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PERSISTENCE AND VERTICAL MOVEMENT OF SELECTED PESTICIDES

IN MICHIGAN POTATO FIELD

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PERSISTENCE AND VERTICAL MOVEMENT OF SELECTED PESTICIDES IN MICHIGAN POTATO FIELD

BY

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ABSTRACT

PERSISTENCE AND VERTICAL MOVEMENT OF SELECTED PESTICIDES IN MICHIGAN POTATO FIELD

BY

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The persistence and movement of pesticides in soil may result in their accumulation over long period of time and cause ground water contamination. A field experiment was designed to study the persistence of two herbicides, metolachlor and metribuzin and an organophosphate insecticide, imidan. The plots consisted of four rows planted with Burbank potatos; all treatments were replicated four times. The soil was sampled four times during the year and analyzed by gas chromatography to determine the concentration of the pesticides in the soil at various depths. No imidan was detected in the soil samples, indicating rapid dissipation. Metolachlor and metribuzin were detected in all the soil samples even before the herbicides were applied. The levels found were low, therefore they should not persist in the soil over long period of time. The results also showed upward and downward movement of the two herbicides in the soil. Reduction of irrigation may help reduce the potential for ground water contamination.

To my uncle Alphonse K. Kadjo, for challenging me to attain the standard that he himself set to high.

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CHAPTER I

BACKGROUND OBJECTIVES

THE IMPORTANCE OF PESTICIDES

The benefits of pesticides to mankind have been the control of insects, vectors of diseases and to increase the yield of many crops. Thus the use of synthetic organic chemical created great expectation; satisfactory control of pests seemed possible. The total pounds of pesticide active ingredients applied on farms increase 170 % between 1964 and 1987, while total acres under cultivation remained relatively constant (US Department of Agriculture, 1984). Herbicide use continues to increase, but insecticides use has stabilized and use patterns have shift away from organochlorine toward organophosphate and carbamate compounds. The total dollar value of the domestic agricultural pesticide market is about $4.0 billion (Association, 1987). Cropland treated with pesticides was recently estimated to be 249 millions acres in the USA and the total amount of pesticides applied was 743 millions lb (Pimentel and Levitan, 1986). Some of the cropped soil receive a pre-emergence herbicide, fungicide, nematicide, systemic insecticide, post emergence herbicide, one or more post-emergence insecticides or fungicides, and defoliant, all in a single season (Nash, 1967). Annual application rates range from several ounces to several pounds per acre, depending upon the crop and the pest problems in a specific fields (T.B. Moorman, 1989). Pesticides have been used and are still used against insects that are vectors of the most debilliting diseases which affect mankind such as malaria, filariasis , and typhus or against termites that destroy houses.

From the economic standpoint as well as health, pesticides will continue to be vital in the production of food and for the protection of man and animal. Chemicals often

do not reach the pest population; 0.1 % of the pesticides applied to crops reaches the target pests (Pimentel and Levitan, 1986). The leftover may move through the environment affecting non target organisms in and into the soil, surface water, and air. These chemicals create a great concern among general public. Nearly half of farmers in a 1989 nationwide survey by Jefferson Davis Associates in Iowa were worried that their use of chemicals poses a danger to themselves and to the environment (Michigan Department of Agriculture, 1990). The cost of agricultural products to the consumer could double or triple if pesticide use were suddenly terminated (Caro, J.H., 1976). A complete cessation of pesticide use is unlikely, but because of increased chemical costs, a better understanding of economic thresholds for pesticide use and increase awareness about environment contamination, many agriculturalist are becoming more prudent about pesticide use.

Assessing all these problems is not easy; a benefit/cost analysis have often been used but quantities involved are not easily quantified. With these consideration in mind, different management strategies (alternative farming systems) have been proposed. Their management strategies seek to enhance and to use biological interactions rather than reduce and suppress them and to exercise prudence use of external inputs. Integrated Pest Management (IPM), the most prevalent of these practices was defined by Jimmy Carter in its presidential message to the congress as "a system approach to reduce pest damage to tolerable levels through a variety of techniques, including predators and parasites, genetically resistant hosts, natural environment modifications, and when appropriate, chemical pesticides". In other words it is a design that conducts continued evaluation of pest control procedures that result in a favorable socio-economic environment (George, W. Bird, 1989). Determining the economic threshold is the difficulty in IPM, because it is not constant. It doesn't always decrease pesticide use, rather it gives more knowledge about pest

population and often increases the number of pesticide applications because of better knowledge of pest population. (Allen et al., 1987).

The responsible use of pesticides requires knowledge of how they are transported, partitioned, detoxified or accumulated in the environment. The understanding of these mechanisms as well as the development of techniques such as analytical techniques and simulation model will prevent the imposition of regulations that unnecessarily restrict the use of certain pesticides.

OBJECTIVES OF THE STUDY

The first objective of this study was to develop analytical techniques (extraction, purification, and chromatography) to determine the residues of three pesticides commonly used in potato production: metolachlor (Dual), metribuzin (Sencor), and phosmet (Imidan). The second objective was to study the persistence of these chemicals under field conditions. The final objective was to compare the movement of these chemicals in soil with regard to soil properties, to weather, and to their characteristics physical and chemical characteristics.

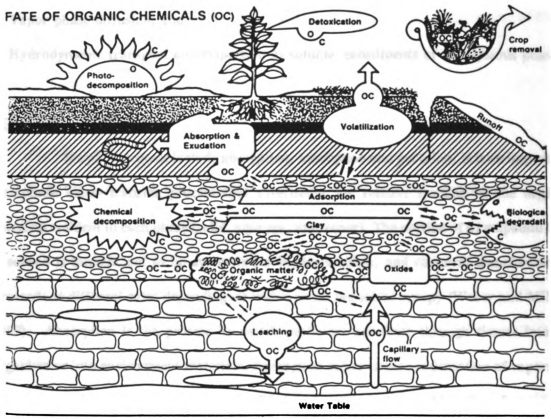
CHAPTER II

REVIEW OF LITERATURE

PESTICIDES IN THE ENVIRONMENT

Upon their introduction into the environment, pesticides are subject to degradation and transfer processes that determine not only their persistence and fate, but their availability for bioactivity.

Figure 1. Processes influencing the behavior and fate of herbicides in the environment (Sawhney, B.L. and Brown, K.W., SSSA Special Publication Nº 22, 1989)



Three specific degradation processes serve to break down the pesticides and change their chemical composition: (1) biological decomposition, (2) chemical decomposition, and (3) photodegradation (Fig 1). These processes are due to the action of diverse types of organisms living in the soil as well as by the physico-chemical interactions between pesticides and the environment.

Organic chemicals are transported by five common transport processes that operate at the subsurface environment (Fig 1). These processes include the following:

1. Absorption, exudation, and retention by crops and crops residues;
2. Run off movement in either the dissolve or sorbed state;
3. Sorption and desorption to organic matter, clays and mineral surfaces;
4. Vapor phase diffusion; and
5. Hydrodynamic transport and dispersion as soluble constituents of the aqueous phase.

TRANSFER PROCESS

Sorption process include absorption, adsorption and partition. It is an important interphase mass- transfer process that determines the relative fraction of the organic chemical resident in each phase (solid, aqueous, and vapor). The portion of a compound that is sorbed is thought not to be available for biodegradation, and chemical transformation proceeds at different rates depending on which phase the solute occupy (Weber and Miller, 1989). Absorption is the process by which pesticides penetrate through tissues into an organism or into environment materials. Adsorption refers to the condensation of vapors or solutes on surfaces or interior pores of solids by physical or chemical bonding. In contrast during partition the organic chemical penetrates into the network of an organic medium by forces common to solution chemodynamics (Boyd, S., 1991).

Adsorption and partition are the processes that govern most the mobility and availability of pesticides in soil. In fact, soil is postulated to behave as a dual sorbent in which the mineral matter functions as a conventional sorbent and the organic matter as a partition medium (Chiou et al., 1985).

PARTITION

The partition uptake is analogous to the extraction of an organic compound from water into an organic phase (Chiou, C.T., 1989). It is has been shown to control the uptake of non ionic organic compounds (NOCs) in soil and water system (Chiou et al, 1983). According to this mechanism soil organic matter act as a solubilizing medium for NOCs and is functionally and conceptually like bulk-phase solvent (e.g octanol) in its uptake of NOCs from water. In soil water systems, the mineral ted as sorbent for NOCs due to strong dipole interactions between water and mineral surfaces (Chiou et al., 1985).

ADSORPTION

Of the processes influencing the fate and behavior of pesticides in soil, adsorption is the most influential and depends on both soil and pesticide properties. The adsorption/desorption process is an equilibrium process and controls the concentration in soil solution and thus removes part of the pesticide from the field of potential action resulting in reduced bioactivity, in reduced chemical degradation, or simply in retarded movement in and through the soil.

There are three major types of adsorption: 1) chemical adsorption- due to coulombic forces which involve the sharing of electrons between the chemical and the adsorptive surface and is characterized by high heats of adsorption; 2) physical adsorption,

due to Van der Waals forces which are attractive forces between dipoles and have low heats of adsorption; and 3) hydrogen bonding, due to bonds between two highly electronegative atoms through the medium of a hydrogen atom (Zabik, 1983).

Adsorption depends on both the soil and the pesticides properties. It is usually greatest in the order organic matter > high charge clays > low charge clays. Bailey and White (1970) have suggested that the nature of the functional groups (OH, CO, COOH, and NH_2), the nature of substituting groups, the stereo position of groups with respect to other functional groups which may enhance or hinder intramolecular bonding, and the presence and magnitude of insaturation in the molecule play an important role on the adsorption and behavior of pesticide chemicals.

The freundlich equation is the simplest equation that describes adsorption:

$$\frac{X}{m} = KC^{\frac{1}{n}}$$

X = Weight of chemical

m = weight of soil

C = Concentration of solution at equilibrium

n = constant = 1 at normal solutions , k = constant that give the extend of binding.

