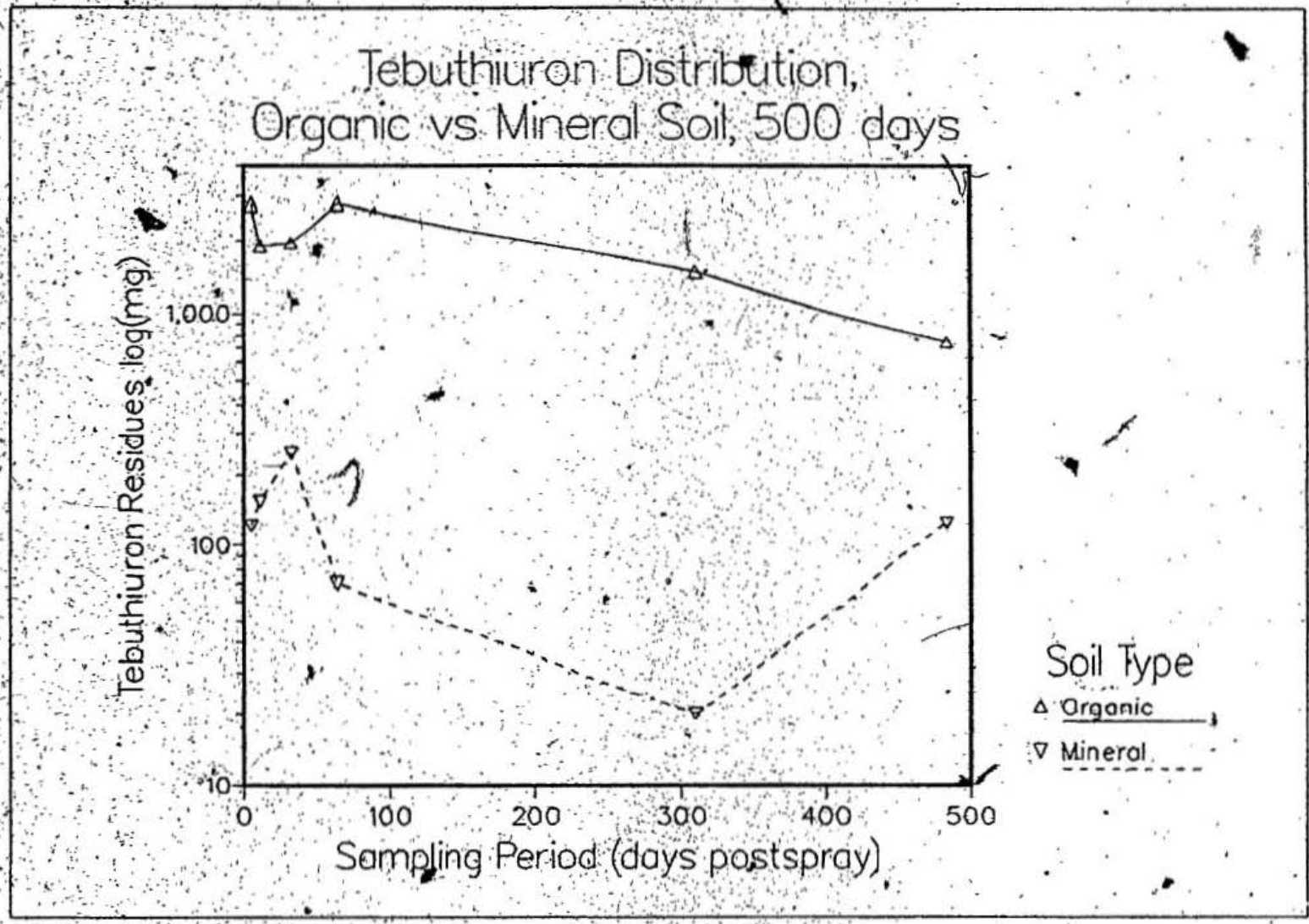

Figure 4-13. Organic versus mineral tebuthiuron distributions

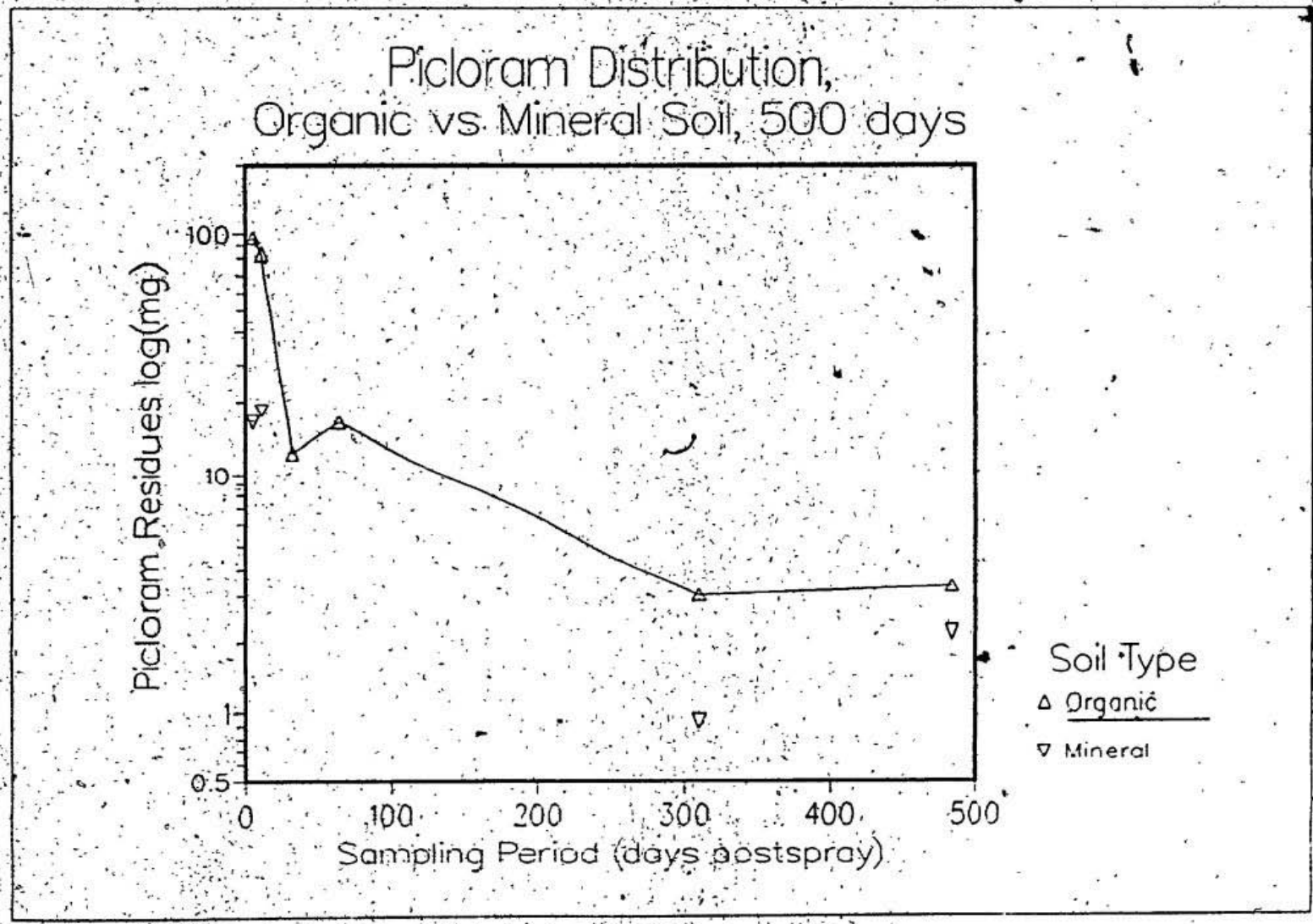

Figure 4-14. Organic versus mineral picloram distributions.

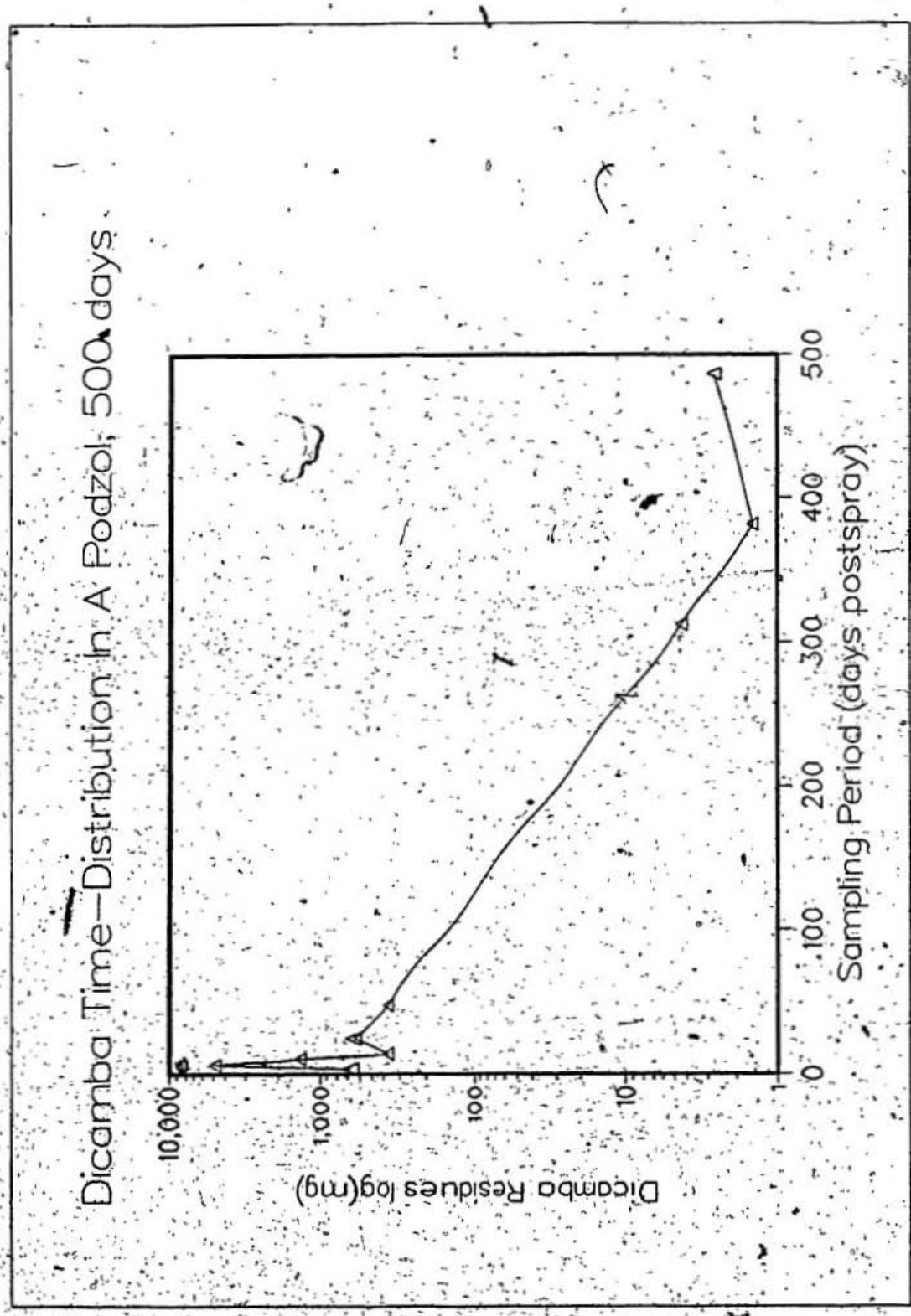

Figure 4-15: Dicamba time distribution

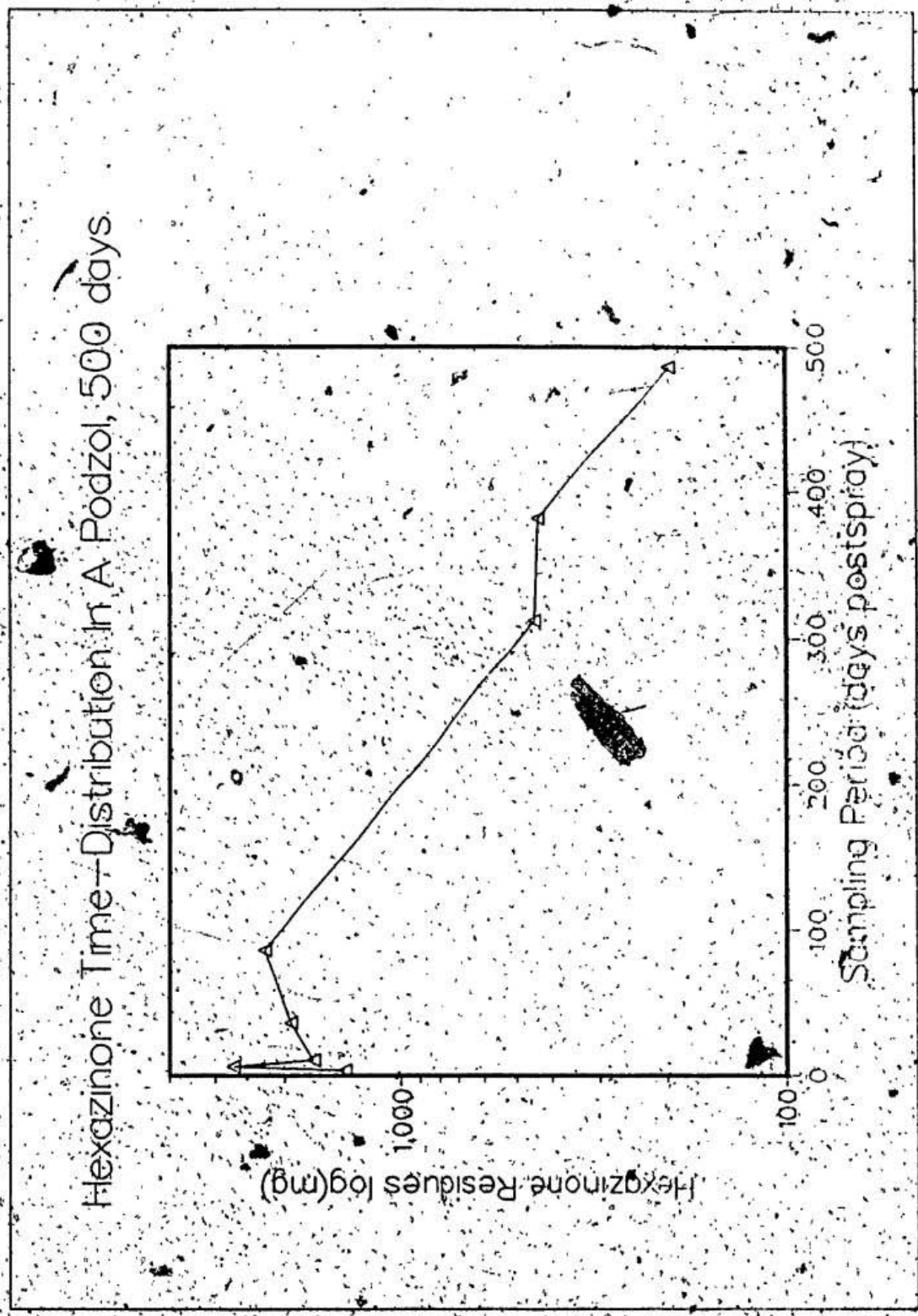

Figure 4-16: Hexazinone time distribution

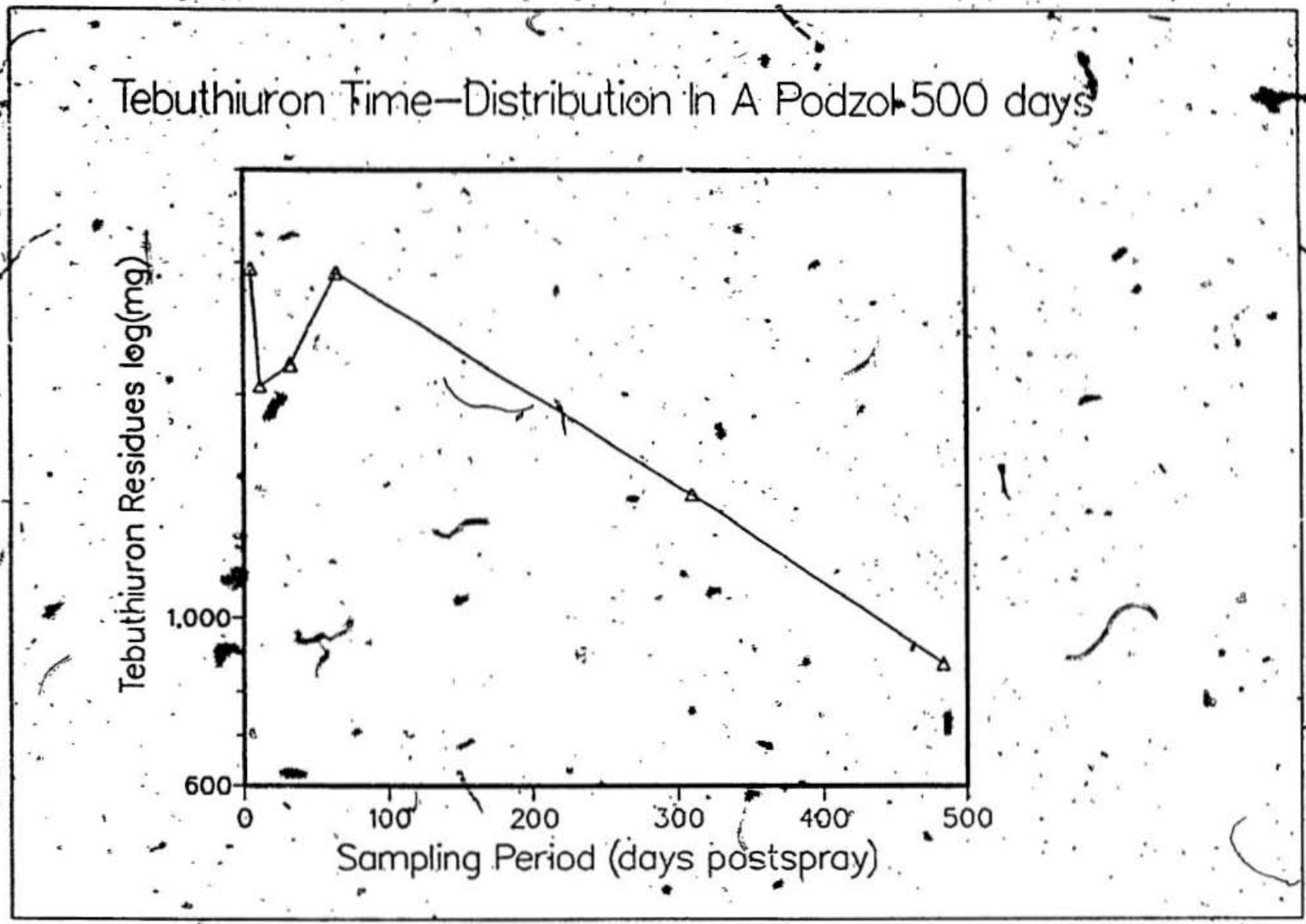

Figure 4-17. Tebuthiuron time distribution

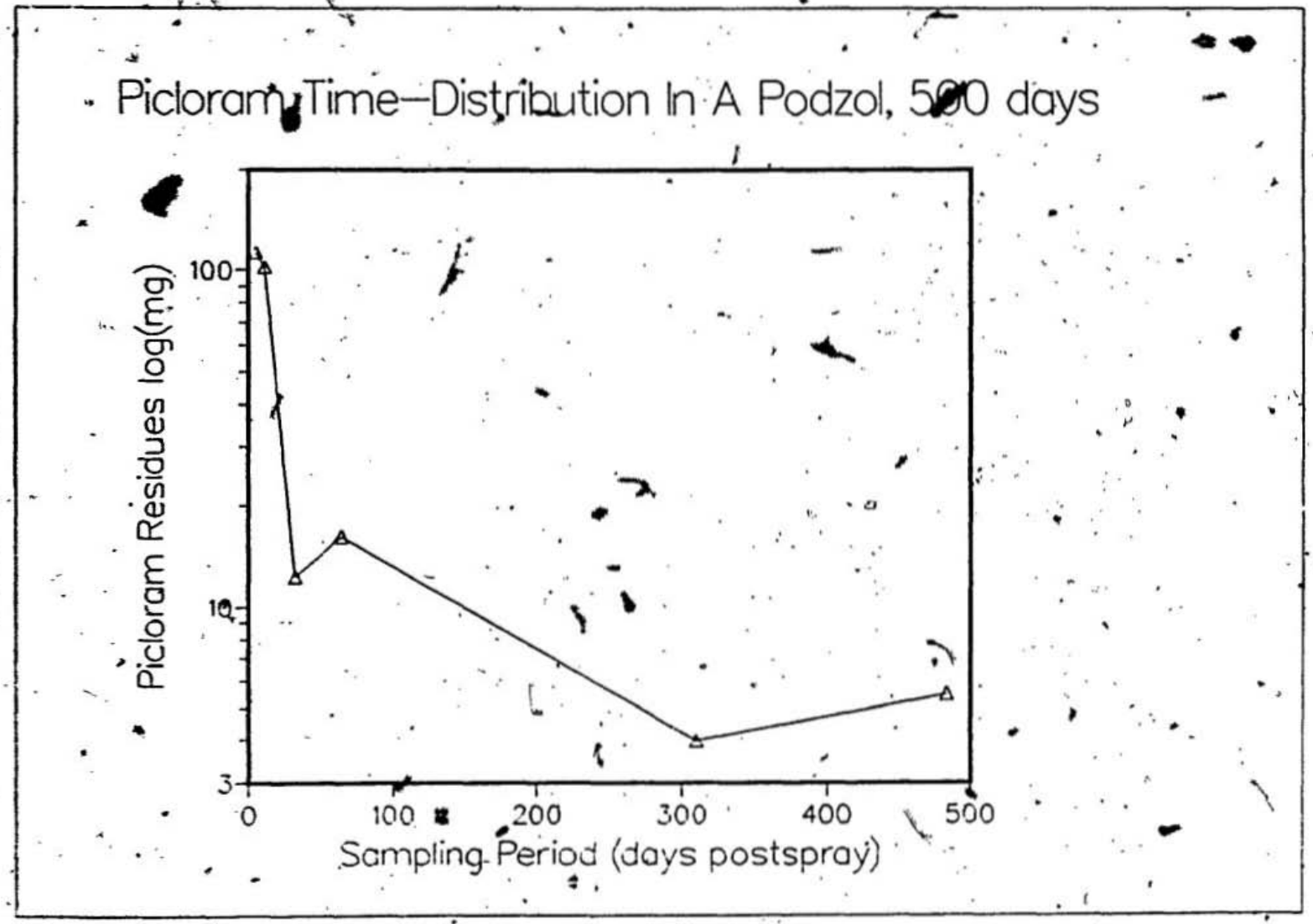

Figure 4-18: Picloram time distribution

first samples were taken after the first storm event. Prior to the rain, the herbicide remained in a dry soil with a soil moisture deficit[12] of 0 and -1 mm for July 21 and 22, respectively. The cumulative rainfall graph which follows clearly outlines the precipitation events recorded on site facilitating the ensuing interpretation (Figure 4-19, page 75). The first rain event on July 23 (day 1 and 2) added 2 mm of precipitation to the soil which did little to increase soil moisture storage but did promote the diffusion of herbicides through the LF, Ae and Bf horizons (Tables 4-6 through 4-9). The next event on July 26 (day 4 and 5) added 26 mm of precipitation which brought the soil moisture storage up from 108 to 131 mm, still below the soil's moisture holding capacity but substantial enough to distribute the herbicides through the soil profile. Similarly, by August 3 (day 11 and 12), the second sample point for tebuthiuron and picloram, 14.9 mm of rain had accumulated, 50 % of which had fallen during the 24 hours prior to sampling. Thus, diffusion and mass flow had distributed the herbicides over a greater surface area of soil particles decreasing the number of hot and cold spots and consequently improving the reliability of the composite samples. This may hold even more so for the organic layer which because of its sponge-like hydrophillic nature could initially account for a more variable distribution (Figures 4-7 through 4-10 and 4-11 through 4-14) and significantly higher values.