For practical purpose, only the distribution coefficient (Kd) is used to compare adsorption among systems

$$K_d = \frac{chemical\ adsorbed(\frac{\mu mol}{Kg})}{chemical \in solution(\frac{\mu mol}{l})}$$

RUNOFF

Runoff losses are of greater concern because of the direct input to water bodies

and because of the possibilities of fish killed and the contamination of other aquatic species. Pesticides may be transported in runoff from land to aquatic habitats in true solution, as small undissolved particles, bound to eroded soil particles and plant debris or dissolved in humic material (Willis, C.H. and Mcdowell, L.L., 1982). Pesticides properties as well as rainfall characteristics, rate and mode of pesticide application, soil texture and topography affect the concentration of pesticides in runoff.

Weber and al. (1980) classified pesticides according to their chemical properties. The basic pesticides are immobile at low Ph and, but can be mobile at high Ph depending on water solubility and structure. acidic pesticides are mobile at normal Ph, but the arsenate and phosphate pesticides, because of their propensity for soil sorption, are usually immobile. The nonionic pesticides are usually sorbed to some extent in the soil, but the degree of sorption depends on water solubility, vapor pressure and chemical structure. Wauchope (1978) conclude in a long-term study that (a) wettable powders produce the highest losses (up to 5% of the amount applied, depending on the slope), (b) water insoluble pesticides (usually applied as emulsion) show losses of 15% or less, and (c) water soluble pesticide (usually applied as aqueous solutions) and soil incorporated pesticides show losses of 0.5% or less. The overall loss of pesticides for all chemical classes ranged from 0 to 15% of that applied.

VOLATILIZATION

Volatilization is the loss of chemicals from surfaces in vapor phase. The potential for volatilization of a chemical is related to its inherent vapor pressure and water solubility, but actually the rates will depend more on environmental conditions and all factors that control behavior of the chemical at the solid-air interface.

Volatilization from soil is difficult to predict because of the many parameters affecting their adsorption, movement and persistence. It involves desorption of the chemical from the soil, movement to the soil surface, and vaporization into the atmosphere (Spencer et al., 1973). The potential for loss through volatilization can be estimated from the physical properties of the pesticide molecule. Knowledge of vapor pressure and water solubility permits calculation of the air/water partition coefficient, and knowledge of the approximate strength of adsorption by soil (Hartley and Graham-Bryce, 1980).

In the study of the factors that could affect volatilization of insecticides from soil, Harris and Lichtenstein (1961) found that volatilization increased with increasing soil moisture. They explained this by the fact that insecticides molecules were displaced from the soil particles by water molecules in the air. The found also that rate of volatilization was function of rate of air movement. Consequently, under field conditions the rate of volatilization of insecticide residue from the soil may be retarded in areas of dense vegetation cover.

DEGRADATION AND METABOLISM

Soil provides an ideal environment for many types of degradative processes. These reactions affect the fate and behavior of pesticides chemicals in the environment. The rate at which a pesticide degrades is in part function of its molecular structure. It is influenced by several soil and weather factors which may vary from site to site and from year to year.

NON-BIOLOGICAL DEGRADATION

Non-biological degradation, is by definition, any decomposition of pesticides that

does not involve microbial processes. It involves reactions such as reduction, oxidation, elimination, substitution, isomerization, and hydrolysis (Lichtenstein, 1977).

For the pesticides in the atmosphere, on foliage or on the soil surface; photodegradation can occur. Photochemical transformation of pesticides are chemical processes that occur when energy in the form of light (usually ultraviolet light) interacts with the pesticide molecule. This reaction involves two operations (Zabik, 1983):

1. absorption of energy leading to excited state, and
2. transformation of the various electronically excited states to chemical products.

The reaction is sometime affected by photosensitizers. These sensitizers can cause increased sensitivity to light by transferring the energy of light into the receptor chemicals (Matsumura, 1973).

The study of photodegradation of every pesticides under actual conditions is not practical, and often impossible, thus two different approaches have been used to predict the photochemical behavior of such compounds (Zabik, 1985). The first model is a model ecosystem in which an attempt is made to include the variables likely to exist in the environment under consideration. The second approach is a mathematical treatment of available data through computer simulation programs. The results are then compared to actual field conditions. An adequate representation of field situation will be to combine both approaches.

Examples of photolysis are those of 4-amino 6-R-3 methylthio s- triazin- 5(4H)-ones R = phenyl, cyclo, hexyl, tert-butyl, isopropyl) in CCl_4, benzene, methanol, water or in crystalline state. These reactions yield the respective 5-hydroxy-6-R-3- (methylthio)-1-2-4-triazin as the major product. The proposed mechanism involves an intramolecular hydrogen abstraction. Minor reactions proceed by routes which include desulfuration, and oxidation

(Pape and Zabik, 1972b).

In the case of organophosphate pesticides, Two majors types of photoproducts have been reported: the oxygen analogs where the structural change is the replacement of a sulfur by oxygen, and products resulting from the cleavage of the P-S, P-O, or C-S, C-O bonds. (Zabik, 1985). The photolysis of phosmet in diethyl ether produce only two major insoluble products in low yield when irradiated at >286 nm. The products, N-methylphthalmide and N-methoxymethylphthalmide, were the same whether the reaction was run in air or under nitrogen. Many minor products were observed but not identified (Tanabe et al., 1974).

Reactions that are involved in the chemical degradation of pesticides are predominantly oxidation along with hydrolysis and isomerization. These reactions destroy the chemicals and thus progressively and permanently decrease their biological effectiveness. The rates of chemical reactions depend greatly on conditions such as temperature, Ph, and the composition of the medium in which the reactions take place. Examples of chemical degradations are alkaline hydrolysis of organophosphorus compounds such as malathion or adsorption catalyzed of chlorotriazines (Hartley and Graham-Bryce, 1980). For pesticides not affected by surface catalysis, degradation might be expected to occur predominantly in solution (Hartley and Graham-Bryce). In this case adsorption would retard degradation by removing the chemical from solution

BIOLOGICAL DEGRADATION

Frehse and Anderson (1982) have suggested that three main variables, apart from concentration, contribute to the rate of biodegradation of pesticides.

1. The quantity of microorganisms or enzyme systems which have the capacity to degrade

the chemical.

2. The availability of the chemical to the organisms or enzyme system responsible for degradation.

3. The activity level or physiological state of the organisms. The structure of the pesticide involved is very important in its attack by soil microorganisms. Introduction of polar groups such as OH, NH_2, NCO, COO^-,NO_2 often afford microbial systems a site of attack. The rate of degradation reaction is further modified by steric and electronic factors on neighboring atoms (Helling et al., 1971).

Environment conditions and soil factors have great impact on microbial degradation. Warm soil temperatures, adequate moisture and the presence of organic matter generally promote microbial activity by providing a suitable environment for microorganisms. For example, the higher the soil temperature, and soil moisture level accelerated decomposition of the insecticides diazinon and thionazin (Getzin, 1968). The same author showed that an increase of soil Ph of 4.3 to 8.1 enhanced the biological breakdown of thiazinon.

PESTICIDE EFFECTS ON SOIL MICROORGANISMS AND MICROBIAL PROCESSES

Soil microorganisms are important in catalyzing many processes such as cycling nutrients from soil and fertilizer or transfer nutrients directly to crops. They mineralize, oxidize, reduce and immobilize elements in soil, and influence their solubilities (Alexander, 1969). These processes can be influenced by pesticides that reach the soil after application and the response of microorganisms depends on the rate and method of application, the toxicity and spectrum of activity, and the persistence and availability of the chemical.

Domsch et al. (1983) have shown that pesticides affect microorganism population, increase ammonium production and depress nitrification but most of the studies concerning pesticide-soil interactions involve pretreated soil that tends to exaggerate the effects of pesticides. Despite this fact, long-term field experiments have indicated that pesticides do not cause critical declines in microbial populations or the processes contributing to soil fertility (Cole, M.A., 1976).

TECHNICAL INFORMATION ON PESTICIDES STUDIED

METOLACHLOR

Metolachlor is an herbicide that provides excellent control of most annual grasses and many broadleaf weeds. The molecular formula of metolachlor, a chloroacetamide hebicide, is $C_{15} H_{22} Cl N O_2$ and appears structurally as shown in Figure 2 (Pesticide Manual, 1983).

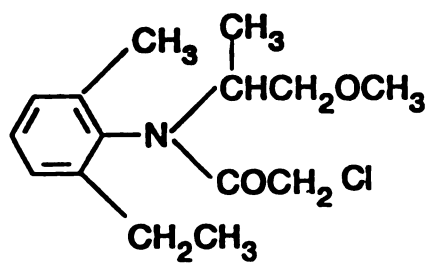


Figure 2. Structure of Metolachlor

Its high level of biological activity and desirable chemical and soil stability (Weber et al., 1981), provide good control of late germinating grasses, especially under conservation tillage system (Lebaron et al., 1983). It is an effective herbicide for control of yellow nutsedge (*Cyperus esculentus* L.). Metolachlor is used selectively in cotton (*Gossypium hirsitum* L.), peanuts (*Arachis hypogaea* L.), corn (*Zea mays* L. Moench), potatoes (*Solanum tuberosum* L.), soybeans (*Glycine max* L.), and other broad-leave crops. (Pesticide Manual, 1983).

Chloroacetamides are presumed to inhibit plant growth (Ashton and Crafts, 1981), their primary biochemical mechanism of action is unknown. Metolachlor inhibits the early development of susceptible weed species (Penner and Hatzios, 1988). The treated seeds of susceptible species usually germinate, but the seedlings either do not emerge from the soil or emerge and exhibit stunted or abnormal growth (Penner and Hatzios, 1988). The basis of selectivity of the chloroacetamide herbicides could be attributed to the ability of resistant plants to metabolize them at a rate sufficient to keep cellular levels of the herbicides bellow that required for growth inhibition (Lebaron et al., 1983). Metolachlor appears to be most efficiently taken up by roots or cotyledons of grasses, while root absorption is very important for uptake by many cotyledoneous plants. Translocation of both herbicides in plants is acropetal (Lebaron et al., 1983). Metolachlor's technical information is summarized in Table 1.