Second, due to the dry condition of the soil, the majority of herbicide remained on the surface with negligible downward movement other than by diffusion and some unknown loss through volatilization and photodegradation. Furthermore, it is likely that the sampling tools (shovels, picks, trowels and plastic lined pails) were contaminated with an unknown proportion of the herbicide. This unknown quantity of herbicide would be lost to detection when cleaning the tools (see page 43, for cleaning procedure) and lost because of adsorption to the inner surface of the disposable plastic bags used to line the pails. If such quantities of herbicides were lost in this way, then an account of the balance could have only been made if the contaminated cleaning solution and plastic liner bags were also analized for residue concentrations.

The second phase of the distribution which shows the steep slope following the peak lasts 4 days for hexazinone, 8 days for dicamba, 53 days for picloram, and does not occur for tebuthiuron. The interpretation of this pattern results in distinguishing the following five factors. First, that a small amount of herbicide has bound to soil colloids and is not easily extractable for detection. Second, that there may be a loss of herbicide out of the sample area through mass flow and/or volatilization. Third, that a larger portion of herbicide has diffused through the soil, complexed and been adsorbed by organometallic compounds thus occupying the majority of available adsorption sites, the balance of which are free to move. Fourth, even greater quantities

[12] Calculations were made using Thornthwaite's method for computing the water balance for a 150 mm soil moisture holding capacity (Thornthwaite and Mather, 1957). The figures change to -1 and -2 mm for a 200 mm soil moisture holding capacity.

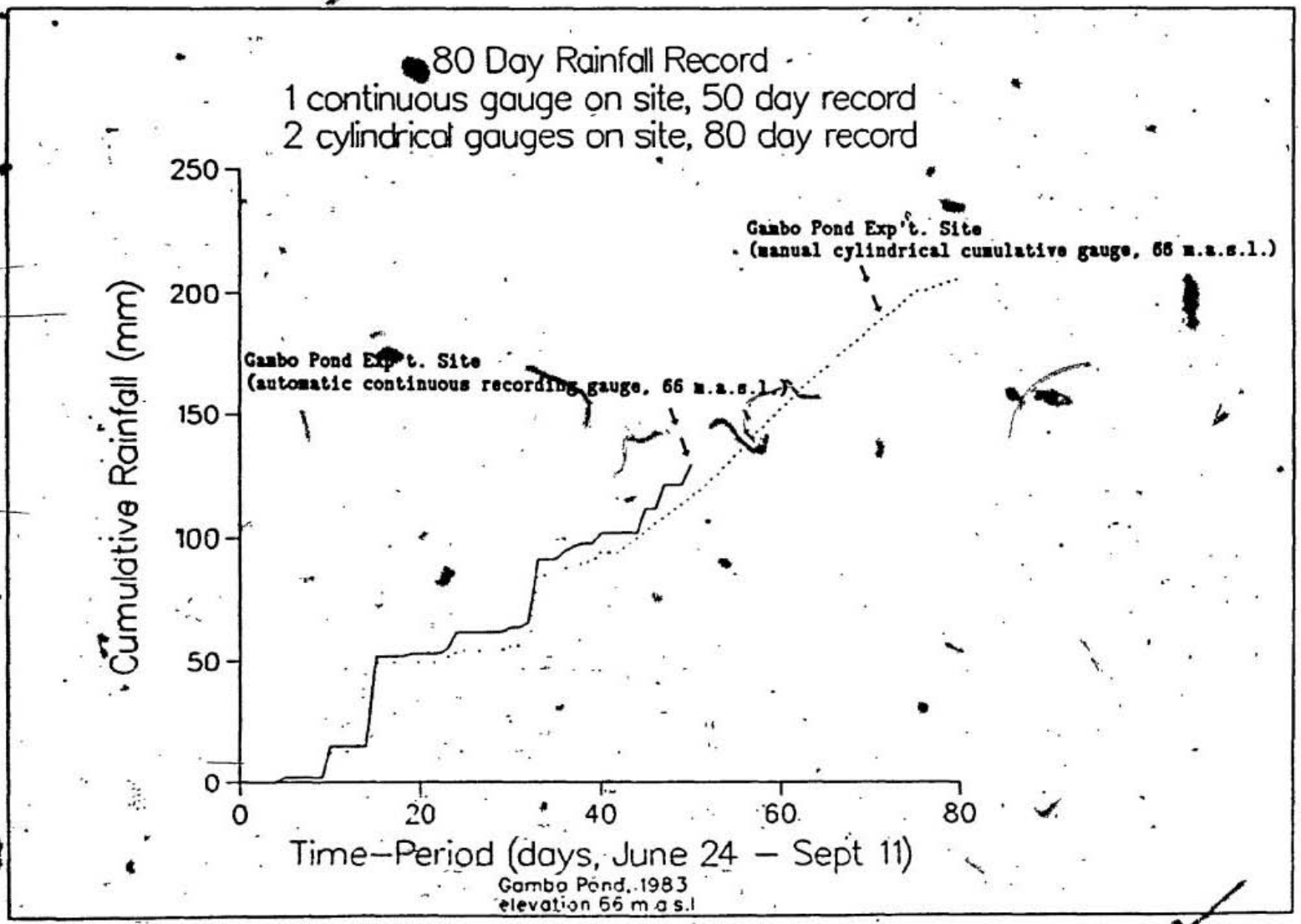

Figure 4-10: Precipitation record, experimental site, summer 1983

of herbicides are performing the task for which they were designed via the uptake and metabolic activity of the target plant species. Fifth, but not least, the original compounds are being transformed into degradation by-products and secondary metabolites by the soil microbiota which has been able to adapt to the new substrates. All these factors are considered as *sinks* and are therefore losses which are not accounted. Though bound residues are adjusted for by appropriate recovery rates, it is not possible to guarantee a specific level of recovery for all bound residues, as small a quantity as they may be. The problems that analytical laboratories have in recovering 100 % of the pesticide applied is exemplified by the results of the blind spike tests shown in Table 4-4, page 79.

The third phase of the distribution exhibits the trend of a slow decline of residue values over the balance of the sample periods which takes, at least, 469 days for dicamba, 476 days for hexazinone, 451 days for tebuthiuron and, 419 days for picloram. This pattern indicates that a number of events must have occurred. First and foremost, there is the ongoing degradation by the soil microbiota. Second, the efficacy of the product has had its major impact on the target species. Third, desorption from soil compounds is continuing but at a decreasing rate. In addition, the natural kinetic degradation of the product is becoming an increasingly greater factor in its disappearance and finally, loss out of the sample area has diminished.

4.4.4. Unadjusted And Adjusted Residue Data

The data for all of the unadjusted and adjusted graphs discussed above can be found in Tables 4-6 through 4-9 (pages 81 - 87). These tables present: The mean horizon thicknesses in cm (rounded to the nearest centimetres, column one), the sample size used to determine the mean horizon thicknesses of column one (count, n, column two), the mean horizon range in cm (centimetres, column three), the data as received in ppm (parts per million, column four), the data as adjusted in mg of a.i. per the above factors (mg of a.i., column five), the distribution of residues in each horizon as a percent relative to the total detected for the associated sample day (percent, column six), and the residues detected as a percent of the total herbicide applied to the ground surface (percent, column seven).

4.5. Graphical Regression And Disappearance Times

Table 4-3 (page 78) is an empirical index in days for a 50, 75, 90 and 95 % reduction in soil residues for the soil profile sampled as a whole. The disappearance times (DTs) given are based on two levels of concentration: In the first set, the DTs are based on the onetime herbicide application at the onset of the experimental period. In the second set, the DTs are based on the total amount of herbicide (sum of LF through C horizons), for a particular day, taken as the maximum detected over all sample days. This allows for a comparison and contrast of values expected (initial rate of application) and values observed (maximum rate detected). It is most likely that the true values, though an unknown identity, fall in the interval between the two calculated DTs. It should be noted that the DTs are only relevant for the concentration of herbicides given, the environmental conditions under which the experiment was conducted and the time period that the herbicides were monitored for (Hamaker,J.W., 1972, pp.276-279).

Table 4-2: Descriptive Regression Equations

Herbicide	Equation	Residual Mean Square	Remarks
Dicamba	$\log(Y_i) = 4.9892 - 1.7386 \times \log(X_i)$	0.1025	
	$\log(X_i) = 2.8156 - .54817 \times \log(Y_i)$	0.0325	n = 8
		corr.= -.976	
Hexazinone	$Y_i = 3.3006 - .00216 \times \log(X_i)$	0.0118	
	$X_i = 1408.0 - 439.06 \times \log(Y_i)$	2396.3	n = 7
		corr.= -.975	
Tebuthiuron	$Y_i = 3.5060 - .00114 \times \log(X_i)$	0.0012	
	$X_i = 3034.8 - 864.66 \times \log(Y_i)$	917.06	n = 4
		corr.= -.994	
Picloram	$\log(Y_i) = 2.6728 - .77463 \times \log(X_i)$	0.0249	
	$\log(X_i) = 3.3830 - 1.2400 \times \log(Y_i)$	0.0399	n = 5
		corr.= -.990	

4.6. Spiked Samples

Table 4-4 shows that for hexazinone and tebuthiuron the spiked samples yield values close to the expected level. This can be interpreted as the utilization of stringent and effective sample preparation procedures prior to detecting herbicide residues in the laboratory. On the other hand, the detected levels for dicamba are significantly lower and for picloram they are significantly higher than the expected levels of detection. This may mean that the dicamba results are underestimated by more than the stated recovery rates, and that the picloram results may be overestimated. For dicamba, hexazinone and tebuthiuron, the uniformly spiked soil samples

Table 4-3: 50, 75, 90 & 95 Percent Disappearance Times For Four Selected Herbicides

Herbicides			Disappearance Time (days@) All Horizons			
Name	Application Rate, kg/ha &	Concentration+	50 %	75 %	90 %	95 %
Dicamba	7.6	1x	25	37	61	89
Hexazinone	10.5	11x	186	318	492	•
Tebuthiuron	8.8	1x	•	•	•	•
Picloram	2.1	1x	7	18	55	131
Name	Maximum Rate Detected kg/ha $	Concentration+	50 %	75 %	90 %	95 %
Dicamba	48.3	6.3x	9	13	22	32
Hexazinone	27.0	15.2x	123	255	430	•
Tebuthiuron	29.4	8.8x	296	•	•	•
Picloram	1.1	0.5x	16	38	119	281

@ = rounded to the nearest day.
kg/ha = kilograms of active ingredient per hectare.
+ = concentration rates are n times the commercially suggested maximum.
• = days computed to be greater than 500 days; only values within the range of given data are valid.
& = disappearance times based on the initial rate of application.
$ = disappearance times based on the maximum herbicide detected over all sample periods.

(homogeneous) generally tend to be lower than those samples which were spiked with a single spot placed in the center of its mass (heterogenous). One interpretation of this pattern is that it is quite possible that, when preparing the soil samples for analysis, the laboratories did not mix the soils as uniformly as possible. This pattern is reversed for picloram (homogeneous > heterogenous) which makes one think that the spot samples were composed of a greater quantity of soil that was not contaminated with picloram. This could be an indication of a soil not well mixed or of a chemical strongly bound to very few soil particles. Table 4-4 below, does not show any obvious relationship between horizon and recovery results, whether it is or is not in conjunction with type of spike (homogeneous vs heterogenous). The difference between mean homogeneous and heterogenous values changes from 5 to 16 to 18 to 24 % for tebuthiuron, dicamba, hexazinone and picloram, respectively. In the final analysis this may suggest that all the samples are well mixed for tebuthiuron, less so for dicamba and hexazinone and, least of all for picloram.

Table 4-4: Results of Spiked Samples

Herbicide	Horizon	Sample Spiked For Detection Level Of (ppm)	Type Of Spike	Actual Detection (ppm)	Percent Recovery (%)
Dicamba	LF	0	none	0.01	err
	Ae	1	homo	0.27	27
	Bf	1	hete	0.43	43
Hexazinone	LF	0	none	<0.02	<0
	Ae	1	homo	0.78 (0.97)	78 (97)
	Bf	1	hete	0.97	97
	BC	1	homo	0.93	93
	C	1	hete	1.20	120
Tebuthiuron	LF	0	none	n.d.	0
	Ae	1000	homo	1100	110
	Bf	1000	hete	1100	110
	BC	1000	homo	1200	120
	C	1000	hete	1300	130
Picloram	LF	0	none	n.d. (n.d.)	0 (0)
	Ae	1	homo	1.42 (1.60)	142 (160)
	Bf	1	hete	1.07 (1.58)	107 (158)
	BC	1	homo	1.55 (1.79)	155 (179)
	C	1	hete	1.39	139

n.d. = none detected.
none = soil not spiked with herbicide.
homo = soil uniformly spiked with herbicide. Soil is spread over a sheet of aluminum foil, the spike solution is then evenly pipetted over the soil as if a fine grid is superimposed, soil is then mixed on the foil, placed in bag, mixed some more and finally sealed.
hete = soil spot spiked with herbicide in center of mass. Soil is clumped in bag, a hole is made to the center of the mass, the spike soution is pipetted in the center and bag is then sealed.
err = detection limit < 0.01 ppm, thus there should be none detected.
<.02 = below detection limit, i.e., none detected.
( ) = bracketed values are duplicates.

4.7. Raw And Transformed Data

Tables 4-6, 4-7, 4-8 and 4-9, (pages, 81, 83, 85 and 87) present in seven columns, for each horizon of the four selected herbicides, the results as described in Subsection 4.4.4, page 76. The sixth column, "Horizon mg As Percent Of Total mg", gives figures describing the distribution of residues within the profile for the specified sample point; these values add up to 100 %. The seventh column, "Percent Of Total Applied Herbicide", presents the residues detected for each horizon and for the sampled soil profile as a whole (*i.e.*, Totals), as a percentage of the original amount of herbicide applied to the soil surface. This indicates the herbicide's persistence; these values should add up to less than 100 %. The percent of the applied herbicide in column five for the mineral horizons (Ae to C) is also representative of that herbicide which has leached from the surface LF horizon. Table 4-5, presents the raw data for the 2,4-D which has not been used because of the reasons given on page 45.

Table 4-5: 2,4-D Residues: Raw data in parts per million

	Unadjusted Residues (ppm)$		Unadjusted Residues (ppm)$
DAY: 3		DAY: 14	
LF:	.041	LF:	.013
AE:	.093	AE:	.055
BF:	.077	BF:	.021
BC:	0.0	BC:	0.0
C:	0.0	C:	0.0
Totals:	.211	Totals:	.089
DAY: 6		DAY: 24	
LF:	69.000	LF:	21.000
AE:	0.0	AE:	.014
BF:	.008	BF:	.006
BC:	0.0	BC:	0.0
C:	0.0	C:	.010
Totals:	69.008	Totals:	21.030
DAY: 10		DAY: 48	
LF:	.067	LF:	.430
AE:	.007	AE:	0.0
BF:	.006	BF:	.013
BC:	0.0	BC:	0.0
C:	.008	C:	0.0
Totals:	.090	Totals:	.443
		DAY: 98•	

$ = Expressed on a fresh weight basis and not corrected for recoveries.
• = Eco-Research Laboratories did not send the results for day 98 (i.e., not received) even after numerous requests had been made.

Table 4-6: Dicamba Residues: mean horizon thickness, ppm, mg, percent of total mg per sample date, and percent of total herbicide applied

	(1) Mean Thickness (cm)	(2) Horizon Count (n)	(3) Range (cm)	(4) Unadjusted Residues (ppm)$	(5) Adjusted Residues (mg)&	(6) Horizon mg As Percent Of Total mg$	(7) Percent Of Total Applied Herbicide+
DAY: 3							
LF:*	6	1	n.a.	11.40	670.9	99.7	81.87
AE:	8	1	n.a.	.01	1.8	.3	.22
BF:	29	1	n.a.	n.d.	0.0	0.0	0.0
BC:*	0	0	0	0.0	0.0	0.0	0.0
C:*	0	0	0	0.0	0.0	0.0	0.0
TOTALS:	43	3	n.a.	11.41	672.7	100.0	82.08
DAY: 6							
LF:*	8	1	n.a.	35.70"	3736.6	77.4	455.83
AE:	8	1	n.a.	.36	66.9	1.4	8.16
BF:	35	1	n.a.	1.08"	968.0	20.0	118.12
BC:	12	1	n.a.	.20	57.1	1.2	6.97
C:*	0	0	0	0.0	0.0	0.0	0.0
TOTALS:	63	4	n.a.	37.34	4827.6	100.0	589.08
DAY: 10							
LF:*	8	36	6.0-21.2	15.40	911.5	65.4	111.23
AE:	5	38	0.0-16.8	1.18"	129.9	9.3	15.85
BF:	30	36	14.6-48.4	.52	336.8	24.1	41.09
BC:	15	36	2.5-20.0	.05	16.1	1.2	1.97
C:	8	11	0.0-15.0	n.d.	0.0	0.0	0.0
TOTALS:	66	155	n.a.	17.15	1394.4	100.0	170.15
DAY: 14							
LF:*	8	38	7.0-25.0	3.67	333.7	90.7	40.72
AE:	8	38	2.3-20.9	.16	28.6	7.8	3.48
BF:	26	38	17.3-42.2	.01	5.5	1.5	.67
BC:	16	38	10.2-20.0	n.d.	0.0	0.0	0.0
C:	10	13	5.0-17.0	n.d.	0.0	0.0	0.0
TOTALS:	68	165	n.a.	4.04	367.8	100.0	44.88
DAY: 24							
LF:*	8	39	5.1-20.8	3.14	189.9	29.4	23.17
AE:	7	39	0.0-10.6	.10	6.7	1.0	.81
BF:	34	39	15.8-44.5	.59	420.1	65.0	51.26
BC:	15	39	10.0-19.8	.09	29.3	4.5	3.58
C:	11	13	4.0-22.0	n.d.	0.0	0.0	0.0
TOTALS:	72	169	n.a.	3.92	646.0	100.0	78.82
DAY: 48							
LF:*	8	38	4.9-19.0	2.24	133.4	36.3	16.28
AE:	7	38	.8-15.[illegible]	.22"	36.4	9.9	4.44
BF:	33	38	13.5-52.[illegible]	.23	165.6	44.6	19.97
BC:	13	38	5.1-18.9	.09	28.6	7.8	3.50
C:	7	11	0.0-16.0	0.03	5.1	1.4	.62
TOTALS:	66	163	n.a.	2.81	367.2	100.0	44.81

continued...

Table 4-6, Dicamba, continued

	(1) Mean Thickness (cm)	(2) Horizon Count (n)	(3) Range (cm)	(4) Unadjusted Residues (ppm)$	(5) Adjusted Residues (ug)&	(6) Horizon ug As Percent Of Total ug@	(7) Percent Of Total Applied Herbicide+
DAY: 98[13]							
DAY: 312							
LF:•	7	40	8.1-17.7	.07	4.3	100.0	.53
AE:	8	40	1.0-14.4	n.d.	0.0	0.0	0.0
BF:	18	40	13.7-24.7	n.d.	0.0	0.0	0.0
BC:	16	40	10.1-20.0	n.d.	0.0	0.0	0.0
C:	10	11	5.0-19.0	n.d.	0.0	0.0	0.0
TOTALS:	59	171	n.a.	.07	4.3	100.0	.53
DAY: 382							
LF:•	9	33	7.8-23.9	.02	1.5	100.0	.19
AE:	5	33	1.0-9.5	rbaa	0.0	0.0	0.0
BF:	27	33	18.7-36.2	rbaa	0.0	0.0	0.0
BC:	15	33	10.2-19.9	rbaa	0.0	0.0	0.0
C:	10	11	4.0-18.0	rbaa	0.0	0.0	0.0
TOTALS:	66	143	n.a.	.02	1.5	100.0	.19
DAY: 486							
LF:•	7	41	7.0-18.1	.03	2.8	100.0	.34
AE:	10	41	1.0-30.9	n.d.	0.0	0.0	0.0
BF:	29	41	18.1-44.2	n.d.	0.0	0.0	0.0
BC:*	0	0	0	0.0	0.0	0.0	0.0
C:*	0	0	0	0.0	0.0	0.0	0.0
TOTALS:	46	123	n.a.	.03	2.8	100.0	.34

$ = Expressed on a fresh weight basis and not corrected for recoveries.
& = Estimate of total ug of residues expressed on a dry weight basis by volume for the specified soil layer of 1m x 1m area and zcm thick (column 1).
@ = Figures in column (6) are expressed as a percent of column (6)'s total showing the herbicide's relative distribution within the profile.
+ = 3,6-dichloro-o-anisic acid applied at the rate of 7.6 kg/ha active ingredient.
• = LF horizon corrected for a 41 percent dilution factor.
I = n=1, where mean is defined by normal random number generator $N(z,\sigma^2)$, using IMSL (International Math & Stats Library, programme GGNML). Where means and std. deviations are as follows: LF, 12.2, 2.1, n=839; Ae, 6.9, 2.6, n=839; Bf, 25.3, 4.9, n=839; BC, 14.7, 1.0, n=734; C, 9.8+, 1.9+, n=69.
* = Mean residue value of duplicate samples.
n.d. = None detected = < 0.01 ppm, limit of detection(0.01 ppm).
: = Horizon not sampled.
n.a. = not applicable.
rbaa = Ontario Research Foundation received samples but were not analyzed.

[13] Moisture values for day 98 are missing. Therefore, day 98 has not been included in constructing tables, graphs or computing the regression equations.