METRIBUZIN

Metribuzin is a heterocyclic basic organic molecule applied as pre-emergence or early post emergence to control annual grasses and numerous broadleaf weeds, including some hard to control weeds, such as cocklebur, velvetleaf, jimsonweed, sicklepod etc (Pesticide

Manual, 1983). Metolachlor which molecular structure is $C_{}$ $H_{}$ $N_{}$ O S presents the structure as depicted in Figure 3 (Pesticide Manual, 1983).

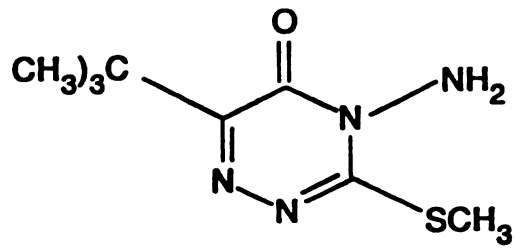


Figure 3. Structure of Metribuzin.

Metribuzin is readily taken up by roots and translocated to the shoots and leaves of treated plants in the apoplast (Schumacher et al.,1974; Falb and Smith, 1984; Fortino and Splittstoesser, 1974). Factors affecting the rate of transpiration, such astemperature, humidity, light intensity, and stomatal aperture would also affect the root uptake of metribuzin (Penner and Hatzios, 1988).

The translocation of metribuzin in the apoplast is not exclusive, it readily penetrates the symplasm of roots or leaves, but because of inability to retain it for long time, metribuzin leached into the apoplast and carried away with the transpiration stream (Penner and Hatzios, 1988).

The symptoms of metribuzin toxicity are those of photosynthetic inhibitor (Fedtke, C., 1982), but metribuzin has been reported to interfere with biochemical and physiological processes of plant metabolism, such as nitrogen metabolism an respiration. The biological and physical properties of metribuzin are summarized by table 2.

PHOSMET

Non systemic acaricide and insecticide used on top fruit (e.g. apples, pears, peaches, apricots, and cherries), citrus, grapes, potatoes, and forestry at rates (0.5 - 1,0 kg a.i./kg) such that it is safe for range of predators of mites and therefore useful in integrated pest management (The pesticide Manual, 1983; The Merck Index, 1983). The molecular structure of phosmet is shown in Figure 3 (The Pesticide Manual, 1983). The biological and physical characteristics are summarized by table 3.

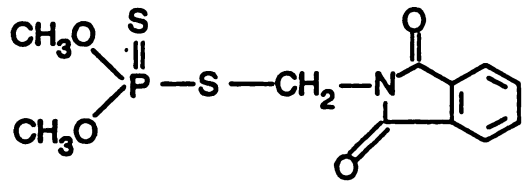


Figure 4. Molecular structure of Phosmet

Table 1. Name, chemical, and biological properties of metolachlor (adapted from Lebaron et al., 1983; Pesticide Manual, 1983)

PROPERTY	DATA or COMMENTS
Chemical name	2-Chloro-6'ethyl-N-(2-methoxy-1-methyl-ethyl)acet-o-toluidide
Common name	Metolachlor
Trade name	Dual
Formulation	DUAL, E.C.(500 or 700 g a.i./l) BICEP, Metolachlor + Atrazine (1.5:1)
Appearance	Colorless to tan
Vapor pressure	$1.3*10^{-4}$ mm Hg at 20°C
Water solubility	530 ppm
Soil photolysis	Stable, but degraded about 50 degree 8 days in natural or artificial light
Soil half life	15-50 days depending on the region
Mode of action	Possible germination inhibitor
Volatilization	Relatively non volatile

Table 2. Name, physical, and biological properties of metribuzin (adapted from Williams, W.M. et al., 1988; Hatzios, K.K., Penner D., 1988; The pesticide Manual, 1983)

PROPERTY	DATA or COMMENTS
Chemical name	4-Amino-6-tert-butyl-3-methylthio-as-triazin-5(4H)-one
Common name	Metribuzine
Trade name	SENCOR, SENCOREX, SENCORAL (Bayer) LEXONE (Dupont)
Formulation	W.P> (350, 500, 700 g a.i./kg); aqueous suspension(420 g/kg)
Appearance	White, Crystalline solid
Vapor pressure	$<10^{-4}$mm Hg at 20°C
Water solubility	1200 ppm at 20°C
LD_{50}	2200 mg/Kg (rat)
Soil photolysis	15-50 days depending on the region
Mode of action	Photosynthetic inhibitor
Volatilization	slightly volatile

Table 3. Name, physical, and biological properties of phosmet (adapted from The pesticide Manual, 1983).

PROPERTY	DATA or COMMENTS
Chemical name	O,O-dimethyl S-phthalimidomethyl phosphorodithiote
Molecular formula	C_{11} H_{12} NO_4 PS_2
Common name	Phosmet
Trade name	Imidan
Formulation	Imidan W.W. (125 or 500 g a.i./kg) Imidan 5 Dust (50 g a.i./kg)
Appearance	Colorless crystalline solid
Vapor pressure	0.997 mm Hg at 30°C
Water solubility	22 mg/l at 25°C
LD_{50}	113 mg/Kg (rat)
Mode of action	Acetylcholinesterase inhibitor
Activity	Non systemic

BEHAVIOR IN THE ENVIRONMENT

METOLACHLOR

Metolachlor is relatively non volatile ($1.2*10^{-4}$ mm Hg), however volatility can cause a minor loss of metolachlor when applied pre-emergence to bare soil or in some conservation tillage situations. Volatilization is influenced by the type of surface to which the herbicide is applied; Parochetti (1978) observed that while only 0.1% of metolachlor was lost from the soil surface, about 11.5 to 36.6% volatilized from the straw surface of various plant residues. Under practical field conditions, only 0.6 to 1.4% of applied metolachlor would volatilize from the soils treated within the first 24 hours (Buckhard, 1977).

Metolachlor is not very strongly adsorbed to soil particles. Buckhard (1978) reported that the Freundlich adsorption constant (K) for metolachlor ranged from 1.54 to 10.0 ug of soil.

Results of the studies of the effect of soil chemistry on metolachlor adsorption are controversial. Strek and Weber (1981) reported that metolachlor adsorption was strongly correlated with organic matter content and cation exchange capacity, clay content had little influence. They also found that the soil organic content has little influence, but greater adsorption occurred on montmorillonite clay.

Movement of metolachlor in soil seemed to be mainly influenced by organic matter and/or clay content. Obrigawitch et al. (1981) reported less leaching of metolachlor in a Pullman clay loam when compared to an Amarillo fine sandy loam and Patricia fine sandy loam.

Although there is evidence of some chemical degradation of metolachor, most of the studies showed that under normal conditions of field use, metolachlor and other acetanilide herbicides are degraded mainly by microbes. McGahen and Tiedje (1975) found that

metolachlor was degraded by the soil fungus *Chaetomium globosum*. Krause et al. (1985) found that an actinomycete strain isolated from soil also metabolized metolachlor.

Degradation proceeded via oxidation of the chloroacetyl group. The major metabolite was the oxalic acid derivative [N-(2'- methoxy - 1 - methylethyl) - 2 - ethyl - methyl - oxalic acid anilide] (Guth, 1981). Chen and al. (1987) have shown that transformation included also dechlorination, dehalogenation, dealkylation, hydroxylation, and indoline ring formation.

METRIBUZIN

The mobility of metribuzin in soils is inversely related to the soil adsorptive capacity. In general metribuzin is relatively mobile in sandy and mineral soils but very immobile in soils with high organic matters . Metribuzin leaching from the zone of soil application is dependent on the amount of rainfall or irrigation that occurs under field conditions (Sharon and Stephenson, 1976). It has been shown that Ph has great influence on leaching of metribuzin (Ladlie et al., 1976). Furthermore they reported that metribuzin leaching in soils increased with increasing soil pH.

It has been shown by (Schmidt, 1973) the existence of high negative correlation of metribuzin phytotoxicity and soil organic matter. It was concluded that the herbicidal inactivation of metribuzin in soils was due to a Ph dependent adsorption of this chemical to the soil organic matter (Schmidt, 1975). The mechanism involved in adsorption of metribuzin to soil particles is the formation of binding forces between the herbicide molecule and soil particles due to electron density of amino groups at C-3 and N-4 positions of the heterocyclic ring.

Most of the studies on metribuzin phototransformation have been conducted

primarily under laboratory conditions rather than field conditions. In this case photodecomposition in the environment under practical conditions is not well understood. Pape and Zabik (1972) have shown that deamination is the major reaction involved in photodecomposition and it yields deamino-metribuzin (D-A) as major metabolic products.

Although it is not always easy to distinguish between the biological and non-biological degradation of a given herbicide in soils , early studies on the fate of metribuzin in soils emphasized the importance of the non-biological degradation of this herbicide. Reports have shown degradation of metribuzin in soil samples awaiting residue analysis and stored at -37 °C (40). Only non-biological activity could account for this degradation since little or no biological activity would be expected at this low temperature. 101 and 114 have reported a slower degradation in samples from deeper horizons rather than in surface soils. This shows that degradation is influenced by soil depth. Since soil components are in vast quantities compared with the herbicide, it degradation should follow a first order kinetics. This has been shown by (Hyzak and Zimdahl, 1974) . He showed that the rate of metribuzin and its isopropyl and cyclohexyl analogs in soils under field and laboratory conditions appears to be best described by first-order kinetics. Common metabolites of non-biological degradation of metribuzin are deamino (DA), deketo (DK), and deamino deketo (DADK) metribuzin.

A number of reports have demonstrated the importance of microbial activity in the degradation of metribuzin in soils. Fumigation, sterilization by autoclaving, irradiation by γ rays, and treatment with microbial inhibitors (Sharon and Stephenson, 1976; Ladlie et al., 1976) have produced marked reductions in the capacity of selected soils to degrade metribuzin. A number of soil bacteria, including *Arthrobacter* and *Pseudomonas* species as well as soil fungi, such as *Rhizopus japonicus* and *Cunninghamella echinulata* Thaxter have

been reported to rapidly deaminated metamitron, a triazine herbicide with relative structure as metribuzin (Engelhardt and Wallnofer, 1978). Metribuzin metabolites that have been detected in soils and are believed to result from microbial degradation include DA, DK, DAAK (Sharon and Stephenson, 1976). Contrary to s-triazine herbicides, the ring of metribuzin or other triazinones could be cleaved by soil microbes. Engelhardt et al. (1982) has reported the formation of benzoyl formic acid, acetylhydrazone and benzoyl formic acid as the result of ring cleavage. Decarboxylation and oxidation can be involved in this degradation and yielded 3-methyl-6-phenyl-1,2,4,5-tetrazine.

PHOSMET

Although Phosmet is not intended for use as soil insecticide, some residues could reach the soil through its use on various crops. But as with most organophosphate insecticides, it degraded fairly rapidly in soils. soil Ph and temperature as well as moisture content seemed to greatly influence the rate of degradation (Menn et al., 1965).

Several microorganisms have been implicated in the degradation of several organophosphate insecticides. Ahmed and Casida (1958) have shown that the yeast *Torulopsis utilis*, the algae *Chlorella pyrenoidosa*, and the bacteria *Pseudomonas fluorescences* and *Thiobacillus thiooxidans* metabolized several dialkyl phenylphosphates and phosphorothioates. Menn et al. (1965) have shown that Phosmet was more stable in autoclaved soil and that partial destruction of soil microorganisms increased the persistence of phosmet. That could only be explained by microbial activity.

Two majors products have been reported in the photolysis of organophosphate: (1). the oxygen analogs where the only structural change is the replacement of sulfur by oxygen, and (2). products resulting from the cleavage of the P-S, P-O,, or C-O, C-S bonds

(Zabik, 1985). When Phosmet is irradiated at > 286 nm in diethyl ether solution, it produced two majors isolable products: N-methylphthalimide and N-methoxymethyl phthalimide (Tanabe et all., 1974).

CHAPTER III

MATERIALS AND METHODS

STUDY DESIGN AND SAMPLE COLLECTION

The soil samples analyzed in this study were obtained from an experiment designed for the study of the leaching potential of nitrogen fertilizer under a potato field (Joern, 1991). The experiment was located at the Michigan State University Montcalm Research Farm. The soil at this area was mapped as a Montcalm-McBride sandy loam complex. Soil characteristics, and weather as well as irrigation records are shown respectively in Tables 4 and 5.

The experimental design selected for this investigation was a randomized complete block with four replications. Each replication consisted of 0.86 m wide x 15 m long plot. The distance between rows was 0.56 m with approximately 25.4 cm planting distance between seed tubers.

Table 4. Initial soil test data.

		Bray-1	---Exchangeable---			Organic	
Year	Ph	P	K	Ca	Mg	Matter	CEC
		----------Kg/ha----------				%	
1988	5.6	672	332	806	120	1.9	6
1989	6.2	597	305	853	151	1.7	5

The two herbicides, metribuzin (Lexone 75%) and metolachlor (Dual 86.4%) were incorporated into the soil at the rate of 0.65 kg/ha and 2.24 kg/ha respectively. Phosmet (Imidan 50 WP) was applied three times during the year after planting but after emergence at the rate of 1.12 kg/ha each time.

Each sampling consisted of two soil samples (3-5 cores 5 cm in diameter) taken across the hill of the two center rows of each plots to a depth of 120 cm . Each core was divided according to the depth. For this study, only depths I (0-15 cm), II (15-30 cm), III (30-45 cm), and IV (45-60 cm) were analyzed. Every Soil sample was mixed thoroughly and air dried, ground, sieved, and fist stored in cardboard boxes. The soil samples were later transferred into glass bottles and stored at -20 °C until laboratory analyses were performed. Table 6 summarized the spraying record as well as the soil sampling periods.

Table 5. Average monthly precipitation, irrigation, air temperature, and radiation data for the experiment site.

Month	Rainfall (mm)		Irrigation (mm)	Temperature (oC)	
	1989	Mean*		1989	mean*
April	62	68	--	7	7
May	68	66	--	12	13
June	123	79	--	19	18
July	21	59	112	22	21
August	140	107	36	19	19
September	34	119	--	14	15
Total	448	498	148		

* Long-term mean

Table 6. 1989 study management and sampling schedule. Michigan State University Montcalm Experimental Station.

Event	Pesticides		
	Metribuzin	Metolachlor	Imidan
Background sample	5/2	5/2	5/2
Treatment	5/26	5/26	6/28-7/6
			7/13-8/3
Planting date	5/4	5/4	5/4
Hilling	----------	5/30	----------
1st sample	6/21	6/21	6/21
2nd sample	8/22	8/22	8/22
Harvest	9/21	9/21	9/21
3rd sample	10/29	10/29	10/29

MATERIALS

GLASSWARE PREPARATION

All glassware (round and flat-bottomed flasks, separatory funnels, funnels, and chromatographic columns) were washed in soaped hot water, rinsed with distillate water followed by acetone. The glassware was further placed in a furnace for drying.

REAGENTS

Solvents: acetone, acetonitrile, dichloromethane, methanol and hexane were pesticide grade solvents and used as received.

Chemicals: reagent grade sodium sulfate (granular, anhydrous); Florosil-PR grade (60-90 mesh) activated at 135 Oc for 4 hours before use; Liquid nitrogen.

Reference chemical standards : metribuzin 99.9 %, metolachlor 98.8 %, Phosmet 98.9% were obtained from the U.S. Environment Protection Agency (EPA), Pesticides and Industrial Chemicals Repository, Research Triangle, N.C.

Miscellaneous: glass wool and Whatman cellulose extraction thimble 25 mm x 80 mm.

EQUIPMENT

Gas chromatograph Varian Aerograph series 1400, Gas chromatograph Beckman GC-65, Gas chromatograph double focussing mass spectrometer (Gc/Ms) Jeol AX505, Spectra Physic integrator SP4270, Hewlett Packard integrator 3390A, and rotary evaporator Buchler Instruments, Soxhlet extractor and soxhlet heater GCA/Precision Scientific.

ANALYTICAL METHODS

The extraction and liquid-liquid partition procedures were adapted from Thorton and Stanley (1977).

EXTRACTION AND CLEANUP OF SOIL SAMPLES

Each soil sample was mixed to homogenized the entire sample. A 25 g aliquot of the mixed soil was weighted into an extraction thimble. 100 ml of 20 % aqueous methanol was measured into a 125 ml flat-bottomed flask and two boilizers were added. The soxhlet apparatus containing the sample was attached to the flask and extracted for 6 hours. The extract was evaporated with a rotary vacuum evaporator until only water remained (10-20 ml). The water extract was transferred into a 250 ml separatory funnel with an additional 50 ml of water. The flask was rinsed with an additional 60 ml of dichloromethane which was added to the separatory funnel. The phases were allowed to separate and 60 ml of dichlolromethane was added to the separatory funnel which was then shacken for three minutes. The lower phase (dichloromethane) was drained through a funnel containing anhydrous sulfate and collected into a 300 ml round-bottomed flask. The partition was

repeated with two additional 60 ml portions of dichloromethane. Three drops of decyl alcohol was added to the flask and the combined dichloromethane extracts were evaporated to nearly dryness on a rotary vacuum evaporator at 35°C. The remaining solvent was removed with liquid nitrogen. The residue was dissolved in 3 ml hexane and analyzed by gas chromatography.

RECOVERY

The recovery study was carried out by spiking three portions of 25 g of soil with 2 ml of a mixture containing 2.10 ppm, 2.25 ppm an 2.0 ppm of metribuzin, metolachlor, and imidan respectively. The soils were left 24 hours to allow binding of pesticide molecules to the soil particles. Then the above procedures for extraction and partition were used . The recoveries were 86%, 90.33% and 84.33% for metribuzin, metolachlor, and imidan as shown by the tble 8.

QUANTIFICATION

The detection of the two herbicides metolachlor and metribuzin in soil samples was performed by using a gas chromatograph equipped with ^{3}H foil electron-capture detector. The following conditions summarized by table 8 were used for the analyses.

Column : DB-5 fused silica capillary column
(30 m x 0.5 mm i.d.) with 0.5 μm phase thickness.

Oven : isothermal temperature 150 °C.

Injector : temperature 190 °C.

Detector : temperature 210 °C.

Carrier gas : helium at the pressure of 140 Kpa.

Integrator : 3390A Hewlett Packard

The insecticide Imidan concentration was quantified with a flame photometric detector (FPD) at the phosphorus mode. The following chromatographic conditions summarized by table 8 were employed.

Column : DB-1301 megabore capillary column

(30 m x 0.53 mm i.d.), film thickness 1.0 μm.

Oven : temperature 170 °C.

Injector : temperature 190 °C.

Detector : temperature 210 °C.

Carrier gas : Helium at a flow rate of 20 cc/min.

Gas flow : Air at 120 cc/min and hydrogen at 150 cc/min.

Integrator : Spectra Physics SP4270.

CONFIRMATION OF THE PESTICIDES

Gas Chromatography-Mass Spectrometry (GC/MS) Jeol AX505 was used for confirmation of pesticide identification. Capillary column DB-1 30 m x 0.25 mm I.D. with 0.25 μm phase thickness was used. The detection was made by using Electron Capture/Negative Chemical Ionization (ECNCI).

Table 8. Percent recovery and standard deviation (Std.dev.) of the pesticides.