Table 4-7. Hexazinone Residues: mean horizon thickness, ppm, mg, percent of total mg per sample date, and percent of total herbicide applied

	(1) Mean Thickness (cm)	(2) Horizon Count (n)	(3) Range (cm)	(4) Unadjusted Residues (ppm)B	(5) Adjusted Residues (mg)A	(6) Horizon mg As Percent Of Total mgB	(7) Percent Of Total Applied Herbicide
DAY: 3							
LF:	7	1	n.a.	73.80	1383.2	98.0	53.64
AE:	7	1	n.a.	.08	8.6	.6	.33
BF:	22	1	n.a.	.06	18.8	1.3	.73
BC:	0	0	0	0.0	0.0	0.0	0.0
C:	0	0	0	0.0	0.0	0.0	0.0
TOTALS:	36	3	n.a.	74.04	1410.6	100.0	54.70
DAY: 6							
LF:	5	1	n.a.	202.00	2520.6	93.2	97.74
AE:	11	1	n.a.	.28	47.4	1.8	1.84
BF:	28	1	n.a.	.28	111.7	4.1	4.33
BC:	14	1	n.a.	.11	25.0	.9	.97
C:	0	0	0	0.0	0.0	0.0	0.0
TOTALS:	58	4	n.a.	202.67	2704.7	100.0	104.88
DAY: 10							
LF:	6	37	4.9-17.4	99.50	1552.0	92.8	60.18
AE:	8	37	0.0-21.9	.16	19.7	1.2	.76
BF:	25	37	15.8-34.2	.08	28.5	1.7	1.11
BC:	15	37	10.3-19.5	.30	72.9	4.4	2.83
C:	8	13	4.0-14.0	n.d.	0.0	0.0	0.0
TOTALS:	62	161	n.a.	100.04	1673.1	100.0	64.88
DAY: 38							
LF:	6	40	5.0-15.0	85.40	1465.2	78.4	56.82
AE:	9	40	0.0-18.5	.85	117.8	6.1	4.57
BF:	20	40	13.1-39.6	.39	144.5	7.5	5.60
BC:	15	40	10.1-19.8	.63	153.2	8.0	5.94
C:	9	15	8.0-18.0	.24	37.2	1.9	1.44
TOTALS:	65	175	n.a.	87.51	1918.0	100.0	74.37
DAY: 66							
LF:	8	43	7.1-17.6	98.20	1991.2	88.3	77.21
AE:	9	43	.8-20.9	.42	58.2	2.6	2.26
BF:	18	43	10.1-25.3	.43	110.3	4.9	4.28
BC:	14	43	10.0-19.3	.31	70.3	3.1	2.73
C:	14	15	8.0-23.0	.10	24.1	1.1	.94
TOTALS:	63	187	n.a.	99.46	2254.2	100.0	87.41

continued...

Table 4-7, Hexazinone, continued

	(1) Mean Thickness (cm)	(2) Horizon Count (n)	(3) Range (cm)	(4) Unadjusted Residues (ppm)$	(5) Adjusted Residues (mg)&	(6) Horizon mg As Percent Of Total mg@	(7) Percent Of Total Applied Herbicide+
DAY: 312							
LF:*	5	37	4.0-13.8	20.30	298.7	66.6	11.58
AE:	8	37	.8-19.8	.12	15.5	3.5	.60
BF:	26	37	16.1-38.7	.20	77.7	17.3	3.01
BC:	16	37	10.0-19.8	.13	33.1	7.4	1.28
C:	13	15	5.0-20.0	.10	23.5	5.2	.91
TOTALS:	67	163	n.a.	20.85	448.5	100.0	17.39
DAY: 382							
LF:*	5	35	4.4-14.5	16.30	232.8	53.1	9.03
AE:	8	35	0.0-16.7	.34	48.0	10.9	1.86
BF:	27	35	12.6-40.5	.22	96.9	22.1	3.76
BC:	15	35	10.0-19.8	.16	44.5	10.1	1.73
C:	12	14	5.0-18.0	.07	16.6	3.8	.64
TOTALS:	67	154	n.a.	17.09	438.8	100.0	17.02
DAY: 486							
LF:*	6	37	5.9-15.4	10.20	192.7	97.4	7.47
AE:	5	37	.3-13.5	.07	5.2	2.6	.20
BF:	27	37	11.6-37.5	n.d:	0.0	0.0	0.0
BC:	15	37	10.7-19.7	n.d.	0.0	0.0	0.0
C:	9	14	3.0-17.0	n.d.	0.0	0.0	0.0
TOTALS:	62	162	n.a.	10.27	197.9	100.0	7.68

$ = Expressed on a dry weight basis and not corrected for recoveries.

& = Estimate of total mg of residues expressed on a dry weight basis by volume for the specified soil layer of 1m x 1m area and xcm thick (column 1).

@ = Figures in column (6) are expressed as a percent of column (6)'s total showing the herbicide's relative distribution within the profile.

\+ = 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine 2,4 (1H,3H)-dione applied at the rate of 10.5 kg/ha of active ingredient.

* = LF horizon corrected for a 41 percent dilution factor.

! = n=1, where mean is defined by normal random number generator $N(\mu,\sigma^2)$, using IMSL (International Math & Stats Library, programme GGNML). Where μ means and std. deviations are as follows: LF, 12.2, 2.1, n=830; Ae, 6.6, 2.8, n=849; Bf, 25.3, 4.9, n=839; BC, 14.7, 1.0, n=734; C, 9.8+, 1.9+, n=69.

\- = Horizon not sampled.

n.d. = None detected = $\leq$ 0.04 ppm, limit of quantification(0.04 ppm).

n.a. = not applicable.

Table 4-8: Tebuthiuron Residues: mean horizon thickness, ppm, mg, percent of total mg per sample date, and percent of total herbicide applied

	(1) Mean Thickness (cm)	(2) Horizon Count (#)	(3) Range (cm)	(4) Unadjusted Residues (ppm)$	(5) Adjusted Residues (mg)&	(6) Horizon mg As Percent Of Total mg@	(7) Percent Of Total Applied Herbicide
DAY: 8							
LF:	8	1	n.a.	40.00	2824.5	95.8	282.03
AE:	8	1	n.a.	.41	54.3	1.8	5.44
BF:	18	1	n.a.	.13	42.7	1.4	4.28
BC:	15	1	n.a.	.10	25.5	.9	2.55
C:	0	0	0	0.0	0.0	0.0	0.0
TOTALS:	49	4	n.a.	40.64	2938.9	100.0	294.30
DAY: 11							
LF:	5	1	n.a.	56.00	1899.8	92.4	190.37
AE:	16	1	n.a.	.23	57.8	2.8	5.75
BF:	25	1	n.a.	.20	75.6	3.7	7.58
BC:	12	1	n.a.	.12	23.9	1.2	2.39
C:	7	1	n.a.	n.d.	0.0	0.0	0.0
TOTALS:	65	5	n.a.	56.55	2056.6	100.0	206.09
DAY: 32							
LF:	7	86	2.5-20.3	60.00	1954.1	88.8	195.81
AE:	4	36	0.0-14.6	.67	42.2	1.9	4.23
BF:	25	36	12.6-41.5	.60	149.4	6.8	14.97
BC:	15	35	10.4-19.6	.18	41.8	1.9	4.19
C:	8	13	0.0-15.0	.10	13.0	.6	1.31
TOTALS:	59	156	n.a.	61.35	2200.6	100.0	220.52
DAY: 64							
LF:	6	38	1.4-20.7	71.00	2833.7	97.6	283.86
AE:	5	38	0.0-16.7	.14	11.7	.4	1.17
BF:	21	38	7.1-40.4	.11	35.4	1.2	3.54
BC:	15	17	10.0-20.0	.09	23.5	.8	2.35
C:	9	11	0.0-24.0	n.d.	0.0	0.0	0.0
TOTALS:	56	181	n.a.	71.34	2904.3	100.0	291.03

continued...

Table 4-8, Tebuthiuron continued

	(1) Mean Thickness (cm)	(2) Horizon Count (n)	(3) Range (cm)	(4) Unadjusted Residues (ppm)$	(5) Adjusted Residues (mg)&	(6) Horizon mg As Percent Of Total mg$	(7) Percent Of Total Applied Herbicide+
DAY: 310							
LF:*	8	41	8.0-21.0	28.00"	1462.8	99.8	145.58
AE:	8	41	0.0-35.3	n.d."	0.0	0.0	0.0
BF:	19	41	8.8-30.3	.07"	20.1	1.4	2.02
BC:	14	41	10.2-19.9	n.d.	0.0	0.0	0.0
C:	12	11	5.0-20.0	n.d.	0.0	0.0	0.0
TOTALS:	61	173	n.a.	28.07	1472.9	100.0	147.59
DAY: 483							
LF:*	8	43	8.0-15.2	14.00"	748.4	85.7	74.79
AE:	6	43	.8-19.4	.20"	19.1	2.2	1.92
BF:	25	43	12.7-36.4	.28"	105.8	12.1	10.61
BC:	16	43	10.1-19.9	n.d.	0.0	0.0	0.0
C:	10	11	3.0-20.0	n.d.	0.0	0.0	0.0
TOTALS:	63	181	n.a.	14.48	871.3	100.0	87.31

$ = Expressed on a fresh weight basis and corrected for recoveries.
& = Estimate of total mg of residues expressed on a dry weight basis by volume for the specified soil layer of 1m x 1m area and xcm thick (column 1).
@ = Figures in column (6) are expressed as a percent of column (6)'s total showing the herbicide's relative distribution within the profile.
+ = N-[5-(1, 1-dimethylethyl)-1, 3, 4-thiadizol-2-yl]N, N,-dimethylurea applied at the rate of 9.8 kg/ha of active ingredient.
* = LF horizon corrected for a 41 percent dilution factor.
| = n=1, where mean is defined by normal random number generator $N(\mu,\sigma^2)$, using IMSL (International Math & Stats Library, programme GGNML). Where means and std. deviations are as follows: LF, 12.2, 2.1, n=839; AE, 6.9, 2.6, n=839; BF, 25.3, 4.9, n=839; BC, 14.7, 1.0, n=734; C, 9.8+, 1.9+, n=69.
" = Mean residue value of duplicate samples.
' = Horizon not sampled.
n.d. = None detected = $\leq$ 0.05 ppm, limit of detection(0.05 ppm).
n.a. = not applicable.

Table 4-9: Picloram Residues: mean horizon thickness, ppm, mg, percent of total mg per sample date, and percent of total herbicide applied

	(1) Mean Thickness (cm)	(2) Horizon Count (n)	(3) Range (cm)	(4) Unadjusted Residues (ppm)*	(5) Adjusted Residues (ug)&	(6) Horizon mg As Percent Of Total mg#	(7) Percent Of Total Applied Herbicide+
DAY: 5							
LF:•	8	1	n.a.	5.500	97.0	85.5	42.32
AE:	10	1	n.a.	.080	10.7	9.4	4.68
BF:	23	1	n.a.	.020	5.7	5.0	2.49
BC:	13	1	n.a.	n.d.	0.0	0.0	0.0
C:•	0	0	0	0.0	0.0	0.0	0.0
TOTALS:	54	4	n.a.	5.600	113.4	100.0	49.49
DAY: 11							
LF:•	5	1	n.a.	7.720	83.8	82.0	36.56
AE:	8	1	n.a.	.078	8.4	8.2	3.65
BF:	27	1	n.a.	.030	10.0	9.8	4.38
BC:	16	1	n.a.	n.d.	0.0	0.0	0.0
C:	9	1	n.a.	n.d.	0.0	0.0	0.0
TOTALS:	65	5	n.a.	7.828	102.2	100.0	44.59
DAY: 32							
LF:•	9	37	9.8-28.0	.60	12.2	100.0	5.33
AE:	6	37	0.0-14.2	n.d.	0.0	0.0	0.0
BF:	21	37	12.7-34.9	n.d.	0.0	0.0	0.0
BC:	14	37	10.3-19.7	n.d.	0.0	0.0	0.0
C:	9	11	3.0-18.0	n.d.	0.0	0.0	0.0
TOTALS:	59	159	n.a.	.60	12.2	100.0	5.33
DAY: 64							
LF:•	7	57	7.7-15.5	1.00	16.3	100.0	7.10
AE:	7	57	2.0-20.7	n.d.	0.0	0.0	0.0
BF:	15	57	5.7-25.7	n.d.	0.0	0.0	0.0
BC:	13	57	10.0-19.9	n.d.	0.0	0.0	0.0
C:	8	11	5.0-14.0	n.d.	0.0	0.0	0.0
TOTALS:	50	239	n.a.	1.00	16.3	100.0	7.10

continued...

Table 4-9, Picloram continued

	(1) Mean Thickness (cm)	(2) Horizon Count (n)	(3) Range (cm)	(4) Unadjusted Residues (ppm)$	(5) Adjusted Residues (ug)&	*(6) Horizon ug As Percent Of Total ug@	(7) Percent Of Total Applied Herbicide+
DAY: 310							
LF:•	8	44	8.0-20.1	.160	3.0	76.4	1.33
AE:	10	44	1.2-25.9	.007	.9	23.6	.41
BF:	28	44	12.5-47.6	n.d.	0.0	0.0	0.0
BC:	14	44	5.5-19.6	n.d.	0.0	0.0	0.0
C:	12	12	3.0-20.0	n.d.	0.0	0.0	0.0
TOTALS:	72	188	n.a.	.167	3.9	100.0	1.74
DAY: 483							
LF:•	0	49	6.8-29.0	.164"	3.3	60.7	1.46
AE:	7	49	0.0-18.0	n.d."	0.0	0.0	0.0
BF:	20	49	16.1-48.2	.006"	2.2	39.3	.94
BC:	15	49	10.1-19.8	n.d.	0.0	0.0	0.0
C:	12	11	3.0-23.0	n.d.	0.0	0.0	0.0
TOTALS:	72	207	n.a.	.170	5.5	100.0	2.40

$ = Expressed on a dry weight basis and corrected for recoveries.
& = Estimate of total ug of residues expressed on a dry weight basis by volume for the specified soil layer of 1m x 1m area and xcm thick (column 1).
@ = Figures in column (6) are expressed as a percent of column (6)'s total showing the herbicide's relative distribution within the profile.
+ = 4-amino-3,5,6-trichloropicolinic acid applied at the rate of 2.1 kg/ha of active ingredient.
• = LF horizon corrected for a 41 percent dilution factor.
* = $\bar{x} \pm 1$, where mean is defined by normal random number generator $N(\bar{x},\sigma^2)$, using IMSL (International Math & Stats Library, programme GGNML). Where means and std. deviations are as follows: LF, 12.2, 2.1, n=839; Ae, 6.9, 2.6, n=839; Bf, 25.3, 4.9, n=839; BC, 14.7, 1.0, n=734; C, 9.8+, 1.9+, n=89.
" = Mean residue value of duplicate samples.
' = Horizon not sampled.
n.d. = None detected = $\leq$ 0.005 ppm, limit of quantification(0.5 ppb).
n.a. = not applicable.

4.8. Conclusion

Despite a degree of experimental variability and some anomalous results, which could mask the objectives of the thesis, there clearly are salient points to be made.

1. The importance of the organic matrix for sorption as inferred from the distinct separation of values between the organic LF horizon and the mineral Ae to C horizons.
2. The active process of herbicide leaching, indicated by the pattern which represents the displacement process where values of the lower horizons (Bf, BC and C) increase as the values of the upper horizons (LF, Ae and Bf) decrease. The Bf horizon fits into both classes because of a lag where during the early phase of the experiment it belongs to the upper class and afterwards it associates with the lower class.
3. The process of podzolization acting upon the herbicides as it does with natural organic compounds as shown by the tendency for the values of the Ae horizon to be less than those of the Bf horizon.
4. The negative linear and negative exponential decay patterns which these herbicides apparently emulate.

Chapter 5
DISCUSSION AND CONCLUSION

5.1. Introduction

This final chapter will begin with a brief discussion of herbicide disappearance from soils comparing and contrasting the DTs of other studies followed by a discussion of some herbicide-soil/climate relationships that exist and how they may fit into this study. Next will be a discussion of problems encountered and identified during the course of the experiment, how they effect the data and whether or not they could be corrected for. The question of herbicide behaviour in soil has implications for forest management which is examined in the Section, "Herbicide Use And Forest Management". The latter Section ends with a Recommendations Subsection which is prescriptive in style intending preventative measures on behalf of society's long term interests in protecting the quality of our boreal environment and improving Canada's forest resources. The Conclusion Section follows with a summary of experimental results and four key topics for future study.

5.2. Discussion

5.2.1. Disappearance Times

The magnitude of herbicide persistance has been shown to vary from study to study. Coincidently, authorities can usually find studies which confirm their own computed DTs. Many field studies are still required in order to develop some sort of disappearance index which would represent all, most or key environments in which herbicides are used. The expected DTs (based on the initial concentration applied) and the observed DTs (based on the maximum concentration detected) are briefly compared and contrasted with the findings of other authorities in the following paragraphs.

DICAMBA: The calculated DT_{50}s of 9 and 25 days compare well with Corbin's and Upchurch's (1967, p.373), DT_{50} of approximately 21 days using prepared and highly organic soils

from North Carolina (*ibid.*, p.370). The calculated DT_{75}s of 0.4 and 1.2 months are within the range of less than 2 months as cited by Kearney *et al.* (1969, p.139).

It is interesting to note that the Ontario Research Foundation, under contract with Velsicol Chemicals, detected 2,4-D on all of the sample days. In their reports of dicamba residues in soil they did not quantify the amounts of 2,4-D detected, but noted that there were detectable amounts up to and including day 486. The DyCleer 24 product has a 2,4-D content of 400 grams/litre and a dicamba content of 200 grams/litre, both present as a dimethylamine salt of which the dicamba application was 7.6 kg/ha of active ingredient. If it is accepted that 2,4-D is a compound of the short-lived "mobility class IV", (Helling, 1971, p.738), with a DT_{90} of less than 1 month (cited in: Klingman and Ashton, 1975, p.76; Hamaker, 1972, p.331), then why is there still detectable amounts of 2,4-D in the dicamba treated soils after 486 days? The first possibility that comes to mind is that the different molecular formulations (*eg.*, low volatile butoxyethyl ester *versus* dimethylamine salt) may be a significant factor (Bailey and White, 1970, pp.43-44). Second, that the presence of other compounds (*i.e.*, dicamba) may be a significant factor; a synergism could possibly be involved (Hamill *et al.*, 1972; Morrill *et al.*, 1982, PP.174-176). Third, that the rates of application could be significant (Hamaker *et al.*, 1967; Altom and Stritzke, 1973; Hance and McKone, 1971). Therefore, it may be suggested that, given the initial concentration and the climatic and edaphic conditions, the 2,4-D as a dimethylamine salt applied in a formulation, which includes dicamba, should persist in the DyCleer 24 treated soil. This then leads to the consideration of further study investigating the behaviour of selected compounds simultaneously used in boreal forests.

HEXAZINONE: The calculated DT_{50}s of 4 and 6 months compare well with the DT_{50}s of Rhodes for two of three sites (1980, p.313) but sharply contrast with the DT_{50}s of Sung (1982, p.21). Rhodes (1980, p.313) calculated DT_{50}s of 3 to 4, 6 to 7 and 10 to 12 months for three different silt loam soils in Illinois, Delaware and Mississippi, respectively. Sung (1982, p.21) calculated DT_{50}s of less than 4 weeks for two soils (loamy sand and a sandy clay loam) in Alabama each at a low and high rate of application, 2 and 4 kg a.i./ha.

It is surprising, that at an application rate elevenfold greater than the suggested maximum, the interpolated DT_{50}s in this study concur with those of Rhodes for the Illinois and Delaware sites but, not with Sung's Alabama sites nor Rhodes' Mississippi site. Furthermore, there is a 9-11 month discrepancy between Sung's results for Alabama and Rhode's results for Mississippi. Considering that Alabama and Mississippi have similar climatic and edaphic regimes this variance suggests that further study may be required. Two considerations for further study would investigate the persistence of hexazinone across latitudinal changes in similar soils or, in different soils at the same latitude. Another consideration for further study would be to examine the behaviour of hexazinone at very high rates of application. This information could be used to

represent a small point source accident over a soil surface. Regardless, the bottom line dictates that until an adequate base of such information is available, it is essential that users strictly adhere to the manufacturer's directions for their proper use. Indeed, it is a contravention of the federal Pest Control Products Act to use these products under unsafe conditions (Environmental Protection Service, 1985, p.2).

TEBUTHIURON: The only calculable disappearance time possible is based on the maximum amount detected at the 50 % level (DT_{50} = 10 months). At the onetime application rate all the calculated values fall outside the range of given data and therefore, the DT_{50} has an indeterminate upper limit greater than 16 months. The calculated DT_{50} of approximately 10 months to 16 months defines a range large enough to include the 12-15 month half life in areas receiving 100 to 150 cm annual rainfall (Elanco technical report, p.3). The report states that the half life is considerably greater in low rainfall areas and in high organic soils regardless of rainfall (*ibid.*). As the total precipitation regime is comparable to that of central Newfoundland (see *climate*, page 7) it would not be unrealistic to think that the majority of DTs outside the range of values reflects the longer half life of residues remaining in the highly organic LF layers. Of the residues detected in the five horizons sampled, those found in the LF horizon account for approximately 92 % of the total per sample period (Table 4-8, page 87, column six, with a mean thickness of 7 cm). The balance of residues detected are found in the remaining four mineral horizons.

PICLORAM: The calculated DT_{50}s of 7 and 16 days are not very different from the DT_{50} of 15 days reported for three soils (Fannin clay loam, Chandler fine sandy loam and, Chester loam) in North Carolina, at two application rates (2.24 and 4.48 kg/ha) (Lutz *et al.*, 1973, p.487). In addition, Lutz (*ibid.*) reported a DT_{90} of 100 days which falls close to the upper limit of the calculated DT_{90}s of 55 and 119 days. However, Altom and Stritzke (1973, p.559) reported that at the end of 100 days from 63 to 77 % of the original concentration remained in the three soils tested from forest and grassland in Oklahoma. Therefore, if 100 days is required for a DT_{23} to DT_{37}, then it can be deduced that a DT_{50} will take longer than 100 days under the conditions set forth in Oklahoma. Meikle *et al.* (1973, p.552) presented the decomposed picloram as a percent of the applied concentration for a variety of soils (clay, clay loam, loam and sandy loam) from Texas, California and Mexico, and indicated a wide range of values for the 423 day period. For this period, percentage of applied concentration that disappeared ranges from 15 % (loam, California), 66 % (sandy loam, Texas), 73 % (clay, Texas), 89 % (clay loam, Texas), 90 % (sandy loam, Mexico) through to 94 % (loam, California).

5.2.2. Herbicide - Climatic/Edaphic Relationships

This study has brought forth a number of relationships between herbicides and soil systems. Although these relationships are not original discoveries, they are relationships which require validation for herbicide use in a cold, moist boreal environment. In the past there have been relatively few quantitative experiments with herbicides in Canada's boreal forests. The following discussion not only validates some of the other herbicide research but adds general information on experimental design which is pertinent to all field studies of herbicide-soil interactions.

One of the many relationships clearly elucidated by this study is that herbicide persistence is inversely related to time. Thus, these organic compounds do disappear (metabolize, volatilize, leach and degrade) with the passing of time. Four of the selected herbicides' time-dependant relationships are described by two negative regression models: one is linear and the other is exponential. The graphs in Figures 4-15 through 4-18, pages 70 through 73, adequately exemplify this relationship. This is not a simple relationship because there are many mechanisms involved in the dissipation of herbicides. However, time does represent the degradation or half-life inherent in all materials.

The calculated DTs are not substantially greater in a northern boreal podzol than the DTs computed by other authorities at more southern latitudes. One would suspect that with low temperatures associated with boreal winters and decreased activity of soil microbiota there would be less herbicide degradation and hence greater herbicide persistence. In fact, the DTs of this study are less than some, comparable with others, and greater than the DTs of those studies reviewed in Chapter 2. Therefore, there is no conclusive evidence suggesting a direct relationship between the relatively long winters of northern latitudes and increased herbicide persistence.

The low clay content of the soils (see Appendix I, page 137), may be sufficient to affect adsorption. However, in this case where there is a relative absence of clay minerals, adsorption is probably greater in soils with high organic matter content than in those soils with little organic matter. The LF and Bf horizons have both higher organic matter content and generally greater herbicide residue content than the Ae, BC or C horizons. If organic matter is not crucial for sorption to take place then the Ae layer, which lies above the Bf horizon, should generally have more residues than the deeper Bf horizon. However, it has been shown that the Ae layer most often has lower residue concentrations the Bf horizon. Hence, there must be a direct positive relationship between herbicide distribution and organic matter distribution in the soil.