COMPOUND	% RECOVERY REPLICATION			MEAN	STD. DEV
	1	2	3		
Metribuzin	87	86	85	86.00	1.53
Metolachlor	90	89	92	90.33	1.53
Imidan	86	84	83	84.33	1.53

Table 9. Chromatographic conditions for the detection of the pesticides in soil samples.

CHROM.TYPE	DETECTOR	COLUMN TYPE	TEMPERATURE (°C) Oven	Inj.	Det.
Varian aerograph Series 1400	^3H	DB-5 fused capillary 30 m x 0.25 mm i.d. 0.25μ phase thickness J&W Scientific	150	190	210
Beckman GC-65	FPD	DB-1301 wide bore 30 m x 0.53 mm i.d. 1.0 phase thickness J&W Scientific	170	190	210
Jeol AX505	ECNI	DB-1 capillary 30 m x 0.25 mm i.d. 0.25um phase thickness	180		

CALCULATION OF PESTICIDES CONCENTRATION

Quantification of pesticides were based on peak heights. Different concentrations of standard solutions were injected and calculation of the pesticides in a sample was accomplished by use of the following equation where response for unknown is compared to the response for a known quantity in a standard solution:

$$ppm = \frac{sample\ area}{std\ area} \times \frac{std.inj.(ng)}{wt\ of\ sample(g)} \times \frac{final\ vol(ml)}{sample\ inj(\mu l)}$$

CHAPTER IV

RESULTS AND DISCUSSION

The concentration of the three pesticides was monitored by analyzing soil samples using gas chromatography (GC). An Electron capture detector (ECD) was used to detect metribuzin and metolachlor. The limit of detection for both compounds was 0.01 ppm. The soil samples had been concentrated from 25 g to 3 ml, therefore the real minimum detectable quantity in the soil should be 0.0012 ppm. The retention time were 5.64 min for metribuzin and 8.89 min for metolachlor as shown by the chromatograms in Figure D3. A Flame photometric detector (FPD) was used for the identification of phosmet. The minimum detectable limit was 0.4 ppm. The detectable limit was therefore 0.048 ppm and the retention time was 6.62 min (Fig D1).

The results of the analyses are reported in appendices A and B and plotted in appendix C.

STATISTICAL ANALYSIS

The experiment was established as a randomized block design with 4 replications. Treatment was represented by the depth. Each replication was sampled 5 times simultaneously. Heterogeneous variances within sampling date within subsample for each replication were found using Bartlett's test. This can be explained by heterogeneity in the pesticide applications. Duncan's multiple range test was employed to determine the significance of residue level difference between depths and between period of sampling at

the significance level of 0.05. The results are shown on the graphics (Appendix C).

PERSISTENCE AND MOVEMENT OF THE PESTICIDES

IMIDAN

This chemical was not detected in any of the soil samples. Its concentration in the soil is certainly below the detection limit of the chromatographic system. Most of the chromatograms as illustrated in Figures D1 and D2 showed a peak at 5.64 min which is different from the retention time for Imidan. This peak can be seen in the standard solutions many days after their preparation. This peak could represent hydrolysis product of imidan or may be imidoxon, a metabolite of imidan as suggested by Bowman (1991) .

The dissipation of imidan may be explained by different processes. Volatilization and photodegradation are two ways by which imidan could be lost in the environment. This could be important since this chemical was applied at the surface of the leaf to control aphids. Chemical decomposition could also account for the disappearance of this pesticide. Menn et al. (1965) have shown that spontaneous hydrolysis was the major factor associated with degradation of imidan. Nearly 50% degradation was observed after 3-19 days. This same study suggested that microbial degradation could account for the degradation. Partial destruction of soil microorganisms increased the persistence by 50%. This rapid rate of degradation may explain the non-detection of imidan in soil samples. Finally, imidan washed from plant leaves may not reach the soil directly but may be subject to soil erosion or runoff.

METRIBUZIN AND METOLACHLOR

For any sample, the concentration of metolachlor in soil was higher than the

concentration of metribuzin as shown in Figures C1 to C4. One explanation for this is the difference between the rate of application of these herbicides. The amount of metolachlor applied (2.24 kg/ha) is four time the amount of metribuzin (0.56 kg/ha). The high water solubility of metribuzin (1200 ppm) in conjunction with the the high soil pH may have increased its hydrolysis and microbial attack as suggested by Ladlie et al. (1976); leading to a decrease of the amount found. On the contrary, metolachlor has a very low water solubility and its distribution coefficient (Kd = 1.60) is higher than the distribution coefficient of metribuzin (Kd = 1.32); therefore it will remain bound to soil particles leading to less degradation.

24 DAYS BEFORE THE TREATMENT (DBT)

There is an appreciable amount of both herbicides found in the soil samples as shown by Figures C. This residue is the expression of the persistence of these chemicals from previous applications. More herbicides were found in the lower layers than the upper layers, with more metolachlor in the third layer and more metribuzin in the fourth (Fig C7). The high water solubility of metribuzin compared to metolachlor may explain its movement and concentration in the fourth layer. The high concentration of these chemicals in the lower layers can be explained by their displacement from the upper layer to the lower layers with water movement leading to their accumulation over long period of time. Since microbial activity is higher in the upper soil layers, increased degradation of these chemicals in these layers may also help explain the observed results. Lock and Sydney (1991) attributed this phenomenon to the reduction of microbial activity with increasing soil depth.

25 DAYS AFTER THE TREATMENT (DAT)

After the treatment there is an increase of the concentration of both chemical in almost all the soil profiles except a decrease of metribuzin in the fourth layer (Fig C7). The concentration found in the samples is still low. The highest concentration found was 0.05 ppm (third layer) which was very low compared to the 0.56 ppm added to the top 6" (0.56 ppm) during the treatment. The herbicides were surface applied, and their persistence may have been reduced by volatility and photodecomposition as observed by Bowman (1991) in the study of the mobility and dissipation of metribuzin and atrazine and their metabolites in plainfield using lysimeters. Chemical and microbial degradation as well as plant uptake may also have contributed to the dissipation of the chemicals. Poor sampling and loss of recovery could also explain this observation. The recovery study was done with spiked soil and extracted the same day, thus the results may have overestimated the extraction efficiency because of residue binding. Degradation during storage may also account for the decrease in the amount found in the samples. Webster and Reimer (1976) have previously observed the loss of metribuzin during cold storage of samples awaiting extraction. After the input from the treatment there was an increase of metolachlor in the first, second, and fourth layers and a decrease in the third layer. The concentration of metribuzin increased in the first three layers and decreased slightly in the fourth layer. Twenty five days after the treatment, potato plants were not well developed, their evapotranspiration and the leaf area index were low. Therefore the available water could move down through the soil profile with the herbicide as proposed by Green and Khan (1987) in a review of the movement of pesticides in the soil. The slight decrease in the concentration of metolachlor in the third layer corresponded to the movement of this chemical downward leading to the slight increase observed in the fourth layer. This can be explained by the presence of high

absorptive sites or less porosity preventing the herbicide from moving with water. This accumulation in certain zones of the soil was also observed by Allan Walter (1973) and he explained it by soil structure. The concentration of metribuzin is higher in the second and third layers compared to the first layer. Because of its mobility metribuzin will move readily with water as observed here. The large decrease in the concentration of metribuzin in the fourth layer may be the result of the downward movement of this chemical and may also have contributed to the increase of the concentration in the third layer due to upward movement.

87 DAYS AFTER THE TREATMENT (DAT)

There was a large increase in the concentration of metolachlor in all the soil layers. Metribuzin slightly increased in the first and fourth layer and slightly decreased in others. This increase in the concentration of metolachlor 87 days after the treatment was not easy to interpret. This high concentration found was probably due to inherent soil characteristics and spatial variability, and has been seen in other studies (Carsel et al, 1988; Ruth and Penner, 1991). This increase in the concentration may also be due to upward movement of the herbicide resulting from the drought situation. Even though there was rainfall and irrigation was done during this period, the soil was dry because of the high uptake of water by potato plants. The plants were at the stage of tuber production, consequently their metabolism and evaporation rates were high therefore there was increase of their evapotranspiration. The chemicals in soil will move upward with water. Metribuzin is a weak acid and may have been subjected to binding to soil particles. This binding could have reduce the movement of metribuzin in the soil as shown by the results. The slight increase of the concentration in the fourth and first layers may have resulted

from some movement of metribuzin from the second and third layer.

157 DAYS AFTER THE TREATMENT (DAT)

Metribuzin concentration increased in the first and third layer and decreased in the fourth layer. The concentration in the second layer remained almost constant. The concentration increase of metribuzin in the third layer could have resulted from the upward movement of this chemical from the fourth layer. The third layer has not been disturbed by tillage, remaining compacted. In this case the aeration is low, reducing microbial activity. Further metribuzin may have move upward to the first layer resulting in the high concentration found in the uppermost layer. Less rainfall occurred during this period contributing to the drought. This would increase upward movement of soil water potentially moving soluble herbicides with it. Potatoes were harvested before this time period and the leaves remaining on the ground may have been incorporated into the soil. The presence of this biomass may have increased the retention of metribuzin resulting in less degradation and less movement. We found a large decrease of metolachlor in all layers. This large concentration decrease of metolachlor may be explained by metabolization. The high microbial activity in the top layers combined with hydrolysis may have increased the dissipation of this chemical. The concentration of metolachlor in the third layer decreased less. This result was observed with metribuzin and could be explained by the same soil compaction.

The overall pattern of the curves can be explained by downward and upward movement of the herbicides in the soil profiles. This movements have been influenced by environmental conditions (rainfall, temperature), plants metabolism (evapotranspiration), and by cultural practices (irrigation, hilling, and harvesting).

CHAPTER 6

CONCLUSION AND FUTURE RESEARCH

Complete metabolism of phosmet was observed with the presence of one preponderant metabolite. Even though further studies should look at the metabolic products, phosmet should not be a serious threat to the environment.