The pedogenic process of podzolization definitely influences the distribution of herbicides in soil. Therefore, it is not unrealistic to suspect that certain pedogenic processes, which influence the development of other soil types, would also influence herbicide distribution in those particular soils. The pedogenic processes active in different climatic and edaphic environments control, to

varying degrees, the accumulation, degradation and movement of soil organic materials and therefore, may similarly influence herbicide accumulation, degradation and movement. In organic soils under dry conditions very limited vertical movement is likely. However, under very moist or saturated conditions herbicide movement would be greater. The pedogenic processes which influence herbicide distribution, probably fall into a class limited to those processes in which water is the primary catalyst for activation. The same class which, in herbicide movement terminology, is referred to as the liquid phase as opposed to movement in the gaseous phase.

The DTs vary between each herbicide which may reflect the different application rates (especially that of hexazinone) and how the individual chemical characteristics of each compound react to the biophysical chemical characteristics of the podzol. However, if all five plots within the site are of the same soil population, subjected to the same climatic events, then dissimilarities in persistence are more likely the result of the diverse nature of each compound used; especially since three of the herbicides were applied for comparable effectiveness. 2,4-D, dicamba, hexazinone, tebuthiuron and picloram belong to the following chemical groups: chlorophenoxy, dihalobenzoic, symmetrical triazine, substituted urea and pyridine acid, respectively. It appears logical that if the chemical nature of the compounds differ, then so may their disappearance times.

5.2.3. Errors

During the early analysis of the results, an error was detected which had to be accounted. This error, the result of a number of conditions, manifested itself as values exceeding 100 % of the application rate (column seven, Tables 4-6 - 4-9). For some of these factors, it was possible to determine a measure for correcting results which were then incorporated into the computations. However, for the remaining factors this was either not possible or practicable. An examination of figures in column seven, Tables 4-6 and 4-9, pages 81 - 87 show some values greater than 100 %, which indicate that some of these indeterminably variant conditions are still in affect. Detection levels in excess of the application rates occur on days 6 and 10 for dicamba and on days 5, 11, 32, 64 and 310 for tebuthiuron. For the following discussion it is important to note that all but one of these seven high values occur in the LF horizon. The one exception occurs in the Bf horizon on day 6 for dicamba. Column seven, Table 4-6, page 81, shows that 118 % of the total applied herbicide was detected on that day in the Bf layer which coincidently, has the second highest mean organic carbon content of the five horizons sampled (Bf horizon: $\bar{x}$ = 6.0 %, n = 12, range = 4.1-9.1 %). The anomalous event of an extreme value in the Bf layer may add further to the argument of a relationship between the organic soil material and organic herbicides. The conditions which may lead to errors and whether or not they were determinable, and therefore incorporated into the calculations, follow:

1. Herbicide overlap along spray swaths (see Figure 3-1, page 39). *Indeterminable.*
2. Inappropriate herbicide applicator (see Figure 3-2, 40). *Indeterminable.*
3. Dilution/concentration problems due to sampling design. *Indeterminable.*
4. Dilution/concentration problems due to sampling equipment. *Nominally determinable.*
5. Reduction in plot areas due to configuration of plots and non soil surfaces within experimental areas (see Figures 4-1 and 5-1, pages 50 and 95). *Determinable.*
6. The misleading assumption of a uniform application due to nonuniform surface geometry (see Figures 4-1 and 5-1, pages 50 and 95). *Indeterminable.*
7. The inability of analytical laboratories to establish consistent recovery rates. *Limited determinability based on laboratories' recovery results.*
8. The problem of extrapolating results from a 10 to 40 g analytical subsample representative of a larger composite sample (600 - 1800 g fresh weight), to an even greater estimated volume of soil (10 - 359 kg; 1 m^2 x X cm thick), when sample variability is unknown, increases the risk of a *Type* II *beta* error. *Indeterminable.*

Figure 5-1: Photograph of the hexazinone plot, August, 1984, showing the nonuniformity of surface geometry and the reduction in plot size due to tree stumps and rock outcrops.

A herbicide application overlap along the borders of the spray swaths occurs because of the inappropriateness of the 'Solo' mist sprayer used for the ground application. Besides the normal expected spray drift there is also drift which is compounded by the use of this mist sprayer. This overlap may be responsible for a two- to fourfold increase in concentration. The increase in concentration would affect the results because a sampling grid was superimposed over the spray swath borders, the area of herbicide overlap. Thus, the sampled soil faces of these pits, which are aligned under the border of the spray swaths, may have received two times more herbicide during application and a further two times increase when applying subsequent swaths.

Great effort was put into becoming skilled at operating and calibrating the 'Solo' mist sprayer used for the herbicide application. Nonetheless, an unknown increase in herbicide concentration would occur if there is a brief delay in the arm movement at the end points of the arc path when applying the herbicide back and forth across the spray swath.

In each of three pits, three sampling units were extracted to contribute to the composite sample of nine. Though the volumes of these sampling units were consistent, their spatial distribution tended to vary because of the nonuniformity of horizon thickness and form. With 100 % of the herbicide applied to the ground surface, dilution of the compound increases with increasing depth. For example, if the nine sampling units drawn from the LF horizon are composed of 50 % of the top layer with given areal dimensions, then those nine units represent a twofold concentration leading to a composite sample which has 200 % more herbicide than the applied rate would indicate. This means that the composite sample for the LF layer actually represents only half of its thickness. Another example shows that of the nine units which comprise the composite sample, if six and three units respectively represent 33 and 50 % of the top layer with given areal dimensions, then two thirds of the composite sample have 300 % and one third has 200 % more herbicide than a composite sample representing 100 % of the layer. Thus, this composite sample would have a concentration of approximately 266 % of the applied rate. For the lower mineral layers this concern is mitigated by the presence of the overlying horizons and the different approach to sampling. The effect of the overlying horizons is to dilute the concentration so that less than 100 % of the herbicide is applied to the Ae layer and even less to subsequent horizons. Thus, the LF layer receives 100 % of the herbicide, the Ae layer receives some percentage less than 100 %, the Bf receives some percentage less than Ae and LF horizons, the BC receives even less than the Bf, Ae and LF layers and, the C receives considerably less than BC, Bf, Ae and LF layers. Fortunately, the LF horizon is also the most significant layer in terms of its adsorptive capacity, giving it a highly positive weight in containing these herbicides (Column six, Tables 4-6 through 4-9). In addition, the sampling of the LF layer in a vertical fashion simplified cutting through vegetative material and minimized surface disturbance. However, it was subsequently found that the vertical sampling did not match well with the horizontal sampling of the Ae through C horizons. The horizontal sampling, being more suitable in obtaining a valid cross section, was accomplished by extracting samples of approximately equal spacing from those areas most representative of the horizon.

In relation to sampling the organic layer another dilution/concentration control problem results from sampling the matrix with a trowel that has a nonuniform shape. A conically shaped trowel contributes more sample from the wider based scoop area than it does from the narrow and pointed insert area. Thus, this sort of sampling tool concentrates herbicide in the sample similar in effect to that mentioned in the previous paragraph but different in scale. On a horizontal basis

the trowel extracts samples of equal depth per sample unit but this is not so for vertical samples which cover a wider range of depths. Thus, due to the adsorptive/desorptive importance of the organic layer a path was sought which would alleviate this problem. A solution was found by comparing the approximate volume of the trowel (trowel was segmented to facilitate the calculation[14]) with that of an ideal cylinder with similar dimensions (height=15.7 cm, radius=4.75 cm). Then the difference (1112.29 - 660.29 = 452.0 cm^3) in volume was used as a weighting factor (41 %) to reduce the thickness of the LF horizon, thereby reducing the affect of herbicide concentration.

The plots were delimited at 11 m x 20 m and the application was applied as uniformly as possible to the ground surface with an apparent area of 220 m^2. However, the hexazinone and tebuthiuron plots are rhombic in shape decreasing their respective areas to 190 and 218 m^2 and thereby increasing the rate of application. In addition, the rate of application increases further when the area of harvested tree stumps and rock outcrops is subtracted from the total area of the plots. Dicamba reduces from 220 to 205 m^2 (3 m^2 = rock outcrop + 12 m^2 = tree stumps); hexazinone reduces from 190 to 166 m^2 (3 m^2 = rock + 21 m^2 = stump); tebuthiuron reduces from 218 to 194 m^2 (1 m^2 = rock + 25 m^2 = stump); and picloram reduces from 220 to 201 m^2 (1 m^2 = rock + 18 m^2 = stump). The area that these items cover reduces the size of the plots because the spray solution runs off the rock outcrops and tree stumps into the ground concentrating the solution around these objects. This situation is reinforced by the fact that the herbicide formulation was highly diluted (80 litres of water + herbicide formulation = spray solution for plot area) to facilitate a uniform application thus supplying ample water to a surface which does not readily absorb it. It might be argued that the tree stumps would absorb the water due to the wood's dryness, however the impervious nature of the bark and the solution's flow velocity along the bark prevented this. Thus, runoff was an important process in distributing herbicide in particular areas, creating chemical 'hot spots' which could significantly increase concentration levels detected. This latter aspect of nonuniform distribution leads to another problem related to uniform applications which is discussed in the following paragraph.

A fundamental assumption for soil residue studies is that the pesticide is uniformly applied to the soil surface. *A priori* to this is the notion that the surface geometry is a two dimensional plane so that the application is uniform. Such a surface may be obtained on level sites which have been modified to resemble a two dimensional plane (*eg.*, agricultural fields with little or no variation in microtopography). However, for natural surfaces this is seldom if ever the case because the earth's surface exists in three dimensions. There are rock outcrops, tree stumps,

[14] Where dimensions in centimetres beginning with trowel's insert area are: 1 cone with ht=1.0 and base=4.4; 13 cylinders with ht=0.8 and radii=2.4, 2.6, 3.2, 3.4, 3.6, 3.7, 3.8, 4.0, 4.1, 4.3, 4.4, 4.5 and 4.6, respectively; 1 cylinder with ht=2.1 and radius=4.7; and 1 cone with ht=1.4 and base=9.2

hummocks or knolls, depressions and vegetation which not only express the microtopography but add two other inhibiting factors to the assumption of a uniform application. One is the nonuniformity of application due to spray shadow effect caused by the variations in microtopography. The sprayward aspects of the terrain receive more spray solution than the leeward surfaces thus, these latter surfaces are referred to as being in the spray shadow. In other words the angle at which the spray solution reaches the ground changes as the geometry changes thereby changing the distribution and quantity that actually contacts the ground. The second factor is the nonuniformity of distribution immediately after the solution has been applied even if the application is one hundred percent uniform. There are some additional concentration/dilution effects due to the differential rates of absorption by the diverse variety of constituents in the organic matrix. Decaying bark, old dead wood, new dead wood, conifer and deciduous foliage, cones, roots, charcoal, animal droppings and moss not only absorb solutions at different rates but have confounded some of the analytical laboratories in working with such a matrix (personal communication: Dr. Ian Borthwick, Eco-Research Laboratories, 1983; Dr. Lincoln Reynolds, Ontario Research Foundation, 1984; Michael Shreve, Kentville Agricultural Pesticides Laboratory, 1984). This latter condition is very important in stressing that, even a perfectly uniform herbicide application terminates once the pesticide is applied and begins to move down through the soil.

Another topic for discussion concerns the recovery rates which are limited by sample preparation and the analytical techniques employed. The results of the spike tests presented in Table 4-4, page 79 are discussed *per se* in Subsection 4.6, page 77. Though, in this context, it suffices to begin with the premise that if blind spike results show a range of values that are substantially different from those stated by the laboratories then it must be assumed that recovery test rates are another source for error. This is clearly expressed in Table 5-1, 99, which shows how the recovery levels contrast between the laboratory spikes and the experimentor spikes. The latter initiated by the author but analysed by the same laboratories. For dicamba, the Ontario Research Foundation reported values ranging from 68 to 74 % which is much greater than the spike test values of 27 and 43 %. For hexazinone, the Kentville Agricultural Pesticides Laboratory reported recoveries ranging from 76 to 90 % which is not substantially different from the test results of 78 through 120 % (mean = 97%, n = 5). Elanco corrected the tebuthiuron data for recovery but their rate is not given so it is not possible to compare or contrast the spike test values of 110, 110, 120 and 130 % with Elanco's recovery rates. Similarly, Dow corrected the picloram data for recovery, but they stated that the data was adjusted for an average recovery of 90 % which is much lower than the spike results ranging from 107 to 179 % (mean = 148%, n = 7). Another aspect of residue recovery, as a source for bias, which considers improper sample preparation is discussed in the Spike Sample Section, page 77.

Finally, there is a problem of scale which may possibly be compounded by the sources as

Table 5-1: Recovery Results Of Laboratory Spikes vs. Those Of Experimentor: *a double check*

		Laboratory Spiked			Experimentor Spiked		
Herbicide	Soil Type	Range of Fortified Recovery Levels, ppm	Average %	Range %	Fortified Recovery Levels, ppm	Average %	Range %
Dicamba	Organic	0.04-40.0	68.3(n=3)	63.5-80.9	0.0	1 (n=1)	n.a.
	Mineral	0.04-40.0	72.8(n=4)	59.6-80.0	1.0	35 (n=2)	27-43
Hexazinone	Organic	0.42	72.5(n=2)	66-79	0.0	n.d.(n=1)	n.a.
	Mineral	0.04-1.00	84.6(n=16)	70-100	1.0	102 (n=4)	93-120
Tebuthiuron	Organic	@	@	@	0.0	n.d.(n=1)	n.a.
	Mineral	@	@	@	1000.0	175 (n=4)	110-130
Picloram	Organic	*	90	*	0.0	n.d.(n=2)	n.a.
	Mineral	*	90	*	1.0	140 (n=7)	107-179

n = Sample size.
n.a. = Not applicable; because organic soil was not spiked.
n.d. = None detected; which is correct because organic soil was not spiked.
@ = Fortified recoveries not reported but residues have been adjusted by Elanco Laboratories, levels unknown.
* = Residue report states an average 90 % recovery without stating which horizons spiked or at what levels the samples were fortified.
@ & * Which mineral horizons were spiked is unknown.

enumerated above. The scalar problem is present in many natural situations where normal sample variability includes an unknown error factor (ϵ_i). When extrapolating to the population this error is multiplied by some representative fraction, exaggerating the error and thus the expression as well. The ϵ_i term inherent to sample variability is often assumed to be small, if not negligible, and could therefore be ignored. Although when sample variability is known to contain test errors, then the ϵ_i term may increase to a statistically significant level which could lead to either an *alpha* error, if the decision is to reject when the hypothesis is true, or a *beta* error, if failing to reject when the hypothesis is false. One limitation of a composite sample is the lack of any measure of variability between sampling units, hence probability can only be discussed in a nominal context. In this case the probability of a *Type* II (β) error is more likely than a *Type* I (α) error as the results are not being rejected. However, because the results have revealed certain evident patterns, there is a better chance that the decision to accept them is a correct one even though β may be larger than desired.

5.3. Herbicide Use And Forest Management

Since the beginning of the forest industry in Canada there has been gross mismanagement or poor management of the forest resource, primarily because our knowledge of forest science and ecology was small(MacGregor, 1982; Macdonald, 1921). In contrast, today, our knowledge of forest ecosystems is considerably increased. Part of that knowledge is a vast storehouse of management techniques including site preparation, planting, fertilizers and pesticides. Forest managers view herbicides as an essential silvicultural tool for vegetation control. Thus, herbicide behaviour in soils can provide crucial information for their use or nonuse in forest management strategies. Herbicide use can make a solid contribution to the forest industry, but only when based on sound ecological principles and used from a standpoint that has long term social and economic benefits in mind. Otherwise, problems can be expected which are environmentally damaging or economically beyond resolve (Oosting and Reed, 1944; Nickerson, 1956; Damman, 1967; Likens *et al.*, 1970; Hall and Richardson, 1972; Jordan, *et al.*, 1972; Richardson and Hall, 1973a, 1973b; Richardson, 1975, 1979a, 1979b; Tamm, 1976; White, 1979; Kardell, 1980; Boring, *et al.*, 1981; and Covington, 1981).

Forest and related industries account for 10 % of employment in Canada and almost as much of our gross national product. One undesirable complication which may arise from improper forest management, compounded through herbicide use, is the common silvicultural practice of scarifying. This is where the mineral soil is exposed as a preparation for planting trees. It is detrimental with regards to herbicide leaching as it tends to decrease the organic matter content of the soil. Therefore, not only would the nutrient-rich organic matter decrease but the potential for herbicide leaching would also increase. This situation is complicated further when it is known that certain tree species such as black spruce prefer a mineral bed for a healthy establishment. This leaves little choice when planting trees but to scarify. Hence, with each rotation cycle replace the depleting levels of organic matter with greater and greater inputs of fertilizers. Drought may introduce another problem. Herbicides are applied on relatively dry days. Under dry summer conditions, which tend to be warm, the herbicides will remain mostly on the surface subjecting them to photodegradation and volatilization; a situation which is wasteful and may be unhealthy.

It may be argued that manual rather than chemical thinning of vegetation is preferred. However, a first experience in Quebec (Boychuk, 1982) indicates the opposite where in the first year of a five year, $675 million tree planting and brush clearing program, 200 of 500 jobs went unfilled because they paid the minimum wage of $150.00/week. Less than 60 % of the scheduled work could be completed. Reforested areas may require three or four manual brush clearings as opposed to one or two chemical treatments. Finally, the costs of manual brush clearing have quadrupled between 1982 and 1984.

The use of herbicides to control unwanted vegetation is in itself not a solution to the severe problems facing our forest industries today. Today forest managers must deal with overmature even-aged stands which are susceptible to budworm, soil degradation in hilly and mountainous terrain which decreases commercial productivity of desirable trees, very dense matchstick type forests which are prone to windthrows, hot ground fires and are of an economically unviable size, and the loss of forested land through the harvesting of marginally productive sites not capable of proper self-regeneration. These problems are historically rooted and until recently the vision of a woodland cornucopia in Canada has been the inertia which has allowed poor management or mismanagement of our forest lands to persist. Indeed, Sir John A. Macdonald showed great foresight concerning our forests in a letter written to the premier of Ontario in June of 1871:

> The sight of the immense masses of timber passing my windows every morning constantly suggests to my mind the absolute necessity there is for looking at the future of this great trade. We are recklessly destroying the timber of Canada, and there is scarcely a possibility of replacing it. ... The Dominion Government, having no lands, has no direct interest in the subject, but it seems to me that it would be a very good thing for the two Governments of Ontario and Quebec to issue a Joint Commission to examine the whole subject and to report:-
> 1st. As to the best means of cutting the timber after some regulated plan, as in Norway and on the Baltic;
> 2nd. As to replanting so as to keep up the supply as in Germany and Norway, and
> 3rd. As to the best means of protecting the woods from fires. ...
>
> (Pope, 1921, p.147)

Canada has come a long way: we are quite proficient at fighting fires. However, in 1982, Canada was importing telephone poles from Finland and railway ties from Malaysia (MacGregor, 1982, pp.10-14). In 1986, Canadians may discover that we are importing eucalyptus cellulose from Brazil, where Kimberly-Clark Corporation is using it to replace the more expensive Canadian softwood fibres used in manufacturing disposable diapers and tissues (King, 1986, p.C8). Why are our fibres more expensive? Is it because of poor management in the past? A better question may be to ask why Brazilian fibres are cheaper; is it because of overexploitation of the tropical rainforests? In both cases the answer points to poor management where the overexploitation of tropical forests today resembles the abusive exploitation of Canada's forests in years past. Macdonald's thoughts were well founded for the white pine (*pinus strobus*), the 'big timbers' which have all but disappeared as a substantial component of Canada's commercial forest industry. The cull species of yesteryear have become Canada's prime species today.

The scientific and technological knowledge to improve forest management does exist (Swan, 1969; Proceedings Cornell Agricultural Waste Management Conference, 1978; Minckler, 1980; Davies, 1985, pp.167-180). Over the last decade, Canadians have become aware of the need for wise management through issues such as those raised by MacGregor (1982), Canadian Press (Globe And Mail, 1983), Boychuk (1984) and King (1986). It is likely that the most sustaining

path for the forest industry would be that which takes a long-term, integrated approach to management. Integrated in the sense partly expressed by Parker (1972, pp.411-412) and Tschirley (1972, p.407) where they advocate a comprehensive systems approach as in agricultural crop protection. This allows for both chemical and manual brush clearing where appropriate, concurrently striving for an economically feasible, total biological control program. With the biophysical and ecological knowledge of natural systems, and sound silvicultural practices, it is possible and necessary to satisfy society's needs and safeguard them for generations to come.

5.3.1. Recommendations For Future Herbicide Research

Depending on the leaching characteristics of the pesticide, or the purpose of the sampling program, there may be the need to sample soil to greater depths than the customary 15 cm[15], especially when the research concerns toxic accumulation in soils or the contamination of groundwaters. In such cases the soil should be sampled to one horizon or incremental depth greater than that suspected of containing residues.

This study has shown that herbicides can leach below the organic surface layer, albeit the quantities detected are very low. As mentioned in subsection 4.4.1, page 53, organic matter has been identified by numerous authorities as a significant sink for herbicide adsorption and graphs 4-11 through 4-14 further exemplify this notion by contrasting the very high residue values in the organic LF layer with the lower residue values in the mineral Ae to C layers. Therefore, it can be logically inferred that without the organic surface layer and its strong adsorptive properties, the potential for leaching through to lower soil horizons and/or the water table is a real possibility. However, in order to prove the definitive importance of the organic layer as a buffer or residue sink it is necessary to examine the leaching patterns of herbicides in forest podzols with and without an organic surface layer: a topic for further study.

Excavation pits and manual labour are at present a very simple way to successfully sample the medium to coarse textured often stony soils, greater than 50 cm deep, found in boreal ecosystems. Of course there are other techniques better suited for a given site, but excavation pits and manual labour can be thought of as a suitable, universally possible common denominator for residue studies from which to build comparative studies. Augers are inadequate as they are responsible for crosscontamination of samples. Oakfield type cores have compaction problems, generally provide samples which are too small in size for analysis, are difficult to clean unless they have a somewhat inert inner sleeve, and are limited in the depth they can sample in stony soils. A rectangular soil corer has been designed (personal communication: Joseph Feng, Forest Pest

[15] Usually associated with agricultural or soil fertility studies.

Management Institute, 1986) which is particularly well suited for soil residue studies but is restricted to shallower depths. Some coring mechanisms which are power driven are acceptable but require machine operators and capital investment not available to all researchers. Furthermore, not all experimental sites may be accessible to these power driven coring machines.

As a precautionary recommendation for herbicide use in similar boreal environments, the coarse textured soil should have an organic surface layer of approximately 10 cm thickness or a clay content which should be at least 20 %; the minimum necessary to identify a soil textural class as a clay loam. In soils of cool, moist environments that do not meet these specifications the water table should be below a tertiary horizon of detection (see Item 1, Subsection 5.4.1, page 103) to prevent any chance of groundwater contamination. As the data suggest, these depths vary with the pesticide: 60 cm for dicamba, 51 cm for tebuthiuron and 42 cm for picloram. Hexazinone is excluded here due to the previously mentioned reasons relating to the high application rate. This work has indirectly demonstrated the sorptive importance of organic matter. This is supported by the literature which states the sorptive strength of both organic matter and clay in soil-pesticide interactions. Thus, from this work, regulatory officials may wish to consider these recommendations in setting minimum standards for the safe use of herbicides.

5.4. Conclusion

5.4.1. Summary

1. Dicamba (3,6-dichloro-o-anisic acid) leached through the first four horizons (LF, Ae, Bf and BC) down to a mean depth of 60 cm (n=4 of a possible 7 valid cases) during the interval after day 3 and until a time not greater than day 312.
   Hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine 2,4 (1H,3H)-dione) leached through the five horizons sampled (LF, Ae, Bf, BC and C) down to a mean depth of 65 cm (n=4 of a possible 6 valid cases) during the period after day 10 and until a time not greater than day 486. As a cautionary note the depth of leaching more likely reflects the high application rate than the nature of the chemical and should not be considered here for any other purpose than what might occur if an accidental spill took place.
   Tebuthiuron (N-[5-(1, 1-dimethylethyl)-1, 3, 4-thiadizol-2-yl]N, N,-dimethylurea) leached through the top four horizons sampled (LF, Ae, Bf and BC) down to a mean depth of 51 cm (n=4 of a possible 6 valid cases) during the interval after day 1 and before day 5 until a time not greater than day 310.
   Picloram (4-amino-3,5,6-trichloropicolinic acid) leached through the first three horizons (LF, Ae and Bf) down to a mean depth of 42 cm (n=3 of a possible 6 valid cases) during the period after day 1 and before day 5 until a time not greater than day 32 and also, specifically on day 483.

2. The organic LF horizon is a very important residue sink with a high buffering capacity (Column six, Tables 4-6 through 4-9). For dicamba a mean of approximately 78 %

(n=9) of residues are detected in the LF layer. This mean value increases to 90 % if two extremely low cases are deleted (n=7). For hexazinone a mean close to 83 % (n=8) of residues are detected in the LF layer. Again, if one low outlier is excluded, this figure increases to 87 % (n=7). For both tebuthiuron and picloram, where no cases are excluded (n=6), the mean percent of residues detected in each respective LF horizon is approximately 93 and 84 %.

3. All four herbicides are eluviated from the Ae horizon and illuviated in the Bf horizon as influenced by podzolization; a pedogenic process found in cool, humid climates under coniferous or mixed vegetation common in the boreal ecosystems of circumpolar countries.

4. The four selected herbicides have 50 % disappearance times which range as follows: 7 to 16 days for picloram; 9 to 25 days for dicamba; 123 to 186 days for hexazinone; and, 296 or more days for tebuthiuron.

5.4.2. Four Topics For Further Study

In a sense this experiment can be treated as a pilot project which has shown the need for further study covering a wide range of topics. Two of these subjects require field work while one is laboratory oriented and the last combines both field and laboratory work.

1. There is a need to investigate leaching patterns in forest podzols under natural conditions, with and without the organic surface layer. This should provide decisive evidence for or against organic material as a significant residue sink. An extension of this study which should yield more detailed information on the sorptive nature of the organic layer follows in the next paragraph.
2. As an extension of the first topic it should be useful to study differential patterns of adsorption/desorption by the individual components of the forest floor organic matrix. This laboratory study should be carried out with the matrix at different moisture levels and at two stages of composition (roughly defined in soil terminology as L and F, Litter and Fiber). The fractions of the H (Humus) stage of decomposition have been examined by a number of authorities, especially by Khan (1972, pp.1-12; 1973a, pp.429-434; 1973b, pp.141-148; 1980, pp.32-36), Grover (1971, pp.417-418) Grover and Smith (1974, pp.179-186) and, Madhun *et al.* (1986, pp.64-68) who have worked extensively on humic and fulvic acids, carbohydrates, resins, lignin and cellulose. This study should help identify some of the raw materials (see subsection 4.4.1, page 98) responsible for the high variation of organic recovery results. Thus, it should be possible to identify the relative importance or rank the sorptive capacities of the components of the organic matrix.
3. Important practical information on spray application criteria should be gained if one was to examine leaching patterns in the field to the depth of groundwater. This should be carried out by sampling soil water (tensiometers made of an appropriately inert material), groundwater (drilling still wells) and the soil itself (excavation pits). This should supply a more accurate balance sheet as to the movement of herbicides in the natural soil environment.
4. As an extension of the first and third topics more detailed knowledge on the leaching behaviour of herbicides should be obtained by studying the movement of herbicides in relatively undisturbed soil columns under selected environmental conditions. A greenhouse in which ambient temperature, moisture, humidity, wind and photoperiod can be controlled is ideal for such an experiment. It should also be possible to check leaching of compounds through soil columns, comparing those with and without the organic surface layer. In addition, the sampling of soil water, soil and leachates should

act as a check on the field leaching study mentioned above. Thus, the first and third field studies enumerated above should be excellent tests of the physical analogue model developed in the greenhouse.

5.4.3. Final Statement

There is no doubt that herbicides are playing an increasing role in our society and this study has brought to the foreground two important points for industry and government to consider. First, the critical role of organic matter as a sink for organic compounds probably increases because podzols are acidic, well drained, medium to coarse in texture and of cool temperature regimes: conditions that are conducive to the leaching of organic compounds. Thus, the second point concerning persistence arises. With leaching below the organic LF horizon a fact, then undesirable contamination below the LF level is a possibility that must be examined further so that the potential for toxic accumulations in the cold, acid, dark and aerobic/anaerobic environment of soil/groundwater systems is addressed. This study indicates that the above concerns are serious if herbicide use is not properly managed, just as real as the degradation of our forest resources if they are not properly managed. As Canadians begin to realize the need for wise management of the land for forestry, they will recognize that this removes it from a wilderness state to a state of control not very different from that of farmland. Hence, when the public's perception of what constitutes Canada's commercial forest lands improves, the safe use of pesticides will be acknowledged as an integral part of forest management.

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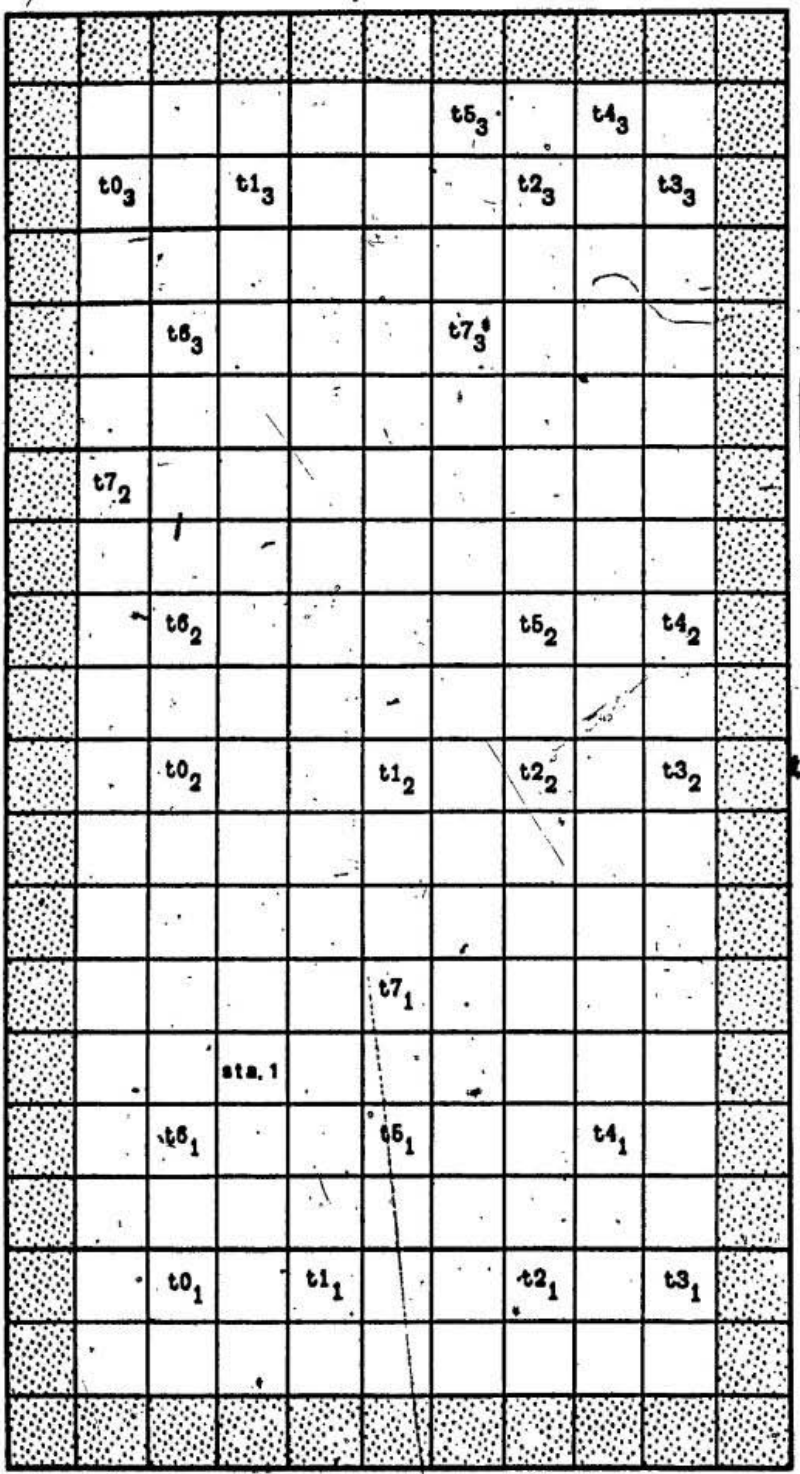
Appendix A

Experimental Field Plots Showing The Location Of Sample Pits



boundary area excluded from sampling.

tn: sample period as per table 3-2, page 56.

tn_1: 1st of 3 pits.

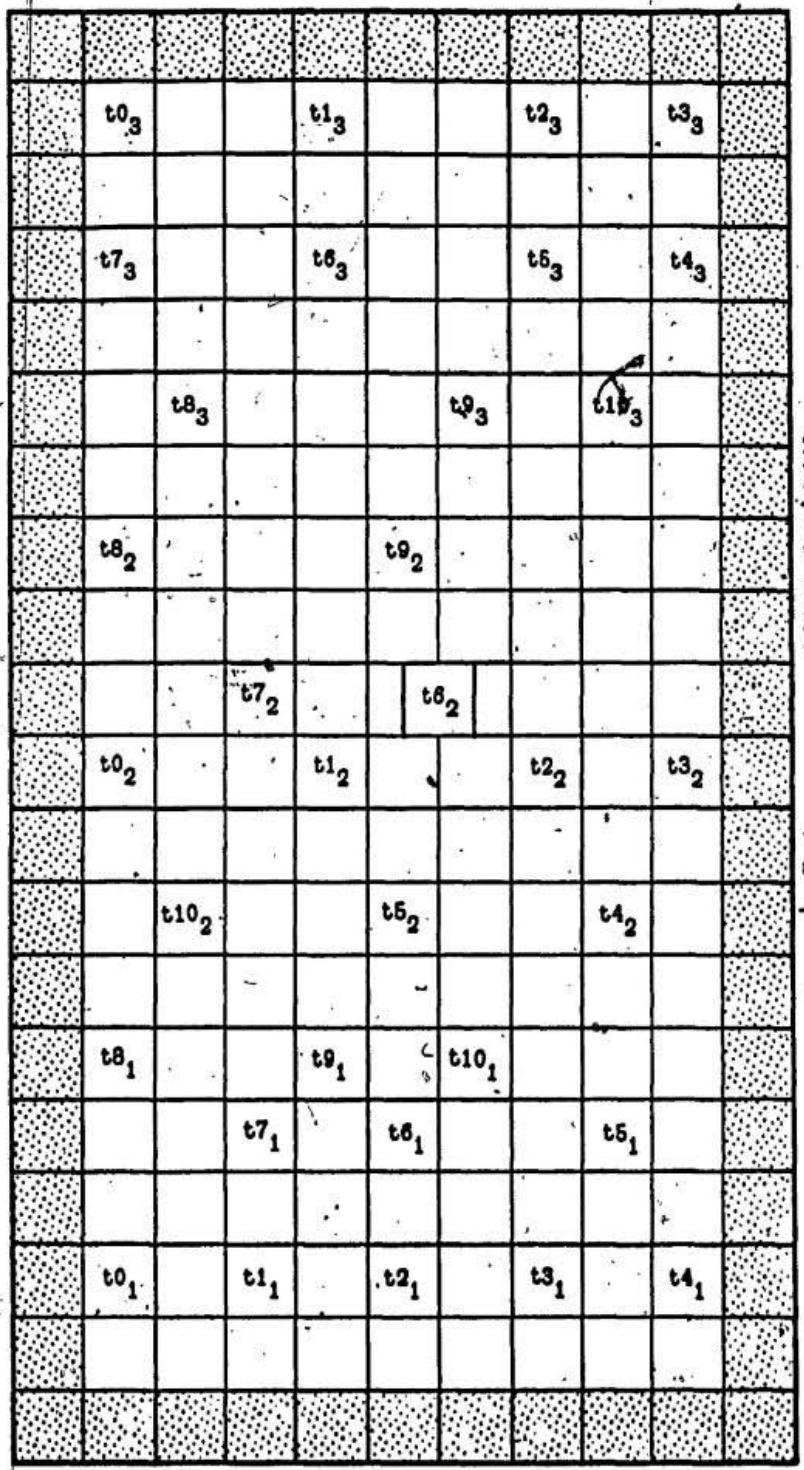
tn_2: 2nd of 3 pits.

tn_3: 3rd of 3 pits.

station 1:
- 1 wedge-type cumulative rain gauge.
- 1 soil temp. probe & 1 soil moisture block both at 9 cm depth.
- 1 soil temp. probe & 1 soil moisture block both at 25 cm depth.

scale: 10 mm = 1 m

Figure A-1: 2,4-D Sample Pits



boundary area excluded from sampling.

tn: sample period as per table 3-2, page 56.

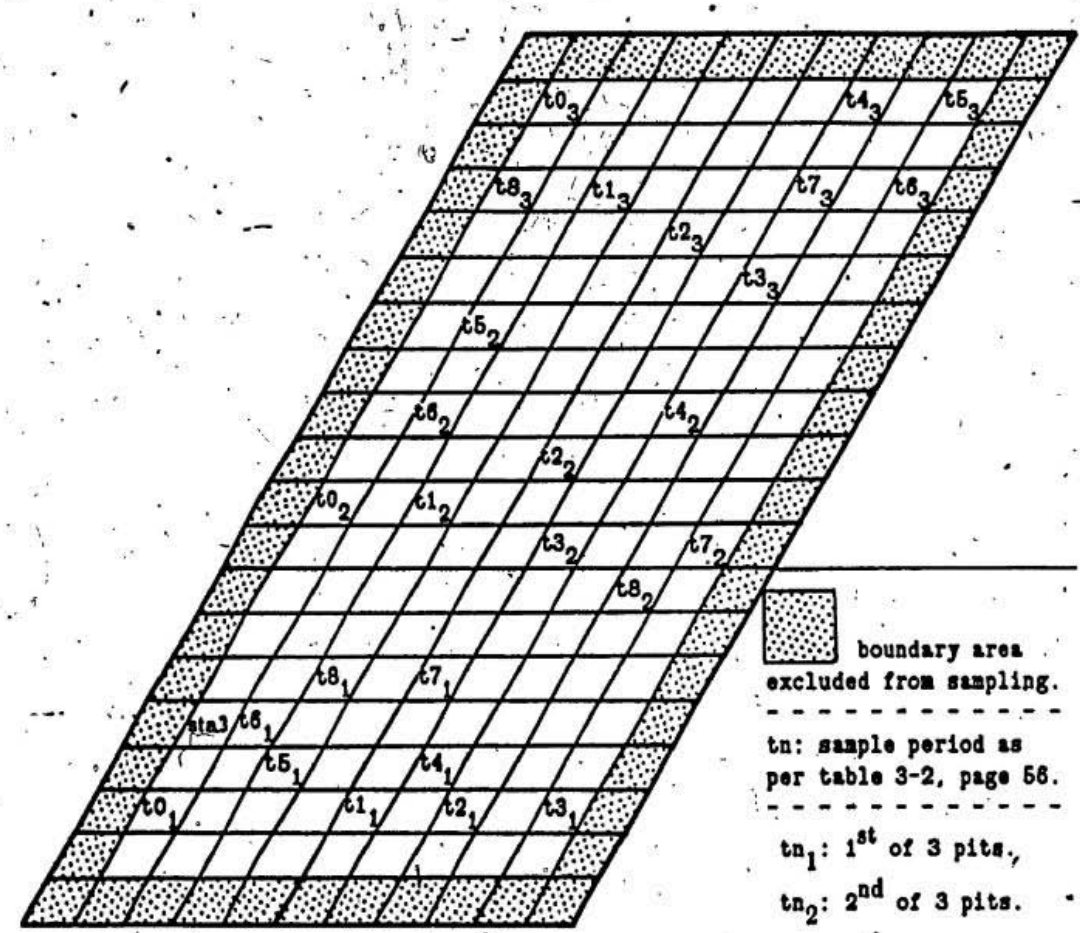
tn_1: 1st of 3 pits.

tn_2: 2nd of 3 pits.

tn_3: 3rd of 3 pits.

scale: 10 mm = 1 m.

Figure A-2: Dicamba Sample Pits



boundary area excluded from sampling.

tn: sample period as per table 3-2, page 56.

tn_1: 1st of 3 pits.

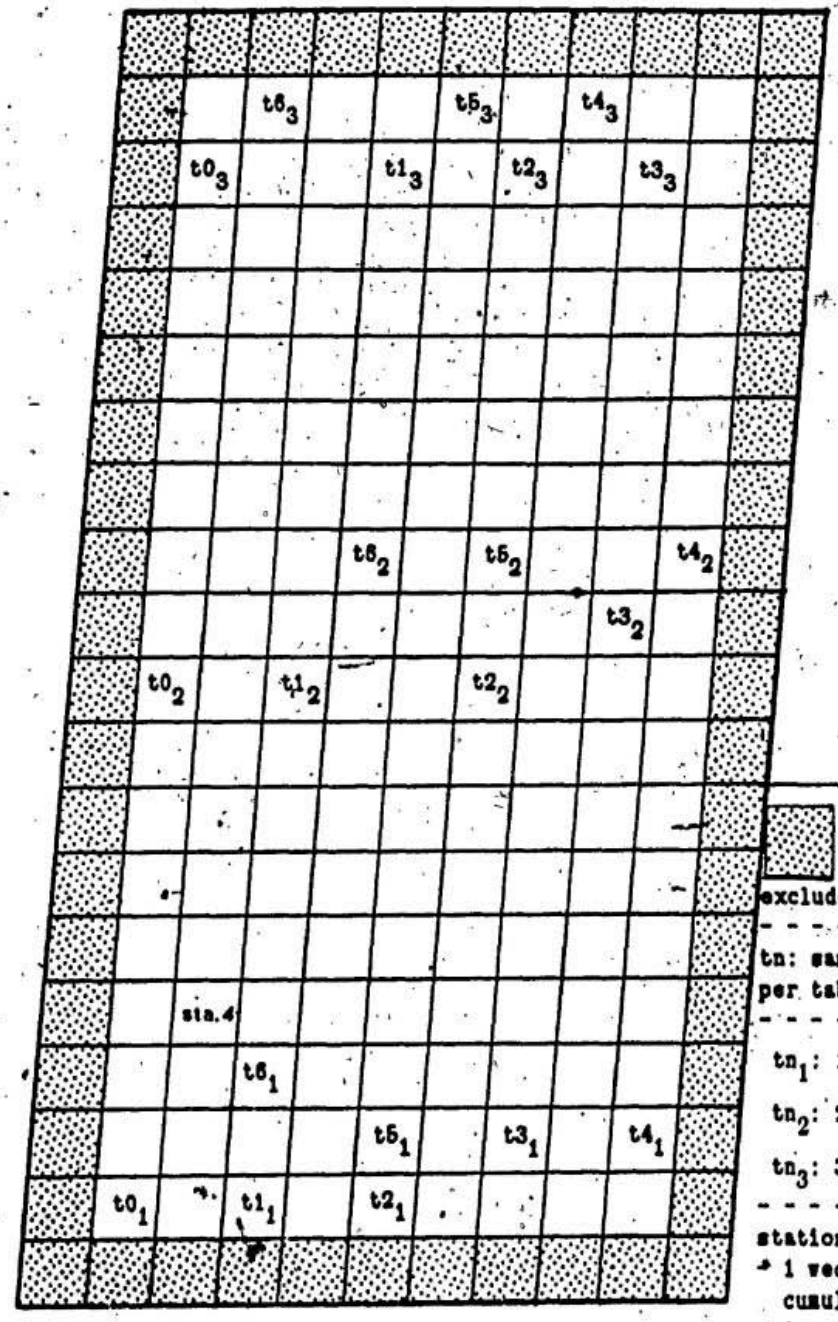
tn_2: 2nd of 3 pits.

tn_3: 3rd of 3 pits.

station 3:
- 1 wedge-type cumulative rain gauge.
- 1 soil temp. probe & 1 soil moisture block both at 14 cm depth.
- 1 soil temp. probe at 16 cm & 1 soil moisture block at 35 cm depth.

scale: 7mm. = 1m

Figure A-3: Hexazinone Sample Pits



boundary area excluded from sampling.

tn: sample period as per table 3-2, page 56.

tn_1: 1st of 3 pits.