We found the two herbicides (metolachlor and metribuzin) in the soil 157 days after treatment. Some herbicides will remain in the soil like those found in the background samples but the amount will be low due to continue degradation occuring in the soil. Thus these herbicides are not likely to pose a problem of carryover and injury to susceptible crops. Furthermore injury problems may be solved by using protectants and antidotes. The concentration of the herbicides in the soil is variable from layer to layer. This difference was explained by variability in soil structure among layers. Soil physical and chemical structures analyses should have helped explain these differences observed.

The large variations observed in the data may be due to the small size of soil samples. For an experiment in plots bearing crops, Hormann et all. (1973) suggested that at least 20 cylinders of soil should be taken and combined for each replication. This number seems to be a good compromise between reproducibility and economy. Their study showed also that if there is a residue pattern in the soil, the sampling must be designed to obtain representative results.

The results obtained show leaching of the herbicides down the profile. This leaching can result in ground water contamination. Since irrigation can not be stopped for productivity reason, farmers should not over irrigate to reduce the amount of herbicides

leached. Other factors such as infiltration, evapotranspiration, root absorption and exudation, lateral transport, vertical percolation and volatilization may also explain the overall results obtained.

The complexity and difficulty in interpreting the results are due to the fact that the length of this study does not allow sufficient time to appreciate all the natural and weather-dependent phenomena such as persitence and leaching. There is also a danger of overinterpreting such data.

APPENDICES

RESULTS OF THE CHROMATOGRAPHIC ANALYSES OF SOIL SAMPLES

Table A1. Concentration of the three pesticides found ion soil samples 24 days before treatment (24 DBT).

SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA	SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA
101-1		0.00	0.07	201-1		0.00	0.07
101-2	NI	0.00	0.07	201-2	NI	0.00	0.09
101-3		0.02	0.05	201-3		0.00	0.10
101-4		0.02	0.05	201-4		0.02	0.17
102-1		0.00	0.03	202-1		0.00	0.10
102-2	NI	0.00	0.20	202-2	NI	0.00	0.18
102-3		0.04	0.26	202-3		0.00	0.45
102-4		0.01	0.15	202-4		0.04	0.10
103-1		0.00	0.01	203-1		0.00	0.10
103-2	NI	0.00	0.17	203-2	NI	0.00	0.05
103-3		0.02	0.2000	203-3		0.09	0.12
103-4		0.04	0.05	203-4		0.07	0.05
104-1		0.00	0.00	204-1		0.00	0.07
104-2	NI	0.00	0.00	204-2	NI	0.00	0.07
104-3		0.03	0.05	204-3		0.00	0.25
104-4		0.02	0.03	204-4		0.01	0.11
105-1		0.01	0.00	205-1		0.00	0.02
105-2	NI	0.00	0.00	205-2	NI	0.00	0.05
105-3		0.09	0.10	205-3		0.00	0.18
105-4		0.05	0.07	205-4		0.00	0.04

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

Table A1.(cont'd)

SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA	SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA
301-1		0.00	0.05	401-1		0.00	0.02
301-2	NI	0.00	0.10	401-2	NI	0.00	0.10
301-3		0.04	0.25	401-3		0.03	0.17
301-4		0.00	0.10	401-4		0.02	0.10
302-1		0.00	0.09	402-1		0.00	0.03
302-2	NI	0.00	0.03	402-2	NI	0.00	0.09
302-3		0.00	0.07	402-3		0.02	0.15
302-4		0.05	0.05	402-4		0.05	0.07
303-1		0.00	0.01	403-1		0.00	0.01
303-2	NI	0.00	0.10	402-2	NI	0.03	0.30
303-3		0.01	0.20	403-3		0.05	0.20
303-4		0.03	0.05	403-4		0.03	0.05
304-1		0.00	0.00	404-1		0.00	0.00
304-2	NI	0.00	0.08	404-2	NI	0.00	0.09
304-3		0.00	0.20	404-3		0.01	0.20
304-4		0.00	0.05	404-4		0.01	0.02
305-1		0.00	0.05	405-1		0.00	0.05
305-2	NI	0.00	0.07	405-2		0.03	0.06
305-3		0.00	0.08	405-3		0.20	0.06
305-4		0.01	0.07	405-4		0.09	0.08

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

Table A2. Concentration of the three pesticides found in soil samples 25 days after treatment (25 DAT).

SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA	SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA
101-1		0.00	0.22	201-1		0.01	0.27
101-2	NI	0.05	0.14	201-2	NI	0.02	0.15
101-3		0.12	0.30	201-3		0.03	0.20
101-4		0.00	0.02	201-4		0.00	0.30
102-1		0.01	0.16	202-1		0.02	0.25
102-2		0.03	0.35	202-2		0.01	0.27
102-3	NI	0.01	0.36	202-3	NI	0.02	0.70
102-4		0.01	0.17	202-4		0.00	0.16
103-1		0.00	0.12	203-1		0.01	0.20
103-2	NI	0.00	0.26	203-2	NI	0.00	0.10
03-3		0.07	0.36	203-3		0.07	0.20
103-4		0.00	0.10	203-4		0.01	0.00
104-1		0.00	0.06	204-1		0.00	0.10
104-2		0.00	0.00	204-2		0.00	0.20
104-3	NI	0.00	0.12	204-3	NI	0.00	0.30
104-4		0.00	0.01	204-4		0.00	0.12
105-1		0.00	0.06	205-1		0.00	0.09
105-2	NI	0.00	0.08	205-2	NI	0.04	0.10
105-3		0.00	0.21	205-3		0.01	0.30
105-4		0.00	0.07	205-4		0.01	0.05

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

Table A2. (cont'd)

SAMPLE	CONCENTRATION (PPM)			SAMPLE	CONCENTRATION (PPM)		
	IMIDAN	MTBZ	METOLA		IMIDAN	MTBZ	METOLA
301-1		0.00	0.16	401-1		0.00	0.10
301-2	NI	0.02	0.30	401-2	NI	0.00	0.20
301-3		0.00	0.35	401-3		0.03	0.20
301-4		0.00	0.13	401-4		0.03	0.12
302-1		0.01	0.20	402-1		0.01	0.11
302-2		0.02	0.10	402-2		0.00	0.17
302-3	NI	0.02	0.10	402-3	NI	0.02	0.20
302-4		0.00	0.01	402-4		0.00	0.07
303-1		0.00	0.12	403-		0.00	0.12
303-2	NI	0.00	0.25	403-2	NI	0.02	0.40
303-3		0.00	0.27	403-3		0.03	0.25
303-4		0.00	0.02	403-4		0.00	0.07
304-1		0.00	0.09	404-1		0.02	0.05
304-2		0.00	0.22	404-2		0.04	0.18
304-3	NI	0.00	0.20	404-3	NI	0.02	0.22
304-4		0.00	0.13	404-4		0.00	0.05
305-1		0.00	0.07	405-1		0.01	0.12
305-2	NI	0.03	0.17	405-2	NI	0.07	0.13
305-3		0.07	0.18	405-3		0.25	0.10
305-4		0.00	0.05	405-4		0.10	0.10

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

Table A3. Concentration of the three pesticides found in soil samples 87 days after treatment (87 DAT)

SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA	SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA
101-1		0.02	0.28	201-1		0.01	0.25
101-2	NI	0.01	0.16	201-2	NI	0.01	0.16
101-3		0.03	0.23	201-3		0.00	0.36
101-4		0.06	0.38	201-4		0.00	0.12
102-1		0.02	0.27	202-1		0.01	0.16
102-2		0.02	0.25	202-2		0.03	0.35
102-3	NI	0.01	0.65	202-3	NI	0.01	0.35
102-4		0.00	0.16	202-4		0.00	0.12
103-1		0.01	0.27	203-1		0.00	0.19
103-2		0.00	0.17	203-2	NI	0.00	0.27
103-3		0.22	0.24	203-3		0.12	0.46
103-4		0.00	0.11	203-4		0.00	0.09
104-1		0.00	0.27	204-1		0.00	0.19
104-2		0.00	0.17	204-2		0.00	0.09
104-3	NI	0.04	0.36	204-3	NI	0.00	0.12
104-4		0.03	0.12	204-4		0.00	0.01
105-1		0.00	0.09	205-1		0.00	0.09
105-2	NI	0.05	0.12	205-2	NI	0.00	0.12
105-3		0.07	0.37	205-3		0.00	0.25
105-4		0.01	0.07	205-4		0.00	0.10

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

Table A3.(cont'd)

SAMPLE		CONCENTRATION (PPM)		SAMPLE		CONCENTRATION (PPM)	
	IMIDAN	MTBZ	METOLA		IMIDAN	MTBZ	METOLA
301-1		0.00	0.17	401-1		0.01	0.16
301-2	NI	0.00	0.25	401-2	NI	0.00	0.35
301-3		0.04	0.36	401-3		0.00	0.33
301-4		0.03	0.12	401-4		0.00	0.01
302-1		0.01	0.11	402-1		0.01	0.22
302-2		0.00	0.17	402-2		0.01	0.11
302-3	NI	0.00	0.23	402-3	NI	0.00	0.25
302-4		0.00	0.07	402-4		0.00	0.01
303-1		0.00	0.12	403-1		0.00	0.12
303-2	NI	0.00	0.42	402-2	NI	0.07	0.21
303-3		0.00	0.22	403-3		0.10	0.33
303-4		0.00	0.16	403-4		0.00	0.02
304-1		0.02	0.09	404-1		0.00	0.09
304-2		0.04	0.18	404-2		0.00	0.22
304-3	NI	0.00	0.18	404-3	NI	0.03	0.25
304-4		0.00	0.05	404-4		0.00	0.12
305-1		0.01	0.12	405-1		0.00	0.05
305-2		0.07	0.13	405-2		0.00	0.21
305-3	NI	0.13	0.10	405-3	NI	0.00	0.22
305-4		0.00	0.10	405-4		0.00	0.11

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

Table A4. Concentration of the three pesticides found in soil samples 157 days after treatment (157 DAT).

SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA	SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA
101-1		0.01	0.09	201-1		0.01	0.03
101-2	NI	0.00	0.16	201-2	NI	0.03	0.04
101-3		0.01	0.16	201-3		0.08	0.11
101-4		0.00	0.05	201-4		0.00	0.01
102-1		0.00	0.09	202-1		0.01	0.09
102-2		0.00	0.12	202-2		0.02	0.10
102-3	NI	0.00	0.22	202-3	NI	0.02	0.10
102-4		0.00	0.11	202-4		0.00	0.01
103-1		0.00	0.12	203-1		0.01	0.12
103-2	NI	0.00	0.12	203-2	NI	0.01	0.16
103-3		0.00	0.07	203-3		0.00	0.16
103-4		0.00	0.02	203-4		0.00	0.08
104-1		0.02	0.12	204-1		0.03	0.13
104-2		0.01	0.12	204-2		0.03	0.13
104-3	NI	0.01	0.07	204-3	NI	0.03	0.16
104-4		0.00	0.02	204-4		0.00	0.08
105-1		0.01	0.14	205-1		0.00	0.07
105-2	NI	0.01	0.15	205-2	NI	0.00	0.12
105-3		0.01	0.15	205-3		0.01	0.13
105-4		0.00	0.10	205-4		0.00	0.11

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

Table A4. (cont'd)

SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA	SAMPLE	CONCENTRATION (PPM) IMIDAN	MTBZ	METOLA
301-1		0.01	0.0 3	401-1		0.01	0.16
301-2	NI	0.03	0.03	401-2	NI	0.01	0.09
301-3		0.08	0.12	401-3		0.00	0.09
301-4		0.00	0.01	401-4		0.01	0.01
302-1		0.04	0.06	402-1		0.00	0.00
302-2		0.04	0.12	402-2		0.00	0.00
302-3	NI	0.04	0.12	402-3	NI	0.00	0.00
302-4		0.00	0.10	402-4		0.00	0.00
303-1		0.02	0.10	403-1		0.02	0.01
303-2	NI	0.02	0.08	402-2	NI	0.03	0.12
303-3		0.16	0.12	403-3		0.03	0.12
303-4		0.00	0.10	403-4		0.00	0.07
304-1		0.00	0.12	404-1		0.00	0.08
304-2		0.01	0.12	404-2		0.04	0.12
304-3	NI	0.01	0.00	404-3	NI	0.04	0.13
304-4		0.00	0.00	404-4		0.00	0.07
305-1		0.01	0.01	405-1		0.00	0.08
305-2	NI	0.01	0.10	405-2	NI	0.05	0.12
305-3		0.00	0.10	405-3		0.07	0.05
305-4		0.00	0.00	405-4		0.00	0.05

MTZ = metribuzin
METOLA = metolachlor
NI = non identified

APPENDIX B

CALCULATED MEAN AND STANDARD DEVIATION FROM CHROMATOGRAPHIC DATA

Table B1. Mean concentration of metribuzin measured at different depths in soil sampled before treatment.

REPLICATION	DEPTH			
	I	II	III	IV
#1	0.005	0.000	0.034	0.028
#2	0.000	0.000	0.018	0.028
#3	0.000	0.000	0.010	0.018
#4	0.000	0.006	0.023	0.040
MEAN	0.001	0.002	0.031	0.029
STD.DEV.	0.003	0.003	0.023	0.009

Table B2. Mean concentration of metolachlor measured at different depths in soil sampled before treatment.

REPLICATION	DEPTH			
	I	II	III	IV
#1	0.054	0.088	0.132	0.070
#2	0.072	0.088	0.220	0.094
#3	0.040	0.076	0.160	0.064
#4	0.000	0.128	0.156	0.064
MEAN	0.042	0.095	0.167	0.073
STD.DEV.	0.031	0.023	0.037	0.014

Table B3. Mean concentration of metribuzin measured at different depths in soil sampled 25 days after treatment.

REPLICATION	DEPTH I	II	III	IV
#1	0.002	0.016	0.046	0.000
#2	0.008	0.014	0.046	0.004
#3	0.002	0.016	0.018	0.000
#4	0.008	0.026	0.070	0.026
MEAN	0.005	0.018	0.045	0.008
STD.DEV.	0.004	0.005	0.021	0.120

Table B4. Mean concentration of metolachlor measured at different depths in soil sampled 25 days after treatment (series 892).

REPLICATION	DEPTH I	II	III	IV
#1	0.124	0.184	0.265	0.074
#2	0.182	0.164	0.340	0.126
#3	0.124	0.208	0.220	0.068
#4	0.100	0.216	0.194	0.068
MEAN	0.133	0.193	0.255	0.084
STD.DEV.	0.035	0.024	0.064	0.028

Table B5. Mean concentration of metribuzin measured at different depths in soil sampled 86 days after treatment (series 893).

REPLICATION	DEPTH I	II	III	IV
#1	0.010	0.012	0.074	0.020
#2	0.004	0.008	0.026	0.020
#3	0.008	0.022	0.034	0.008
#4	0.004	0.016	0.026	0.000
MEAN	0.007	0.015	0.040	0.012
STD.DEV.	0.003	0.006	0.023	0.009

Table B6. Mean concentration of metolachlor measured at different depths in soil sampled 86 days after treatment (series 893).

REPLICATION	DEPTH I	II	III	IV
#1	0.738	0.854	0.370	0.784
#2	0.683	0.704	0.308	0.280
#3	0.514	0.224	0.218	0.100
#4	0.128	0.220	0.293	0.076
MEAN	0.516	0.501	0.297	0.310
STD.DEV.	0.276	0.327	0.062	0.329

Table B7. Mean concentration of metribuzin measured at different depths in soil sampled 153 days after treatment (series 89F).

REPLICATION	DEPTH I	II	III	IV
#1	0.007	0.022	0.028	0.002
#2	0.066	0.022	0.058	0.000
#3	0.010	0.018	0.028	0.000
#4	0.088	0.004	0.080	0.000
MEAN	0.043	0.017	0.049	0.000
STD.DEV.	0.041	0.008	0.025	0.001

Table B8. Mean concentration of metolachlor measured at different depths in soil sampled 153 days after treatment (series 89F).

REPLICATION	DEPTH I	II	III	IV
#1	0.083	0.113	0.128	0.033
#2	0.064	0.090	0.308	0.036
#3	0.088	0.110	0.132	0.052
#4	0.094	0.112	0.120	0.060
MEAN	0.082	0.106	0.172	0.045
STD.DEV.	0.013	0.011	0.090	0.013

Table B9. Metribuzin concentration in soil at different sampling period at four soil depths.

SAMPLING SERERIES	DEPTH I	II	III	IV
24 DBT	0.001	0.002	0.031	0.029
25 DAT	0.005	0.018	0.045	0.008
87 DAT	0.007	0.015	0.040	0.012
157 DAT	0.043	0.017	0.049	0.000
MEAN	0.018	0.017	0.045	0.007
STD.DEV.	0.021	0.001	0.005	0.006

Table B10. Metolachlor concentration in soil at different sampling period at four soil depths.

SAMPLING PERIOD	DEPTH I	II	III	IV
24 DBT	0.042	0.095	0.167	0.073
25 DAT	0.133	0.193	0.255	0.084
87 DAT	0.516	0.501	0.297	0.310
157 DAT	0.082	0.106	0.172	0.045
MEAN	0.244	0.266	0.241	0.146
STD.DEV.	0.237	0.208	0.064	0.143

APPENDIX C

PLOTS OF THE RESULTS

Figure C1. Mean concentration of metribuzin in different soil layers. Mean with the same letter at the same sampling period are not significantly different at the 0.05 significance level according to Duncans's Multiple Range test.

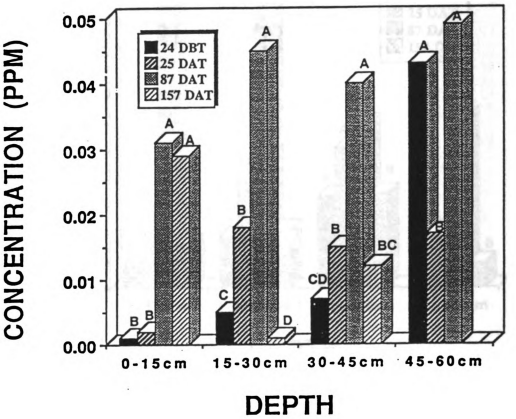


Figure C2. Mean concentration of metolachlor in different soil layers. Mean with the same letter at the same sampling period are not significantly different at the 0.05 significance level according to Duncans's Multiple Range test.

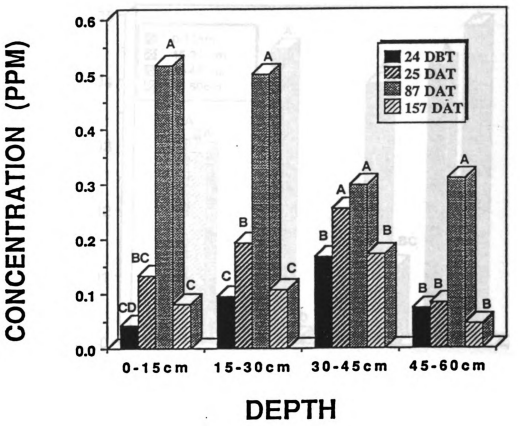


Figure C3. Mean concentration of metribuzin in different layers for each sampling period. Mean with the same letter at the same DAT are not significantly different at the 0.05 significance level according to Duncans's Multiple Range test.