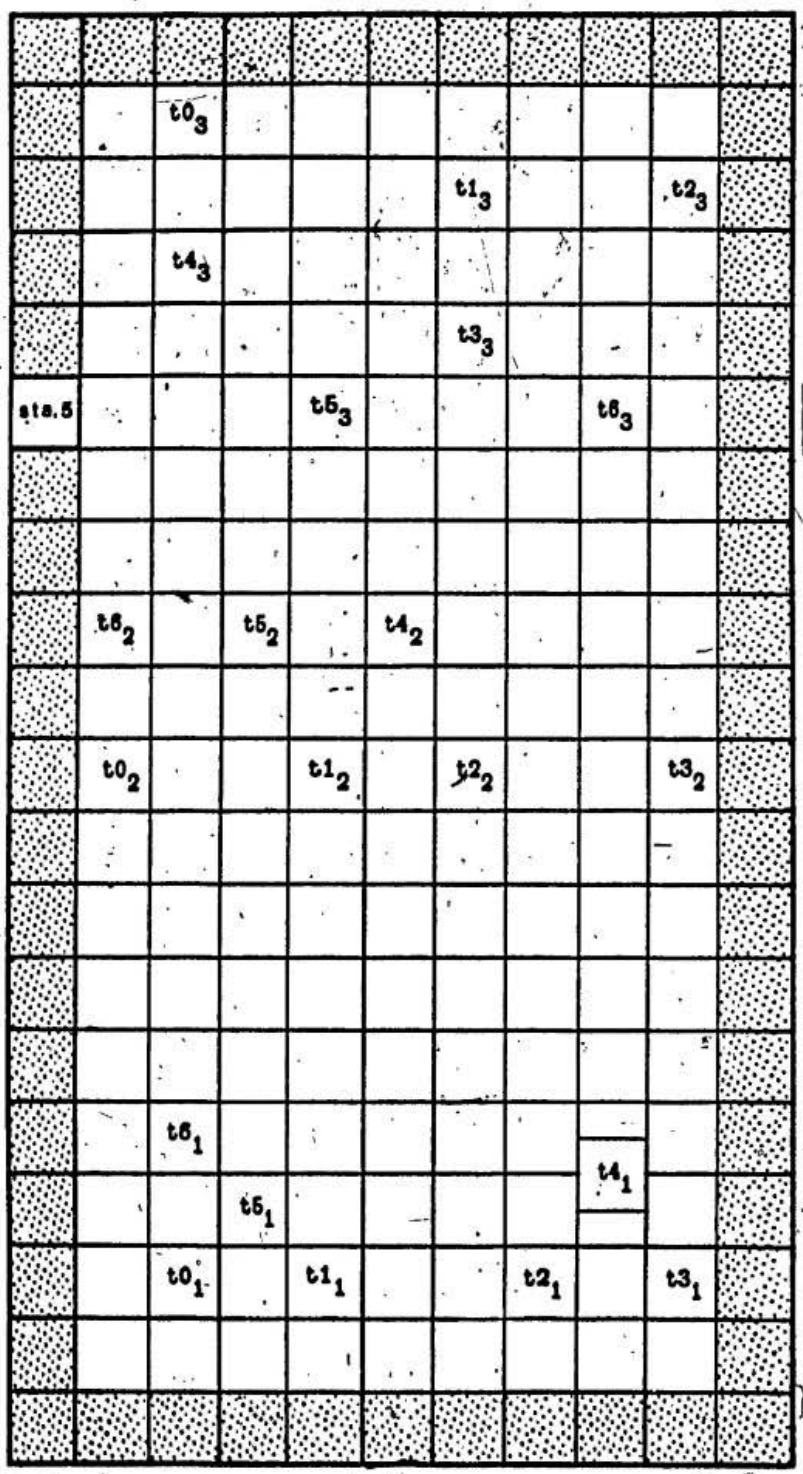
tn_2: 2nd of 3 pits.

tn_3: 3rd of 3 pits.

station 4:
- 1 wedge-type cumulative rain gauge.
- 1 soil temp. probe at 7 cm & 1 soil moisture block at 5 cm depth.
- 1 soil temp. probe & 1 soil moisture block both at 50 cm depth.

scale: 9mm = 1m

Figure A-4: Tebuthiuron Sample Pits



boundary area excluded from sampling.

tn: sample period as per table 3-2, page 56.

tn_1: 1st of 3 pits.

tn_2: 2nd of 3 pits.

tn_3: 3rd of 3 pits.

station 5:
- 1 wedge-type cumulative rain gauge.
- upper soil temp. probe & soil moisture block disturbed.
- 1 soil temp. probe at 44 cm & 1 soil moisture block at 43 cm depth.

scale: 10 mm = 1 m

Figure A-5: Picloram Sample Pits

Appendix B

Checklist For:
Soil Sampling Materials And Supplies Used In The Field

Table B-1: Field Checklist For Soil Sampling

1. 2 - long-handled, round-pointed shovels.
2. 1 - spare shovel handle.
3. 2 - heavy picks.
4. 1 - spare pick handle.
5. 2 - army surplus-type spade/pick for cleaving a clean face from profile for sampling.
6. 1 - metre stick.
7. 1 - folding "Sweva" type saw for large roots.
8. 1 - sharp axe or hatchet for large roots.
9. 2 - 4 pairs of work gloves.
10. 2 - 4 rain suits or high rubber boots.
11. 1 - camera with film.
12. 2 - or more styrofoam coolers and an adequate supply of ice packs (rinse clean 2 litre plastic pop bottles, they make excellent ice packs).
13. 1 - clip board.
14. 1 - soil temperature meter.
15. 1 - soil moisture meter.
16. 1 - set of soil moisture/temperature and weather data sheets.
17. Field note books and water resistant pens.
18. 1 - soil sampling kit:
    a. 2 - pointed garden trowels.
    b. Heavy duty plastic baggies (double bag samples) and ties.
    c. Rubber bands.
    d. Large garbage bags for double bagged soil samples.
    e. Paper towels.
    f. Disposable latex gloves.
    g. Wire brush.
    h. Aluminum foil to cover composite sample pails while in field.
    i. Bring a supply of the following for 3 well marked wash bottles:
        i. One for petroleum ether (wrap in foil to inhibit evaporation).
        ii. One for soap water.
        iii. One for distilled water.

Appendix C

Permeability Tests, July And August, 1983

Table C-1: Field Permeability Tests : plug method *

	Volume of Water (l/181.4 cm^2)	Time Interval (min,sec)	Rate of Flow (l/min/cm^2)	Ground Surface Condition
1	0.78	0,05.1	0.05	Moss growth on
2	7.57	2,23.2	0.02	level ground.
3	7.57	0,54.9	0.05	
4	7.57	0,54.1	0.05	
5	7.57	1,18.8	0.03	n = 13
6	7.80	2,05.2	0.02	
7	7.80	3,01.9	0.01	mean flow
8	7.80	1,28.8	0.03	= 0.04 l/min/cm^2
9	8.48	1,19.0	0.04	
10	11.36	0,59.1	0.06	s.d. = 0.02 l/min/cm^2
11	11.36	1,37.0	0.04	
12	11.36	3,51.0	0.02	
13	15.14	2,02.7	0.04	
tot:	113.14	21,28.0		
1	7.57	1,22.5	0.03	Little or no growth
2	7.57	4,21.0	0.01	on compacted
3	7.57	6,32.6	0.01	surface of skid
4	11.36	2,33.7	0.02	tracks, level
5	11.36	2,09.2	0.03	ground.
6	11.36	5,06.4	0.01	
7	11.36	2,15.3	0.03	n = 9
8	11.36	9,14.8	0.01	
9	15.14	6,04.8	0.01	mean flow = 0.02 l/min/cm^2
tot:	94.65	39,48.0		s.d. = 0.01 l/min/cm^2

* = water applied in a PVC tube with inside diameter of 15.2 cm (181.46 cm^2) and set approximately 5 cm into the ground.

Appendix D
Field Description Of Soil Profile

Table D-1: Field Description Of Control Section Profile

Characteristic	Horizon LF	Aegj	Bf	BC	C
Depth (cm):	12 - 0	0 - 10	10 - 23	23 - 33	33 - 108+
Colour (moist):	----	5YR 7/2m	5YR 5/8m	10YR 6/3m	2.5Y 6.2m,
Texture (moist):	fiberous	loamy sand	sandy loam	sandy loam	silty loam
Mottles:					
abundance-	----	none	none	none	many
size-	----	none	none	none	medium
contrast-	----	none	none	none	distinct
Horizon boundary:					
form-	wavy	wavy	wavy	wavy	wavy
distinctness-	gradual	abrupt	gradual	gradual	diffuse
Structure:					
size-	----	medium	medium	medium	fine
type-	----	granular	granular	granular	psuedo platy
distinctness-	----	weak	moderate	moderate	mod - strong
Stoniness and rockiness:	----	graditic blocks near surface	[---silt caps in lower Bf to C,----- ---many rounded and angular blocks]		
Consistence:					
stickness-	----	slightly	slightly	slightly	slightly
plasticity-	----	slightly	slightly	slightly	slightly
Cementation:	----	none	weakly	none	none
Roots:	many medium to fine, horiz.	many fine, random.	[few, medium, horizon.]		very few.
Pores:					
abundance-	----	many,	few,	few,	many,
size-	----	medium,	fine,	fine,	very fine,
continuity-	----	discontinuous,	[- - - c o n t i n u o u s - - -]		
type-	----	root & interstitial	[- - i n t e r s t i s i a l - -]		
Clay films:	----	none	none	none	none
Drainage:	well	well	[m o d e r a t e l y w e l l]		
Landforms, slope:	[m o r a i n a l i n c l i n e, 15 - 23 percent slope]				

m = Munsell colour scheme.
---- = Not applicable.

Appendix E
Soil Bulk Density Determination

Table E-1: Summary Of Bulk Densities (gm/cm^3)

Control section core: a) 1.35 | Excavation cores' mean = 1.24. Includes LF,
b) 1.33 | Ae & part of Bf layer & coarse fragments that
Ridge-top core: c) 1.12 | are excluded from the Oakfield corer.

			LF	Ae	Bf	BC	C
Vertical cores:			0.26	1.12	1.07	---	---
Horizontal cores:	Plot 2,	Pit 1,	0.47*	1.16	1.11	1.24	1.24
		Pit 2,	0.30	0.89	1.06	1.04	1.38
		Pit 3,	0.23	1.18	1.05	1.25	1.18
	Plot 3,	Pit 1,	0.21	0.97	0.85	1.01	1.06
		Pit 2,	0.17	1.08	0.93	1.17	1.28
		Pit 3,	0.23	1.15	0.90	1.13	1.14
Mean bulk density:			0.23	1.08	1.00	1.14	1.21

* = This outlier value of 0.47 excluded from the computation of the mean bulk density for the LF horizon.

note: The organic layer (LF) should have a B.D. of about 0.23 and as there are no stones in this layer the Oakfield core samples should suffice. The mineral layers (BC & C) should have higher B.D. where the silts and clays have been translocated. In any case the oakfield core samples for the stony mineral layers (Ae - C) should be adjusted for coarse fragments (stones > 2 cm dia.) using the excavation cores' mean of 1.24 gm/cm^3 as follows:

Horizon	Excavation cores' mean	x	Oakfield cores	=	Adjusted B.D.
Ae	1.24	x	1.08	=	1.34
Bf	1.24	x	1.00	=	1.24
BC	1.24	x	1.14	=	1.41
C	1.24	x	1.21	=	1.50

Table E-2: Vertical Core Samples: Oakfield Corer (i.d. = 19.05 mm)

Vertical Core Samples (every 7.5 meters for 30 metres)

Horizon	Sample Size n	Total Length Of Core (cm)	Total Volume Of Core (cm^3)	Oven-Dry (105°) Weight (gm)	Bulk Density (gm/cm^{-3})
LF	9	43.0	121.9	32.2	0.26
Ae	7	31.5	89.3	100.2	1.12
Bf	3	43.5	123.3	131.4	1.07

Table E-3: Excavation Core Samples

Sample	Core# Radius (cm)	Height (cm)	Volume (cm^3)	Weight (gm)~	Bulk Density (gm/cm^{-3})
Control section*: a)	7.62	40.5	7387.8	10000.0	1.35
b)	7.62	20.0	3649.3	4860.0	1.33
Ridge-top*: c)	7.62	53.0	9668.0	10810.0	1.12
Mean:			6901.4	8556.7	1.24

\# = Excavation corer is a PVC tube equipped with a steel cutting edge.
Includes LF, Ae & part of Bf horizons.
~ = Oven-dry weight of core at 105 deg. celsius for 24 hours.
* = Mid-slope, lower center location of site.
* = Ridge-top, upper center location of site.

Table E-4: Horizontal Core Samples: Oakfield Corer (i.d. = 19.05 mm)

Plot #	Horizon	Pit, 1 ht	vm	wt	bd	Pit, 2 ht	vm	wt	bd	Pit, 3 ht	vm	wt	bd
2	LF	23.0	65.2	30.4	0.47	23.0	65.2	19.8	0.30	44.5	126.2	28.4	0.23
	Ae	26.5	75.1	89.7	1.19	26.0	73.7	65.4	0.89	19.0	53.9	63.6	1.18
	Bf	43.0	121.9	135.7	1.11	44.0	124.8	132.7	1.06	29.5	83.6	87.6	1.05
	BC	37.5	106.3	131.6	1.24	36.5	103.5	108.1	1.04	22.5	63.8	79.7	1.25
	C	25.0	70.9	88.9	1.24	27.0	76.5	105.6	1.38	21.5	61.0	72.2	1.18
3	LF	44.0	124.7	25.9	0.21	41.0	116.2	20.2	0.17	41.5	116.2	26.8	0.23
	Ae	38.0	107.7	104.7	0.97	35.5	100.6	109.0	1.08	21.5	61.0	70.0	1.15
	Bf	60.5	171.5	146.3	0.85	38.5	109.2	101.0	0.93	43.5	123.3	110.5	0.90
	BC	35.5	100.6	101.6	1.01	37.0	104.9	122.3	1.17	38.5	109.2	123.5	1.13
	C	26.5	75.1	79.5	1.06	34.5	97.8	125.2	1.28	38.0	107.7	123.0	1.14

plot #: 2 = second plot, dicamba. 3 = third plot, hexazinone.
i.d. = Inside diameter (mm).
ht = Length of soil core sample (cm).
vm = Volume of soil core sample (cm^3).
wt = Weight of soil core sample (gm), oven-dry at 105 deg. celsius for 24 hours.
bd = Bulk density of soil core sample (gm/cm^{-3}).

Appendix F
Soil Moisture Content

Table F-1: Field Moisture Determinations: gravimetric method

Date dd/mm/yy	Percent Soil Moisture LF	Ae	Bf	BC	C	total	n	mean
24/07/83	63	15	11	na	na	89	3	--
27/07/83	73	18	32	17	na	140	4	--
31/07/83	53	14	19	8	11	105	5	21
3/08/83	64	14	18	15	14	125	5	25
4/08/83	68	15	17	9	8	117	5	23
14/08/83	60	15	17	9	8	99	5	20
24/08/83	50	15	17	9	8	99	5	20
25/09/83	66	20	19	[illegible]	13	137	5	27
26/05/84	66	15	18	[illegible]	13	126	5	25
27/05/84	64	16	22	14	13	129	5	26
4/08/84	53	17	16	11	11	108	5	22
17/11/84	72	16	18	14	12	132	5	26
18/11/84	74	16	21	na	na	111	3	--
total:	816	206	245	139	111			
n:	13	13	13	11	10			
mean:	63	16	19	13	11			

na = data not available.

Appendix G

Horizon Thicknesses As Determined By Sampling Pits And Digitized Horizon Thicknesses

Table G-1: Summary: Horizon Thickness Statistics (cm)

Horizon*	n	Mean	Standard Deviation	Standard Error of Mean	Range Min	Range Max
LF	839	12.2	2.1	0.130	1.4	29.0
As	839	6.9	2.6	0.181	0.0	35.3
Bf	839	25.3	4.9	0.299	5.7	52.3
BC	734	14.7	1.0	0.103	2.5	20.0
C@	243	9.8	1.9	0.121	0.0	24.0

* = All herbicide sample pits.
@ = Upper limit of C only.

Appendix H
Organic Carbon Content

Table H-1: Organic Carbon Content: loss-on-ignition

	Carbon Content (percent by weight)					
Horizon:	LF	Ae	Bf	BC	C	
	93.2	0.8	7.2	1.6	1.0	
	87.8	1.0	4.2	1.6	7.7	
	92.6	2.2	7.4	2.8	1.5	
	81.2	1.6	9.1	2.2	1.8	
	92.0	1.3	5.0	1.9	1.2	
	87.6	2.1	6.2	2.1	1.7	
	93.6	1.0	5.1	2.1	1.0	
	95.8	1.2	6.8	1.8	1.1	
	87.9	0.8	4.1	1.3	0.8	
	90.2	1.1	6.2	2.0	1.5	
	91.0	0.9	4.9	2.0	1.1	
	91.3	1.0	5.1	1.6	0.8	
						Grand
mean:	90.4	1.2	6.0	2.0	1.8	20.2
n:	12	12	12	12	12	N = 60
standard deviation:	3.85	.48	1.5	.39	1.9	35.4
minimum:	81.2	0.8	4.1	1.3	0.8	0.8
maximum:	95.8	2.2	9.1	2.8	7.7	95.8

Appendix I
Particle Size Determination

Table I-1: Summary Of Particle Size Determination: hydrometer method

The particle size data for the following table is listed in appendix J (pages 140 - 142). This is a summary and associated-statistics table.

Horizon	Particle Size*	Sample Size	Mean	Standard Deviation	Minimum	Maximum
Ae	Sand	12	74.8	1.65	71.0	77.7
Ae	Silt	12	16.9	1.52	14.7	19.4
Ae	Clay	12	8.2	0.77	7.3	9.6
Bf	Sand	12	68.5	2.72	62.5	70.8
Bf	Silt	12	22.8	2.75	19.7	27.9
Bf	Clay	12	8.6	1.59	5.5	10.1
BC	Sand	12	58.0	9.08	46.3	81.1
BC	Silt	12	29.1	7.20	10.7	36.0
BC	Clay	12	12.8	2.52	7.9	17.8
C	Sand	12	61.7	8.52	53.0	85.6
C	Silt	12	24.2	6.08	7.2	31.1
C	Clay	12	14.0	3.06	7.2	18.1
Total: All Horizons:	Sand	48	65.8	8.99	46.3	85.6
	Silt	48	23.3	6.50	7.2	36.0
	Clay	48	10.9	3.31	5.5	19.1

* = Particle size where:

1) 2.00 mm < sand ≥ 0.05 mm,

2) 0.05 mm < silt ≥ 0.002 mm,

3) 0.002 mm < clay (McKeague, 1978, pp. 15-25).

Appendix J

Soil Chemical And Physical Properties: analysis at Memorial University

Table J-1: Orthic Humo-Ferric Podzol Properties: M.U.N. ~

Location* / Property	Horizon				
Plot 3, Pit 1:	LF	Ae	Bf	BC	C
pH = 0.1 $CaCl_2$	3.51	3.20	4.50	4.70	4.60
% Carbon@	92.6	2.24	7.36	2.82	1.46
Particle Size#					
% Sand		74.3	67.9	57.9	56.0
% Silt		17.6	25.2	31.0	27.9
% Clay		8.0	6.8	11.1	16.1
Plot 3, Pit 2:					
pH	3.20	3.31	4.75	5.28	5.10
% Carbon	81.2	1.63	9.10	2.23	1.85
Particle Size					
% Sand		75.6	69.0	57.1	62.8
% Silt		15.4	20.9	29.0	23.1
% Clay		8.8	10.1	13.9	14.1
Plot 3, Pit 3:					
pH	3.35	3.50	4.50	5.30	5.00
% Carbon	92.0	1.34	5.01	1.90	1.23
Particle Size					
% Sand		71.0	70.8	54.8	58.2
% Silt		19.4	22.9	32.8	27.0
% Clay		9.6	6.3	12.4	13.9
Plot 3, Composite Of All Pits:					
pH	3.47	3.20	4.62	4.90	4.95
% Carbon	87.6	2.06	8.09	2.10	1.71
Particle size					
% Sand		74.4	69.0	64.2	55.5
% Silt		17.5	20.5	25.7	29.6
% Clay		8.1	10.3	10.1	14.0

~ = Memorial University of Newfoundland.
* = Location: Plots 1, 2, 3, 4, & 5 represent 2,4-D, Dicamba, Hexazinone, Tebuthiuron & Picloram respectively.
@ = Carbon loss-on-ignition.
\# = Particle size as defined in Appendix I, Table I-1, hydrometer method.

continued...

Table, J-1, continued

Location	Horizon				
Plot 1, Pit 2:	-LF	Ae	Bf	BC	C.
Property					
pH = 0.1 $CaCl_2$	3.80	3.80	4.70	5.30	5.28
% Carbon@	93.2	0.82	7.17	1.56	1.04
Particle Size*					
% Sand		75.4	69.2	81.1	85.6
% Silt		16.0	21.4	10.8	7.2
% Clay		[illegible]	9.4	7.9	7.2
Plot 4, Pit 1:					
pH	3.00	4.50	3.20	4.55	4.55
% Carbon	93.8	0.98	5.13	2.10	0.93
Particle Size					
% Sand		75.7	63.5	49.9	53.2
% Silt		16.8	27.6	36.0	31.1
% Clay		7.5	8.9	14.1	15.7
Plot 4, Pit 2:					
pH	2.55	3.30	4.50	4.60	4.60
% Carbon	95.8	1.20	6.82	1.80	1.13
Particle Size					
% Sand		76.0	69.4	60.4	59.1
% Silt		14.7	20.6	28.4	24.9
% Clay		9.3	10.0	11.2	16.0
Plot 4, Pit 3:					
pH	3.21	3.20	4.19	4.45	4.59
% Carbon	97.9	0.85	4.13	1.29	0.85
Particle Size					
% Sand		78.9	70.6	57.7	64.9
% Silt		13.3	21.3	26.9	23.2
% Clay		7.8	8.1	15.4	11.9

* = Location: Plots 1, 2, 3, 4, & 5 represent 2,4-D, Dicamba, Hexazinone, Tebuthiuron & Picloram respectively.

@ = Carbon loss-on-ignition.

* = Particle size as defined in Appendix I, Table I-1, hydrometer method.

continued...

Table, J-1, continued

Location	Horizon				
Plot 2, Pit 2:	LF	Ae	Bf	BC	C
Property					
pH = 0.1 $CaCl_2$	3.40	3.48	4.50	5.09	5.00
% Carbon$	87.8	0.96	4.15	1.64	7.75
Particle Size*					
% Sand		78.7	70.5	51.4	61.5
% Silt		19.0	24.0	36.0	25.6
% Clay		7.3	5.5	12.6	12.9
Plot 5, Pit 1:					
pH	3.80	3.30	4.60	4.95	5.00
% Carbon	90.2	1.11	6.21	2.01	1.47
Particle Size					
% Sand		75.7	68.6	57.9	63.4
% Silt		16.5	21.5	29.4	20.6
% Clay		7.8	9.9	12.7	16.0
Plot 5, Pit 2:					
pH	3.70	3.40	4.70	5.30	5.20
% Carbon	91.0	0.86	4.89	1.95	1.11
Particle Size					
% Sand		74.3	62.5	46.3	53.0
% Silt		17.1	27.9	35.9	28.9
% Clay		8.6	9.6	17.8	18.1
Plot 5, Pit 3:					
pH	2.90	3.38	4.50	4.85	4.60
% Carbon	91.3	0.98	5.11	1.64	0.84
Particle Size					
% Sand		77.7	69.5	54.2	59.1
% Silt		14.9	21.1	31.7	24.9
% Clay		7.3	9.4	14.1	16.0

* = Location: Plots 1, 2, 3, 4, & 5 represent 2,4-D, Dicamba, Hexazinone, Tebuthiuron & Piclorah respectively.

$ = Carbon loss-on-ignition.

* = Particle size as defined in Appendix I, Table I-1, hydrometer method.

Appendix K

Soil Chemical And Physical Properties: analysis at C.B.R.I., Ottawa

Table K-1: Orthic Humo-Ferric Podzol Properties: C.B.R.I. ~ *

	Horizon						
	Aegj	Bf		BC		C	
C.B.R.I. Analytical Laboratory Number:	84-912	-913	-914	-915	-916	-917	-918
Property							
pH, 1:2, $CaCl_2$	3.5	4.7	4.5	4.7	4.6	4.4	4.2
% Carbon	0.64	2.10	3.59	1.00	0.62	0.16	0.10
% Nitrogen	0.00	0.10	0.09	0.03	0.01	0.01	0.00
Sodium Pyrophosphate							
% Iron	0.01	0.09	0.22	0.02	0.02	0.02	0.16
% Aluminum	0.03	0.51	0.83	0.26	0.21	0.14	0.07
Exchangeable Cations *me/100gm*, 2*N* NaCl							
Calcium	0.37	0.33	0.50	0.16	0.16	0.25	0.46
Magnesium	0.26	0.10	0.15	0.08	0.07	0.14	0.32
Potassium	0.10	0.08	0.11	0.07	0.08	0.10	0.13
Aluminum	1.47	0.11	0.30	0.08	0.08	0.17	0.47
Bray Phosphorus *µg/gm* soil	13	3	3	8	25	77	52
Water Retention							
4 *bar*	2.7	11.8	16.4	6.6	6.1	7.1	9.2
15 *bar*	2.0	9.5	12.9	5.1	4.5	6.0	5.1
Particle Size*							
% Sand	69.6	69.6	67.5	73.1	67.8	46.8	48.4
% Silt	29.0	27.6	28.5	25.2	28.3	45.1	40.5
% Clay	1.4	2.8	4.0	1.7	3.9	8.2	11.0

~ = Chemistry and Biological Research Institute, Ottawa, Ontario.

* = Particle size where:

1) 2.00 mm < sand ≥ 0.05 mm,

2) 0.05 mm < silt ≥ 0.002 mm,

3) 0.002 mm < clay ≥ 0.0002 mm (McKeague, 1978, pp. 15-25).

Appendix L
Humic And Fulvic Acid

Table L-1: Ash, Moisture And Elemental Composition Of Humic Substances

Percent By Weight

Acids	Elemental Composition				Ash	Moisture
	Carbon	Hydrogen	Nitrogen	Sulfur		
Fulvic	10.64	1.26	0.22	0.24	86.99	0.05
Humic	52.00	5.84	1.58	0.35	7.84	1.44

Appendix M
Available Phosphorous

Table M-1: Extractable Phosphorus: bray method

Plot #	Pit #	Extractable Phosphorus (Kg/Ha) Horizon					
		LF	Ae	Bf	BC	C	
1	2	160	100	160	400	1020	
2	2	175	100	205	470	810	
3	1	165	110	205	330	715	
3	2	150	140	200	305	1070	
3	3	150	120	240	250	1025	
4	1	150	180	170	505	1140	
4	2	115	95	160	375	605	
4	3	115	125	240	315	460	
5	1	150	150	300	430	750	
5	2	110	180	300	625	660	
5	3	125	180	250	650	1105	
							grand
total:		1565	1400	2430	4655	9360	19410
mean:		142.3	127.3	220.9	423.2	850.9	352.9
variance:		496.8	986.8	2504.1	16831.4	53509.1	88247.9
std. dev.:		22.3	31.4	50.0	129.7	231.3	297.1

Appendix N

SPSSX Computer Programs For Distribution Graphs And Descriptive Statistical Tables

Dicamba SPSSX Graph And Table Computations

```
TITLE  DICAMBA DISTRIBUTION AND PERSISTENCE COMPUTATIONS
FILE HANDLE  /Resdata/ name="ZEROMAT7.DAT"
DATA LIST/  File=Resdata Free/Herb  Time  Days  Y1 to Y5  TotHerb  TotArea
          AreaSamp  SS1 SS2  D1 TO D5  M1 TO M5  RECA RECB  samp1 to samp5
VARIABLE LABELS  Herb "Herbicide"     Time "Sampling Periods (sample num)"
  Days "Days Postspray"   Y1 "LF Residues (ppm)"    Y2 "Ae Residues (ppm)"
  Y3 "Bf Residues (ppm)"  Y4 "BC Residues (ppm)"    Y5 "C Residues (ppm)"
  TotHerb "Total Herbicide Applied (gm)"   AREASAMP "SAMPLED AREA = 3 SQ. M."
  SS1 "Mass of Org Soil Sampled (gm)"   SS2 "Mass of Min. Soil Sampled (gm)"
  D1 "LF THICKNESS (CM)"  D2 "AE THICKNESS (CM)"  D3 "BF THICKNESS (CM)"
  D4 "BC THICKNESS (CM)"  D5 "C THICKNESS (CM)"   M1 "LF MOISTURE (% BY WT)"
  M2 "AE MOISTURE (% BY WT)"   M3 "BF MOISTURE (% BY WT)"
  M4 "BC MOISTURE (% BY WT)"   M5 "C MOISTURE (% BY WT)"
  RECA "MEAN RECOVERY OF SPIKED ORGANIC SAMP %"
  RECB "MEAN RECOVERY OF SPIKED MINERAL SAMP %"
VALUE LABELS  Herb 1 "2,4-D" 2 "Dicamba" 3 "Hexazinone" 4 "Tebuthiuron"
                   5 "Picloram"/
              Time 1 "Sample 1" 2 "Sample 2" 3 "Sample 3" 4 "Sample 4"
                   5 "Sample 5" 6 "Sample 6" 7 "Sample 7" 8 "Sample 8"
                   9 "Sample 9" 10 "Sample 10" 11 "Sample 11"/
     Y4 TO Y5 999 'SOIL NOT SAMPLED'
MISSING VALUES  Y4 TO Y5 (999)
RECODE  Y4 TO Y5(999=0)
NUMERIC  MM1 TO MM5(F4.3)/  AY1 TO AY5(F6.3)/  TOTAY(F7.3)/  TOTY(F7.3)/
        PMG1 TO PMG5/  TPMG/ PRT1 TO PRT5/  TPRT/  ID(F4.0)/ TS/ AD1/
        ORMG/  ORPMG/  ORPRT/  MINMG/  MINPMG/  MINPRT/  S1 TO S5
SELECT IF HERB = 2
COMMENT
COMMENT  HERB: 2,  "DICAMBA PERSISTENCE CURVES"
COMMENT
COMMENT  ANALYSIS WAS CARRIED OUT BY THE ONTARIO RESEARCH FOUNDATION IN
         MISSISSAUGA, ONTARIO.  RESULTS EXPRESSED ON A FRESH WEIGHT BASIS.
COMMENT
COMMENT  MM1 TO MM5 ARE SOIL DRYNESS BY WEIGHT EXPRESSED AS A UNIT FRACTION.
             WHERE:  M1 TO M5 = SOIL MOISTURE (% BY WEIGHT).
                     .01 = CONVERSION FACTOR FOR PERCENT TO UNITS.
                     1 - (R * .01) = SOIL DRYNESS (% BY WEIGHT) EXPRESSED
                                     AS A UNIT FRACTION.
COMMENT
DO REPEAT  R = M1 TO M5/ S = MM1 TO MM5
COMPUTE  S = 1 - (R * .01)
END REPEAT
COMMENT  AD1= LF HORIZON THICKNESS CORRECTED FOR REPRESENTATIVE SAMPLING VOLUME.
COMPUTE  AD1= D1 - (0.41 *D1)
COMMENT
COMMENT  S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
          (D * 100**2)= TERM WHICH EXPRESSES SOIL VOLUME FOR 1 SQUARE METER
           SAMPLE AREA, WITH SPECIFIED HORIZON D CENTIMETERS THICK.
                    Where:  D1 - D5 = Horizon thicknesses (cm).
                            100**2= 10000 square centimeter sample area.
       0.23 - 1.50 = BULK DENSITY (gm*cm**3) OF LF - C HORIZONS.
COMPUTE  S1 = 100**2 * AD1 * 0.23
COMPUTE  S2 = 100**2 * D2 * 1.34
COMPUTE  S3 = 100**2 * D3 * 1.24
COMPUTE  S4 = 100**2 * D4 * 1.41
COMPUTE  S5 = 100**2 * D5 * 1.50
COMMENT
COMPUTE  TS = S1 + S2 + S3 + S4 + S5
COMMENT
COMMENT  AY1 TO AY5 ARE RESIDUE VALUES ADJUSTED FOR SOIL MOISTURE CONTENT,
         BULK DENSITY, HORIZON THICKNESS AND RECOVERY RATES EXPRESSED IN
         TOTAL mg A.I. (ACTIVE INGREDIENT) per VOLUME OF SOIL HORIZON.
  WHERE: [(Y * (100/REC) / MM] = RESIDUE VALUES EXPRESSED ON A DRY WEIGHT BASIS
                                 AND ADJUSTED FOR RECOVERIES (ppm).
                    Where:  Y1 - Y5 = Residue values (ppm).
                            (100/RECA) = Factor for LF recovery rate.
```

```
                (100/RECB) = Factor for AE - C recovery rates.
                MM1 - MM5 = Soil dryness (unit fraction).
        S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
        10**-3  = FACTOR TO CONVERT ug TO mg AND m TO cm.
COMMENT
COMPUTE AY1= [Y1 * (100/RECA) / MM1] * S1 * 10**-3
COMPUTE AY2= [Y2 * (100/RECB) / MM2] * S2 * 10**-3
COMPUTE AY3= [Y3 * (100/RECB) / MM3] * S3 * 10**-3
COMPUTE AY4= [Y4 * (100/RECB) / MM4] * S4 * 10**-3
COMPUTE AY5= [Y5 * (100/RECB) / MM5] * S5 * 10**-3
COMMENT
COMMENT TOTY= TOTAL UNADJUSTED RESIDUES IN SOIL PROFILE FOR ALL HORIZONS.
COMPUTE TOTY= Y1 + Y2 + Y3 + Y4 + Y5
COMMENT
COMMENT TOTAY= TOTAL ADJUSTED RESIDUES IN SOIL PROFILE FOR ALL HORIZONS.
COMPUTE TOTAY= AY1 + AY2 + AY3 + AY4 + AY5
IF  (Y1 EQ 0.00)  AY1= 0.00
IF  (Y2 EQ 0.00)  AY2= 0.00
IF  (Y3 EQ 0.00)  AY3= 0.00
IF  (Y4 EQ 0.00)  AY4= 0.00
IF  (Y5 EQ 0.00)  AY5= 0.00
COMMENT TD= SUM OF LF, AE, BF, BC AND C HORIZON THICKNESSES.
COMPUTE TD= AD1 + D2 + D3 + D4 + D5
COMMENT
COMMENT PMG1 TO PMG5= THE RESIDUES (mg) IN EACH HORIZON EXPRESSED AS A %
        OF THE TOTAL RESIDUES DETECTED IN THE SOIL PROFILE.
COMPUTE PMG1= (AY1 / TOTAY) * 100
COMPUTE PMG2= (AY2 / TOTAY) * 100
COMPUTE PMG3= (AY3 / TOTAY) * 100
COMPUTE PMG4= (AY4 / TOTAY) * 100
COMPUTE PMG5= (AY5 / TOTAY) * 100
COMMENT
COMMENT TPMG= THE SUM OF PMG1 TO PMG5 PERCENTAGES WHICH = 100
COMPUTE TPMG= PMG1 + PMG2 + PMG3 + PMG4 + PMG5
COMMENT
COMMENT PRT1 TO PRT5= THE RESIDUES (mg) IN EACH HORIZON EXPRESSED AS
        A % OF THE TOTAL HERBICIDE APPLIED TO THE 205 SQ M SAMPLE AREA;
        (TOTHERB * 1000) CONVERTS GM TO MG.
COMPUTE PRT1= AY1 / [(TOTHERB * 1000) / 205] * 100
COMPUTE PRT2= AY2 / [(TOTHERB * 1000) / 205] * 100
COMPUTE PRT3= AY3 / [(TOTHERB * 1000) / 205] * 100
COMPUTE PRT4= AY4 / [(TOTHERB * 1000) / 205] * 100
COMPUTE PRT5= AY5 / [(TOTHERB * 1000) / 205] * 100
COMMENT
COMMENT TPRT= THE SUM OF PRT1 TO PRT5 SHOULD BE LESS THAN 100 PERCENT.
COMPUTE TPRT= PRT1 + PRT2 + PRT3 + PRT4 + PRT5
COMMENT
COMMENT ORMG= MG OF RESIDUES IN THE ORGANIC SURFACE HORIZON WHICH HAS
        NOT LEACHED FROM THE SURFACE.
COMPUTE ORMG= AY1
COMMENT
COMMENT ORPMG= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED AS A
        PERCENT OF THE TOTAL RESIDUES FOUND IN THE SOIL PROFILE
        FOR A GIVEN TIME, "X".
COMPUTE ORPMG= (ORMG / TOTAY) * 100
COMMENT
COMMENT ORPAT= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED
        AS A PERCENT OF THE TOTAL HERBICIDE APPLIED TO THE
        205 SQ. M. TEST PLOTS; (TOTHERB * 1000) CONVERTS GM TO MG.
COMPUTE ORPAT= ORMG / [(TOTHERB * 1000) / 205] * 100
COMMENT
COMMENT MINMG= MG OF RESIDUES IN THE 4 MINERAL HORIZONS, AS A MINIMUM VALUE,
        AND AS THE DIFFERENCE FROM THE TOTAL AND THE VERY HIGH VALUES (MG)
        FOUND IN THE LF HORIZON.  THIS VALUE ALSO INDICATES THAT AMOUNT OF
        HERBICIDE WHICH HAS LEACHED FROM THE SURFACE LAYER.
COMPUTE MINMG= TOTAY - AY1
COMMENT
COMMENT MINPMG= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED AS A PERCENT
        OF THE TOTAL RESIDUES IN THE SOIL PROFILE FOR A GIVEN TIME, "X".
COMPUTE MINPMG= (MINMG / TOTAY) * 100
COMMENT
COMMENT MINPAT= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED
        AS A PERCENT OF THE TOTAL HERBICIDE APLLIED TO THE 205
        SQ. M. TEST PLOTS;  (TOTHERB * 1000) CONVERTS GM TO MG.
COMPUTE MINPAT= MINMG / [(TOTHERB * 1000) / 205] * 100
VARIABLE LABELS
```

```
  AY1 'LF RESIDUES (ng) FOR SAMP'    AY2 'AE RESIDUES (ng) FOR SAMP'
  AY3 'BF RESIDUES (ng) FOR SAMP'    AY4 'BC RESIDUES (ng) FOR SAMP'
  AY5 'C RESIDUES (ng) FOR SAMP'     TOTAY 'TOT ADJ RES (ng) FOR 3 PITS'
  PMG1 'LF RES (ng) AS % OF TOT RES IN PROFILE'
  PMG2 'AE RES (ng) AS % OF TOT RES IN PROFILE'
  PMG3 'BF RES (ng) AS % OF TOT RES IN PROFILE'
  PMG4 'BC RES (ng) AS % OF TOT RES IN PROFILE'
  PMG5 'C RES (ng) AS % OF TOT RES IN PROFILE'
  TPMG 'SUM OF PTMG1 TO PTMG5 = 100 %'
  PRT1 'LF RESIDUES (ng) AS % OF TOT HERB APPLD'
  PRT2 'AE RESIDUES (ng) AS % OF TOT HERB APPLD'
  PRT3 'BF RESIDUES (ng) AS % OF TOT HERB APPLD'
  PRT4 'BC RESIDUES (ng) AS % OF TOT HERB APPLD',
  PRT5 'C RESIDUES (ng) AS % OF TOT HERB APPLD'
  TPRT 'TOT RES (ng) AS % OF TOT HERB APPLIED'
  ORMG 'RESIDUES (ng) IN ORGANIC LF HORIZ'
  ORPMG 'ORG LF RES (ng) AS % OF TOT RES IN PROF'
  ORPRT 'ORG LF RES (ng) AS % OF TOT HERB APPLD'
  MINMG 'RESIDUES (ng) IN MINERAL AE-C HORIZ'
  MINPMG 'MINERAL RES ng AS % OF TOT RES IN PROF'
  MINPRT 'MINERAL RES ng AS % OF TOT HERB APPLD'
  TD 'SUM OF ALL HORIZON THICKNESSES'
DO IF (TIME EQ 1)
PRINT EJECT/'HERBICIDE:' HERB(T12,F1.0)/ 'HORIZ. THICK.' 14 ' RES:PPM  ' 29
  '   RES:NG    ' 38 'PCT OF NG' 52 '  PCT OF HERB ' 62
PRINT SPACE
END IF
PRINT
 /'   DAY:' DAYS(T9,F3.0)
 /' LF:' AD1(T18,F2.0) Y1(T28,F5.2) AY1(T39,F6.1) PMG1(T53,F4.1) PRT1(T65,F6.2)
 /' AE:' D2(T18,F2.0) Y2(T28,F5.2) AY2(T39,F6.1) PMG2(T53,F4.1) PRT2(T65,F6.2)
 /' BF:' D3(T18,F2.0) Y3(T28,F5.2) AY3(T39,F6.1) PMG3(T53,F4.1) PRT3(T65,F6.2)
 /' BC:' D4(T18,F2.0) Y4(T28,F5.2) AY4(T39,F6.1) PMG4(T53,F4.1) PRT4(T65,F6.2)
 /'  C:' D5(T18,F2.0) Y5(T28,F5.2) AY5(T39,F6.1) PMG5(T53,F4.1) PRT5(T65,F6.2)
 /'    TOTALS:' TD(T18,F2.0) TOTY(T28,F5.2) TOTAY(T39,F6.1) TPMG(T52,F5.1)
 TPRT(T65,F6.2)
 /
EXECUTE
FINISH
```

Hexazinone SPSSX Graph And Table Computations

NOTE: In the remaining 4 programs, variable labels, value labels, print formats, print comands and selected comments are deleted to avoid repetition and facilitate reading.

```
TITLE  HEXAZINONE DISTRIBUTION AND PERSISTENCE STATISTICS
FILE HANDLE  Resdata/ name='ZERONAT7.DAT'
DATA LISTS  File=Resdata Free/Herb  Time  Days  Y1 to Y5  TotHerb  TotArea
          AreaSamp  SS1 SS2  D1 TO D5  M1 TO M5  RECA RECB  samp1 to samp5
MISSING VALUES  Y4 TO Y5 (999)
RECODE   Y4 TO Y5(999=0)
NUMERIC  AY1 TO AY5(F6.3)/   TOTAY(F7.3)/   TOTY(F7.4)/   PMG1 TO PMG5/   IPMG/
         IPRT/   PRT1 TO PRT5/   TD(F4.0)/   ORMG/   ORPMG/   ORPRT/   MINMG/
         MINPMG/   MINPRT/   S1 TO S5/   TS/  AD1
SELECT IF HERB = 3
COMMENT
COMMENT  HERB: 3,  'HEXAZINONE PERSISTENCE CURVES'
COMMENT
COMMENT  AD1= LF HORIZON THICKNESS CORRECTED FOR REPRESENTATIVE SAMPLE VOLUME.
COMPUTE  AD1= D1 - (0.41 * D1)
COMMENT
COMMENT  S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
         (D * 100**2)= TERM WHICH EXPRESSES SOIL VOLUME FOR 1 SQUARE METER
          SAMPLE AREA, WITH SPECIFIED HORIZON D CENTIMETERS THICK.
                 Where:  D1 - D5 = Horizon thicknesses (cm).
                         100**2= 10000 square centimeter sample area.
         0.23 - 1.50 = BULK DENSITY (gm*cm**3) OF LF - C HORIZONS.
COMPUTE  S1 = 100**2 * AD1 * 0.23
COMPUTE  S2 = 100**2 * D2 * 1.34
COMPUTE  S3 = 100**2 * D3 * 1.24
COMPUTE  S4 = 100**2 * D4 * 1.41
COMPUTE  S5 = 100**2 * D5 * 1.50
COMMENT
COMMENT  RAW RESIDUE VALUES HAVE BEEN ADJUSTED FOR MOISTURE BY ATLANTIC
         PESTICIDES LABORATORY, KENTVILLE, NOVA SCOTIA.  RESULTS
         EXPRESSED ON A DRY WEIGHT BASIS.
COMMENT  AY1 TO AY5 ARE RESIDUE VALUES ADJUSTED FOR SOIL MOISTURE CONTENT,
         BULK DENSITY, HORIZON THICKNESS AND RECOVERY RATES EXPRESSED IN
         TOTAL ug A.I. (ACTIVE INGREDIENT) per VOLUME OF SOIL HORIZON.
  WHERE: [(Y * (100/REC)] = RESIDUE VALUES ADJUSTED FOR RECOVERIES (ppm).
                 Where:  Y1 - Y5 = Residue values (ppm).
                         (100/RECA) = Factor for LF recovery rate.
                         (100/RECB) = Factor for AE - C recovery rates.
         S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
         10**-3  = FACTOR TO CONVERT ug TO mg AND m TO cm.
COMMENT
COMPUTE  AY1= [Y1 * (100/RECA)] * S1 * 10**-3
COMPUTE  AY2= [Y2 * (100/RECB)] * S2 * 10**-3
COMPUTE  AY3= [Y3 * (100/RECB)] * S3 * 10**-3
COMPUTE  AY4= [Y4 * (100/RECB)] * S4 * 10**-3
COMPUTE  AY5= [Y5 * (100/RECB)] * S5 * 10**-3
COMMENT
COMMENT  TOTY= TOTAL UNADJUSTED RESIDUES IN SOIL PROFILE FOR ALL HORIZONS.
COMPUTE  TOTY= Y1 + Y2 + Y3 + Y4 + Y5
IF  (Y1 EQ 0.00)  AY1= 0.00
IF  (Y2 EQ 0.00)  AY2= 0.00
IF  (Y3 EQ 0.00)  AY3= 0.00
IF  (Y4 EQ 0.00)  AY4= 0.00
IF  (Y5 EQ 0.00)  AY5= 0.00
COMMENT  TOTAY= TOTAL ADJUSTED RESIDUES IN SOIL PROFILE FOR ALL
               HORIZONS 'D' CM DEEP & 1 M SQ.
COMPUTE  TOTAY= AY1 + AY2 + AY3 + AY4 + AY5
COMMENT
COMMENT  TD= SUM OF LF, AE, BF, BC AND C HORIZON THICKNESSES.
COMPUTE  TD= AD1 + D2 + D3 + D4 + D5
```

```
COMMENT
COMMENT  TS = TOTAL WE[illegible]g) OF SOIL TO cm THICK AND 1 METRE SQUARE.
COMPUTE  TS= S1 + S2 [illegible] S4 + S5
COMMENT
COMMENT  PMG1 TO PMG5= THE RESIDUES (ug) IN EACH HORIZON EXPRESSED AS A %
             OF THE TOTAL RESIDUES DETECTED IN THE SOIL PROFILE. *
COMPUTE  PMG1= (AY1 / TOTAY) * 100
COMPUTE  PMG2= (AY2 / TOTAY) * 100
COMPUTE  PMG3= (AY3 / TOTAY) * 100
COMPUTE  PMG4= (AY4 / TOTAY) * 100
COMPUTE  PMG5= (AY5 / TOTAY) * 100
COMMENT
COMMENT  TPMG= THE SUM OF PMG1 TO PMG5 PERCENTAGES WHICH = 100
COMPUTE  TPMG= PMG1 + PMG2 + PMG3 + PMG4 + PMG5
COMMENT
COMMENT  PRT1 TO PRT5= THE RESIDUES (ug) IN EACH HORIZON EXPRESSED AS
         A % OF THE TOTAL HERBICIDE APPLIED TO A 1 SQ M SAMPLE AREA;
         (TOTHERB * 1000 / 166) CONVERTS GM TO MG FOR A 1 SQ M-AREA.
COMPUTE  PRT1= [AY1 / (TOTHERB * 1000 / 166)] * 100
COMPUTE  PRT2= [AY2 / (TOTHERB * 1000 / 166)] * 100
COMPUTE  PRT3= [AY3 / (TOTHERB * 1000 / 166)] * 100
COMPUTE  PRT4= [AY4 / (TOTHERB * 1000 / 166)] * 100
COMPUTE  PRT5= [AY5 / (TOTHERB * 1000 / 166)] * 100
COMMENT
COMMENT  TPRT= THE SUM OF PRT1 TO PRT5 SHOULD BE LESS THAN 100 PERCENT.
COMPUTE  TPRT= PRT1 + PRT2 + PRT3 + PRT4 + PRT5
COMMENT
COMMENT  ORMG= MG OF RESIDUES IN THE ORGANIC SURFACE HORIZON WHICH HAS
             NOT LEACHED FROM THE SURFACE.
COMPUTE  ORMG= AY1
COMMENT
COMMENT  ORPMG= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED AS A PERCENT OF
             THE TOTAL RESIDUES FOUND IN THE SOIL PROFILE FOR A GIVEN TIME, *X*.
COMPUTE  ORPMG= (ORMG / TOTAY) * 100
COMMENT
COMMENT  ORPRT= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED AS A
             PERCENT OF THE TOTAL HERBICIDE APPLIED TO A 1 SQ. M. SAMPLE
             AREA; (TOTHERB * 1000 / 166) CONVERTS GM TO MG FOR A 1 SQ M AREA.
COMPUTE  ORPRT= [ORMG / (TOTHERB * 1000 / 166)] * 100
COMMENT
COMMENT  MINMG= MG OF RESIDUES IN THE 4 MINERAL HORIZONS, AS A MINIMUM VALUE,
             AND AS THE DIFFERENCE FROM THE TOTAL AND THE VERY HIGH VALUES (MG)
             FOUND IN THE LF HORIZON.  THIS VALUE ALSO INDICATES THAT AMOUNT OF
             HERBICIDE WHICH HAS LEACHED FROM THE SURFACE LAYER.
COMPUTE  MINMG= TOTAY - AY1
COMMENT
COMMENT  MINPMG= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED AS A PERCENT
             OF THE TOTAL RESIDUES IN THE SOIL PROFILE FOR A GIVEN TIME, *X*.
COMPUTE  MINPMG= (MINMG / TOTAY) * 100
COMMENT
COMMENT  MINPRT= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED AS A
             PERCENT OF THE TOTAL HERBICIDE APPLIED TO A 1 SQ. M. SAMPLE
             AREA;  (TOTHERB * 1000 / 166) CONVERTS GM TO MG FOR A 1 SQ M AREA.
COMPUTE  MINPRT= [MINMG / (TOTHERB * 1000 / 166)] * 100
FINISH
```

Tebuthiuron SPSSX Graph And Table Computations

```
TITLE  TEBUTHIURON DISTRIBUTION AND PERSISTENCE STATISTICS
FILE HANDLE  Resdata/ name='ZERONEW'.DAT'
DATA LISTS  File=Resdata Free/Herb  Time  Days  Y1 to Y5  TotHerb  TotArea @
          AreaSamp  SS1 SS2  D1 TO D5  M1 TO M5  RECA RECB  samp1 to samp5
MISSING VALUES  Y4.TO Y5 (999)
RECODE   Y4 TO Y5(999=0)
NUMERIC  MM1 TO MM5(F4.3)/  AY1.TO AY5(F6.3)/  TOTAY(F7.3)/  TOTY(F7.3)/
         PMG1 TO PMG5/  TPMG/ PRT1 TO PRT5/  TPRT/  TD(F4.0)/  ORMG/
         ORPMG/  ORPRT/  MINMG/  MINPMG/  MINPRT/  S1 TO S5/  TS/ AD1
SELECT IF HERB = 4
COMMENT
COMMENT  HERB: 4,  'TEBUTHIURON PERSISTENCE CURVES'
COMMENT
COMMENT  RAW RESIDUE VALUES HAVE BEEN ADJUSTED FOR RECOVERY RATES BY ELANCO
         LABORATORIES, GREENFIELD, INDIANA.  RESULTS EXPRESSED ON A FRESH
         WEIGHT BASIS.
COMMENT
COMMENT  MM1 TO MM5 ARE SOIL DRYNESS BY WEIGHT EXPRESSED AS A UNIT FRACTION.
             WHERE:  M1 TO M5 = SOIL MOISTURE (% BY WEIGHT).
                     .01 = CONVERSION FACTOR FOR PERCENT TO UNITS.
                     1 - (R * .01) = SOIL DRYNESS (% BY WEIGHT) EXPRESSED
                                     AS A UNIT FRACTION.
DO REPEAT  R = M1 TO M5/ S = MM1 TO MM5
COMPUTE  S = 1 - (R * .01)
END REPEAT
COMMENT  AD1= LF HORIZON THICKNESS CORRECTED FOR REPRESENTATIVE SAMPLE VOLUME.
COMPUTE  AD1 = D1 - (0.41 * D1)
COMMENT  S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
          (D * 100**2)= TERM WHICH EXPRESSES SOIL VOLUME FOR 1 SQUARE METER
           SAMPLE AREA, WITH SPECIFIED HORIZON D CENTIMETERS THICK.
                  Where:  D1 - D5 = Horizon thicknesses (cm).
                          100**2= 10000 square centimeter sample area.
          0.23 - 1.50 = BULK DENSITY (gm*cm**3) OF LF - C HORIZONS.
COMPUTE  S1 = 100**2 * AD1 * 0.23
COMPUTE  S2 = 100**2 * D2 * 1.34
COMPUTE  S3 = 100**2 * D3 * 1.24
COMPUTE  S4 = 100**2 * D4 * 1.41
COMPUTE  S5 = 100**2 * D5 * 1.50
COMPUTE  TS = S1 + S2 + S3 + S4 + S5
COMMENT
COMMENT  AY1 TO AY5 ARE RESIDUE VALUES ADJUSTED FOR SOIL MOISTURE CONTENT,
         BULK DENSITY, HORIZON THICKNESS AND RECOVERY RATES EXPRESSED IN
         TOTAL ug A.I. (ACTIVE INGREDIENT) per VOLUME OF SOIL HORIZON.
  WHERE:  (Y / MM) = RESIDUE VALUES EXPRESSED ON A DRY WEIGHT BASIS (ug/gm).
                  Where:  Y1 - Y5 = Residue values (ppm).
                          MM1 - MM5 = Soil dryness (unit fraction).
           S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
          10**-3= FACTOR TO CONVERT ug TO mg AND m TO cm.
COMMENT
COMPUTE  AY1= (Y1 / MM1) * S1 * 10**-3
COMPUTE  AY2= (Y2 / MM2) * S2 * 10**-3
COMPUTE  AY3= (Y3 / MM3) * S3 * 10**-3
COMPUTE  AY4= (Y4 / MM4) * S4 * 10**-3
COMPUTE  AY5= (Y5 / MM5) * S5 * 10**-3
COMMENT
COMMENT  TOTY= TOTAL ADJUSTED RESIDUES IN SOIL PROFILE FOR ALL HORIZONS.
COMPUTE  TOTY= Y1 + Y2 + Y3 + Y4 + Y5
IF  (Y1 EQ 0.00)  AY1= 0.00
IF  (Y2 EQ 0.00)  AY2= 0.00
IF  (Y3 EQ 0.00)  AY3= 0.00
IF  (Y4 EQ 0.00)  AY4= 0.00
IF  (Y5 EQ 0.00)  AY5= 0.00
COMMENT  TOTAY= TOTAL ADJUSTED RESIDUES IN SOIL PROFILE FOR ALL HORIZONS.
COMPUTE  TOTAY= AY1 + AY2 + AY3 + AY4 + AY5
COMMENT
COMMENT  TD= SUM OF LF, AE, BW, BC AND C HORIZON THICKNESSES.
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```
COMPUTE  TD= AD1 + D2 + D3 + D4 + D5
COMMENT
COMMENT  PMG1 TO PMG5= THE RESIDUES (ug) IN EACH HORIZON EXPRESSED AS A %
             OF THE TOTAL RESIDUES DETECTED IN THE SOIL PROFILE.
COMPUTE  PMG1= (AY1 / TOTAY) * 100
COMPUTE  PMG2= (AY2 / TOTAY) * 100
COMPUTE  PMG3= (AY3 / TOTAY) * 100
COMPUTE  PMG4= (AY4 / TOTAY) * 100
COMPUTE  PMG5= (AY5 / TOTAY) * 100
COMMENT
COMMENT  TPMG= THE SUM OF PMG1 TO PMG5 PERCENTAGES WHICH = 100
COMPUTE  TPMG= PMG1 + PMG2 + PMG3 + PMG4 + PMG5
COMMENT
COMMENT  PRT1 TO PRT5= THE RESIDUES (ug) IN EACH HORIZON EXPRESSED AS
         A % OF THE TOTAL HERBICIDE APPLIED TO THE 194 SQ M SAMPLE AREA;
         (TOTHERB * 1000) CONVERTS GM TO MG.
COMPUTE  PRT1= AY1 / [(TOTHERB * 1000) / 194] * 100
COMPUTE  PRT2= AY2 / [(TOTHERB * 1000) / 194] * 100
COMPUTE  PRT3= AY3 / [(TOTHERB * 1000) / 194] * 100
COMPUTE  PRT4= AY4 / [(TOTHERB * 1000) / 194] * 100
COMPUTE  PRT5= AY5 / [(TOTHERB * 1000) / 194] * 100.
COMMENT
COMMENT  TPRT= THE SUM OF PRT1 TO PRT5 SHOULD BE LESS THAN 100 PERCENT.
COMPUTE  TPRT= PRT1 + PRT2 + PRT3 + PRT4 + PRT5
COMMENT
COMMENT  ORMG= MG OF RESIDUES IN THE ORGANIC SURFACE HORIZON WHICH HAS
             NOT LEACHED FROM THE SURFACE.
COMPUTE  ORMG= AY1
COMMENT
COMMENT  ORPMG= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED AS A PERCENT OF
             THE TOTAL RESIDUES FOUND IN THE SOIL PROFILE FOR A GIVEN TIME, %X%.
COMPUTE  ORPMG= (ORMG / TOTAY) * 100
COMMENT
COMMENT  ORPRT= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED AS A PERCENT OF
             THE TOTAL HERBICIDE APPLIED TO THE 194 SQ. M. TEST PLOTS;
             (TOTHERB * 1000) CONVERTS GM TO MG.
COMPUTE  ORPRT= ORMG / [(TOTHERB * 1000) / 194] * 100
COMMENT
COMMENT  MINMG= MG OF RESIDUES IN THE 4 MINERAL HORIZONS, AS A MINIMUM VALUE,
             AND AS THE DIFFERENCE FROM THE TOTAL AND THE VERY HIGH VALUES (MG)
             FOUND IN THE LF HORIZON.  THIS VALUE ALSO INDICATES THAT AMOUNT OF
             HERBICIDE WHICH HAS LEACHED FROM THE SURFACE LAYER.
COMPUTE  MINMG= TOTAY - AY1
COMMENT
COMMENT  MINPMG= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED AS A PERCENT
             OF THE TOTAL RESIDUES IN THE SOIL PROFILE FOR A GIVEN TIME, %X%.
COMPUTE  MINPMG= (MINMG / TOTAY) * 100
COMMENT
COMMENT  MINPRT= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED
             AS A PERCENT OF THE TOTAL HERBICIDE APLLIED TO THE 194
             SQ. M. TEST PLOTS;  (TOTHERB * 1000) CONVERTS GM TO MG.
COMPUTE  MINPRT= MINMG / [(TOTHERB * 1000) / 194] * 100
FINISH
```

```
TITLE  PICLORAM DISTRIBUTION AND PERSISTENCE STATISTICS
FILE HANDLE  Resdata/ name='ZEROMAT7.DAT'
DATA LISTS  File=Resdata Free/Herb  Time  Days  Y1 to Y5  TotHerb  TotArea
            AreaSamp  SS1 SS2  D1 TO D5  M1 TO M5  RECA  RECB  samp1 to samp5
MISSING VALUES  Y4 TO Y5 (999)
RECODE  Y4 TO Y5(999=0)
NUMERIC  AY1 TO AY5(F8.3)/  TOTAY(F7.3)/  TOTY(F7.3)/  PNG1 TO PNG5/  TPNG/
         TD(F4.0)/  PRT1 TO PRT5/  TPRT/  ORNG/  ORPNG/  ORPRT/  MINNG/
         MINPNG/  MINPRT/  S1 TO S5/  TS/  AD1
SELECT IF HERB = 5
COMMENT
COMMENT  HERB: 5,  'PICLORAM PERSISTENCE CURVES'
COMMENT
COMMENT  AD1= LF HORIZON THICKNESS CORRECTED FOR REPRESENTATIVE SAMPLE VOLUME.
COMPUTE  AD1= D1 - (0.41 * D1)
COMMENT
COMMENT  S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
          Where:  (100**2 * D)= TERM WHICH SOIL VOLUME FOR 1 SQUARE METER
                  SAMPLE AREA, WITH SPECIFIED HORIZON D CENTIMETERS THICK.
                   Where:  D1 - D5 = Horizon thicknesses (cm).
                           100**2= 10000 square centimeter sample area.
                  0.23 - 1.50 = BULK DENSITY (gm*cm**3) OF LF - C HORIZONS.
COMPUTE  S1 = 100**2 * AD1 * 0.23
COMPUTE  S2 = 100**2 * D2 * 1.34
COMPUTE  S3 = 100**2 * D3 * 1.24
COMPUTE  S4 = 100**2 * D4 * 1.41
COMPUTE  S5 = 100**2 * D5 * 1.50
COMPUTE  TS = S1 + S2 + S3 + S4 + S5
COMMENT
COMMENT  RAW RESIDUE VALUES HAVE BEEN ADJUSTED FOR AN AVERAGE 90 % RECOVERY
         RATE AND MOISTURE CONTENT BY DOW, MIDLAND, MICHIGAN.  RESULTS
         EXPRESSED ON A DRY WEIGHT BASIS.
         AY1 TO AY5 ARE RESIDUE VALUES ADJUSTED FOR SOIL MOISTURE CONTENT,
         BULK DENSITY, HORIZON THICKNESS AND AN AVERAGE 90 % RECOVERY RATE
         EXPRESSED IN TOTAL ug A.I. (ACTIVE INGREDIENT) per VOLUME OF SOIL
         HORIZON.
  WHERE:  Y1 - Y5 = RESIDUE VALUES (ppm).
          S1 - S5 = DRY WEIGHT (gm) OF SOIL VOLUME (1 m sq. x D cm thick).
          10**-3 = FACTOR TO CONVERT ug TO mg AND m TO cm.
COMMENT
COMPUTE  AY1= Y1 * S1 * 10**-3
COMPUTE  AY2= Y2 * S2 * 10**-3
COMPUTE  AY3= Y3 * S3 * 10**-3
COMPUTE  AY4= Y4 * S4 * 10**-3
COMPUTE  AY5= Y5 * S5 * 10**-3
COMMENT
COMMENT  TOTY= TOTAL UNADJUSTED RESIDUES IN SOIL PROFILE FOR ALL HORIZONS.
COMPUTE  TOTY= Y1 + Y2 + Y3 + Y4 + Y5
IF  (Y1 EQ 0.00)  AY1 = 0.00
IF  (Y2 EQ 0.00)  AY2 = 0.00
IF  (Y3 EQ 0.00)  AY3 = 0.00
IF  (Y4 EQ 0.00)  AY4 = 0.00
IF  (Y5 EQ 0.00)  AY5 = 0.00
COMMENT  TOTAY= TOTAL ADJUSTED RESIDUES IN SOIL PROFILE FOR ALL HORIZONS.
COMPUTE  TOTAY= AY1 + AY2 + AY3 + AY4 + AY5
COMMENT
COMMENT  TD= SUM OF LF, AE, BF, BC AND C HORIZON THICKNESSES.
COMPUTE  TD= AD1 + D2 + D3 + D4 + D5
COMMENT
COMMENT  PNG1 TO PNG5= THE RESIDUES (ng) IN EACH HORIZON EXPRESSED AS A %
             OF THE TOTAL RESIDUES DETECTED IN THE SOIL PROFILE.
COMPUTE  PNG1= (AY1 / TOTAY) * 100
COMPUTE  PNG2= (AY2 / TOTAY) * 100
COMPUTE  PNG3= (AY3 / TOTAY) * 100
COMPUTE  PNG4= (AY4 / TOTAY) * 100
COMPUTE  PNG5= (AY5 / TOTAY) * 100
```

```
COMMENT
COMMENT  TPMG= THE SUM OF PMG1 TO PMG5 PERCENTAGES WHICH = 100
COMPUTE  TPMG= PMG1 + PMG2 + PMG3 + PMG4 + PMG5
COMMENT
COMMENT  PRT1 TO PRT5= THE RESIDUES (ug) IN EACH HORIZON EXPRESSED AS
         A % OF THE TOTAL HEABICIDE APPLIED TO A 1 SQ M SAMPLE AREA;
         (TOTHERB * 1000 / 201) CONVERTS GM TO MG FOR A 1 SQ M AREA.
COMPUTE  PRT1= [AY1 / (TOTHERB * 1000 / 201)] * 100
COMPUTE  PRT2= [AY2 / (TOTHERB * 1000 / 201)] * 100
COMPUTE  PRT3= [AY3 / (TOTHERB * 1000 / 201)] * 100
COMPUTE  PRT4= [AY4 / (TOTHERB * 1000 / 201)] * 100
COMPUTE  PRT5= [AY5 / (TOTHERB * 1000 / 201)] * 100
COMMENT
COMMENT  TPRT= THE SUM OF PRT1 TO PRT5 SHOULD BE LESS THAN 100 PERCENT.
COMPUTE  TPRT= PRT1 + PRT2 + PRT3 + PRT4 + PRT5
COMMENT
COMMENT  ORMG= MG OF RESIDUES IN THE ORGANIC SURFACE HORIZON WHICH HAS
             NOT LEACHED FROM THE SURFACE.
COMPUTE  ORMG= AY1
COMMENT
COMMENT  ORPMG= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED AS A PERCENT OF
             THE TOTAL RESIDUES FOUND IN THE SOIL PROFILE FOR A GIVEN TIME, "X".
COMPUTE  ORPMG= (ORMG / TOTAY) * 100
COMMENT
COMMENT  ORPRT= THE RESIDUES IN THE ORGANIC HORIZON EXPRESSED AS A
         PERCENT OF THE TOTAL HERBICIDE APPLIED TO A 1 SQ. M. SAMPLE
         AREA; (TOTHERB * 1000 / 201) CONVERTS GM TO MG FOR A 1 SQ M AREA.
COMPUTE  ORPRT= [ORMG / (TOTHERB * 1000 / 201)] * 100
COMMENT
COMMENT  MINMG= MG OF RESIDUES IN THE 4 MINERAL HORIZONS, AS A MINIMUM VALUE,
             AND AS THE DIFFERENCE FROM THE TOTAL AND THE VERY HIGH VALUES (MG)
             FOUND IN THE LF HORIZON.  THIS VALUE ALSO INDICATES THAT AMOUNT OF
             HERBICIDE WHICH HAS LEACHED FROM THE SURFACE LAYER.
COMPUTE  MINMG= TOTAY - AY1
COMMENT
COMMENT  MINPMG= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED AS A PERCENT
             OF THE TOTAL RESIDUES IN THE SOIL PROFILE FOR A GIVEN TIME, "X".
COMPUTE  MINPMG= (MINMG / TOTAY) * 100
COMMENT
COMMENT  MINPRT= THE RESIDUES IN THE 4 MINERAL HORIZONS EXPRESSED AS A
         PERCENT OF THE TOTAL HERBICIDE APPLIED TO A 1 SQ. M. SAMPLE
         AREA;  (TOTHERB * 1000 / 201) CONVERTS GM TO MG FOR A 1 SQ M AREA.
COMPUTE  MINPRT= [MINMG / (TOTHERB * 1000 / 201)] * 100
FINISH
```

Appendix O

BMDP Computer Programs For Descriptive Regression Analysis Of Persistence Curves

Dicamba BMDP Regression Computations

```
/ PROBLEM  TITLE IS 'DICAMBA NEGATIVE EXPONENTIAL REGRESSION,
                    EXCLUDES CASES 1 & 7'.
/ INPUT    VARIABLES ARE 3.    FORMAT IS FREE.     FILE = 'DICREG.DAT'.
/ VARIABLE NAMES ARE DAY, TOTY, TOTAY, LOGY, LOGAY, LGDAY.
           ADD = 3.
/ TRAN     LOGY = LOG(TOTY + 1).
           LOGAY = LOG(TOTAY).
           LGDAY = LOG(DAY).
           IF(CASE EQ 1 OR CASE EQ 7) THEN USE = 0.
/ REGRESS  DEPENDENT IS LOGAY.
           INDEPENDENT IS LGDAY.
/ PRINT    NEWS. MATRICES = RESI. CASE = 10. NO SHADE.
/ PLOT     YVAR ARE LOGAY, LOGAY, LGDAY, LGDAY.
           XVAR ARE LGDAY, PREDICTD, LOGAY, PREDICTD.
           NORMAL. HISTOGRAM. SIZE = 40, 25. STATISTICS.
/ END
```

Hexazinone BMDP Regression Computations

```
/ PROBLEM  TITLE IS 'HEXAZINONE NEGATIVE LINEAR REGRESSION, EXCLUDES CASE 1'.
/ INPUT    VARIABLES ARE 3.    FORMAT IS FREE.    FILE = 'HEXREG.DAT'.
/ VARIABLE NAMES ARE DAY, TOTY, TOTAY, LOGY, LOGAY, LGDAY.
           ADD = 3.
/ TRAN     LOGY = LOG(TOTY).
           LOGAY = LOG(TOTAY).
           LGDAY = LOG(DAY).
           IF (CASE EQ 1) THEN  USE = 0.
/ REGRESS  DEPENDENT IS LOGAY.
           INDEPENDENT IS DAY.
           METHOD = NONE.
/ PRINT    MATRICES = RESI.    CASE = 8.    NO SHADE.
/ PLOT     YVAR ARE LOGAY, LOGAY, RESIDUAL, RESIDUAL.
           XVAR ARE DAY, PREDICTD, PREDICTD, DELRESID.
           NORMAL.    SIZE IS 40, 25.    STATISTICS.
/ END
```

Tebuthiuron BMDP Regression Computations

```
/ PROBLEM  TITLE IS 'TEBUTHIURON NEGATIVE LINEAR REGRESSION,
                     EXCLUDES CASES 2 & 3'.
/ INPUT    VARIABLES ARE 3.    FORMAT IS FREE.    FILE = 'TEBREG.DAT'.
/ VARIABLE NAMES ARE DAY, TOTY, TOTAY, LOGY, LOGAY.
           ADD = 2.
/ TRAN     LOGY = LOG(TOTY).
           LOGAY = LOG(TOTAY).
           IF (KASE EQ 1 OR KASE EQ 2 OR KASE EQ 3) THEN  USE = 0.
/ REGRESS  DEPENDENT IS LOGAY.
           INDEPENDENT IS DAY.
           METHOD = NONE.
/ PRINT    MATRICES = RESI.   CASE = 6.    NO SHADE.
/ PLOT     YVAR IS LOGAY, LOGAY, RESIDUAL, RESIDUAL.
           XVAR IS DAY, PREDICTD, PREDICTD, DELRESID.
           NORMAL.     SIZE = 40, 25.     STATISTICS.
/ END
```

Picloram BMDP Regression Computations

```
/ PROBLEM  TITLE IS 'PICLORAM NEGATIVE EXPONENTIAL REGRESSION, EXCLUDES CASES'.
/ INPUT    VARIABLES ARE 3.    FORMAT IS FREE.    FILE = 'PICREG.DAT'.
/ VARIABLE NAMES ARE DAY, TOTY, TOTAY, LOGY, LOGAY, LGDAY.
           ADD = 3.
/ TRAN     LOGY = LOG(TOTY).
           LOGAY = LOG(TOTAY).
           LGDAY = LOG(DAY).
           IF (KASE EQ 3)  THEN  USE = 0.
/ PRINT    CASE = 6.    MATRICES = RESI.   NO SHADED.
/ REGRESS  DEPENDENT IS LOGAY,
           INDEPENDENT IS LGDAY.
           METHOD = NONE.
/ PLOT     YVAR  = LOGAY, LOGAY, RESIDUAL, RESIDUAL.
           XVAR = LGDAY, PREDICTD, PREDICTD, DELRESID.
           NORMAL.    SIZE = 40, 25.    STATISTICS.
/ END
```