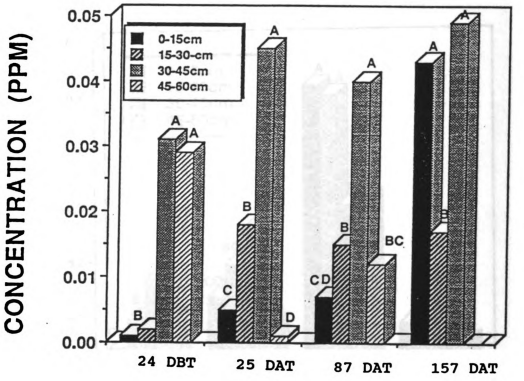


Figure C4. Mean concentration of metolachlor in different layers for each sampling period. Mean with the same letter at the same DAT are not significantly different at the 0.05 significance level according to Duncans's Multiple Range test.

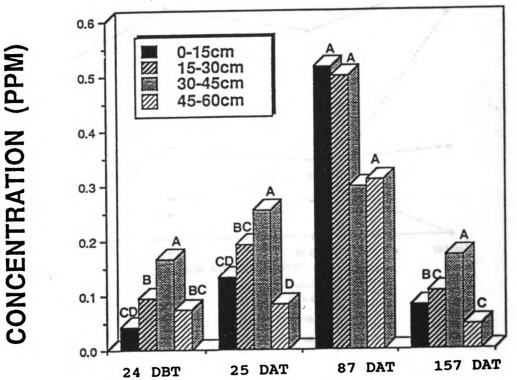


Figure C5. Metribuzin concentration found in soil samples

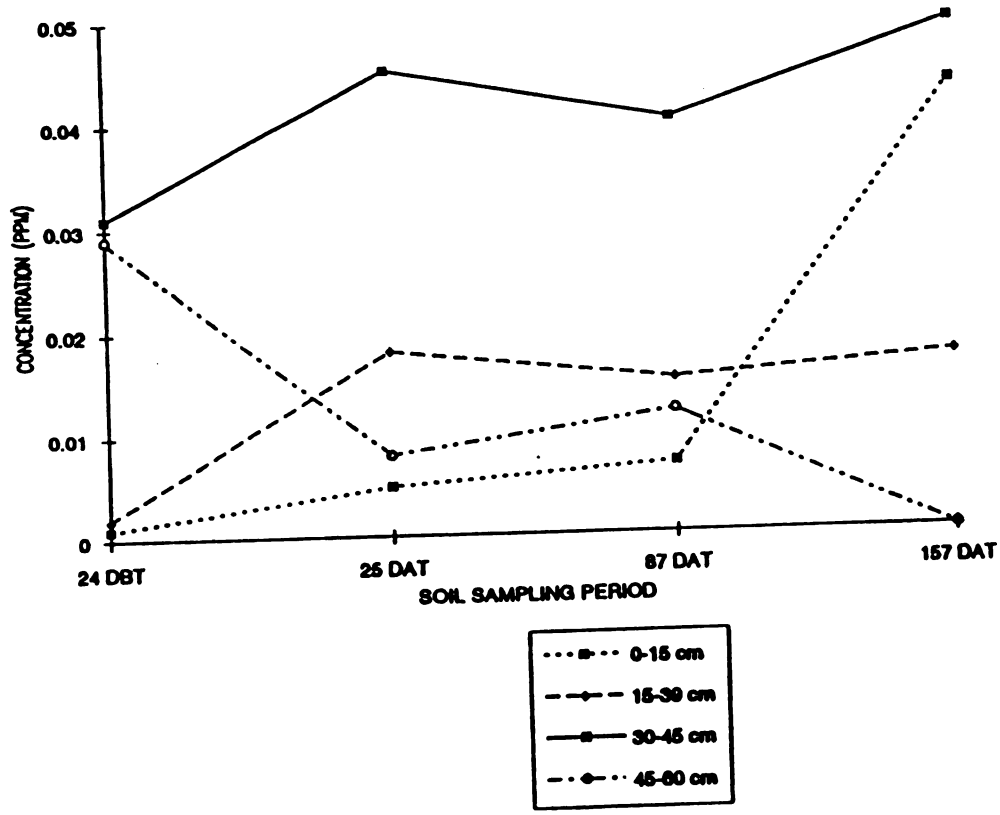
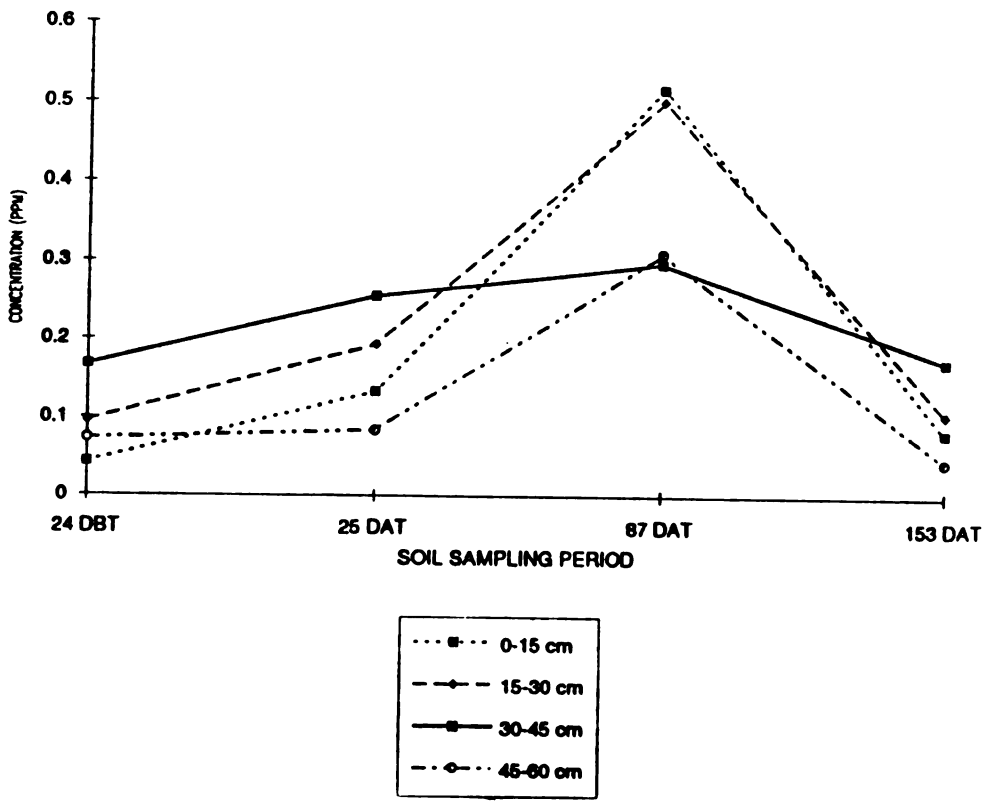
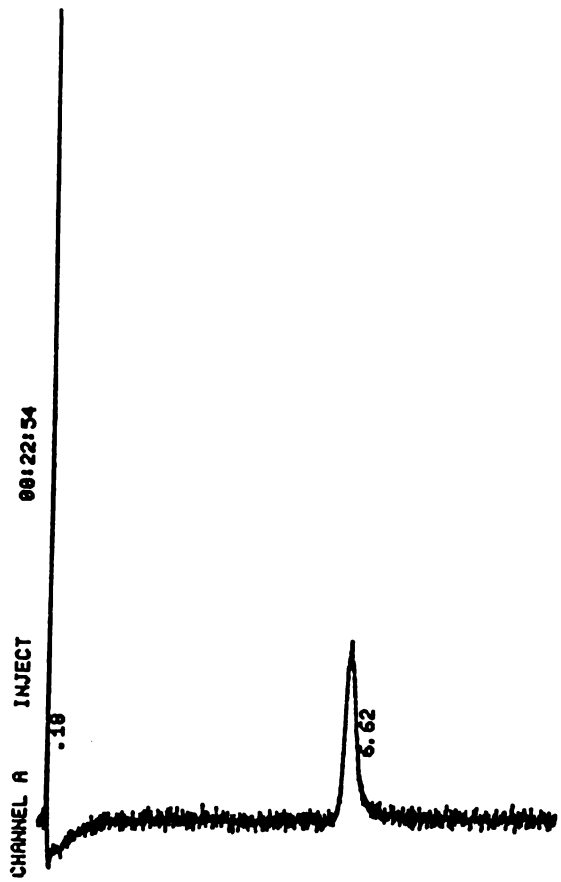


Figure C6. Metolachlor concentration found in soil samples



APPENDIX D

CHROMATOGRAMS OF THE ANALYSES

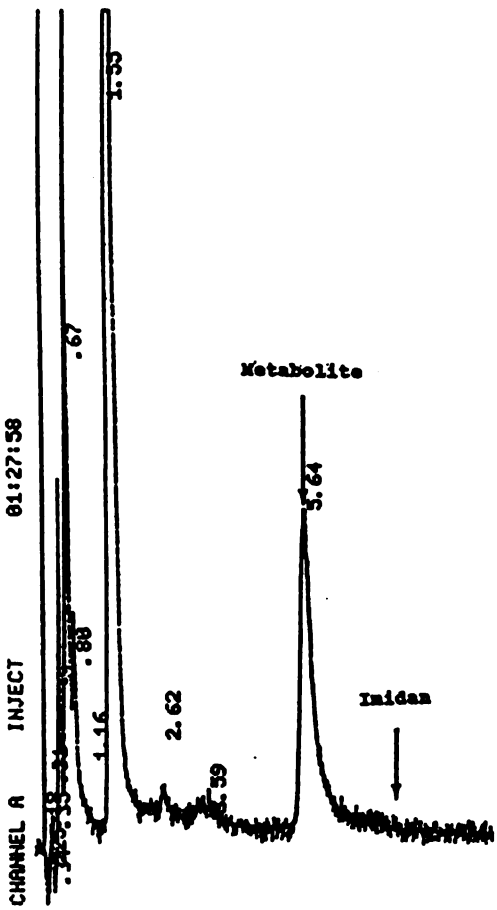


00:22:54

FILE 0. METHOD 0. RUN 2 INDEX 2

PEAK#	AREA%	RT	AREA	BC
1	58.057	0.18	52184	01
2	41.943	6.62	37700	01
TOTAL	100.		89884	

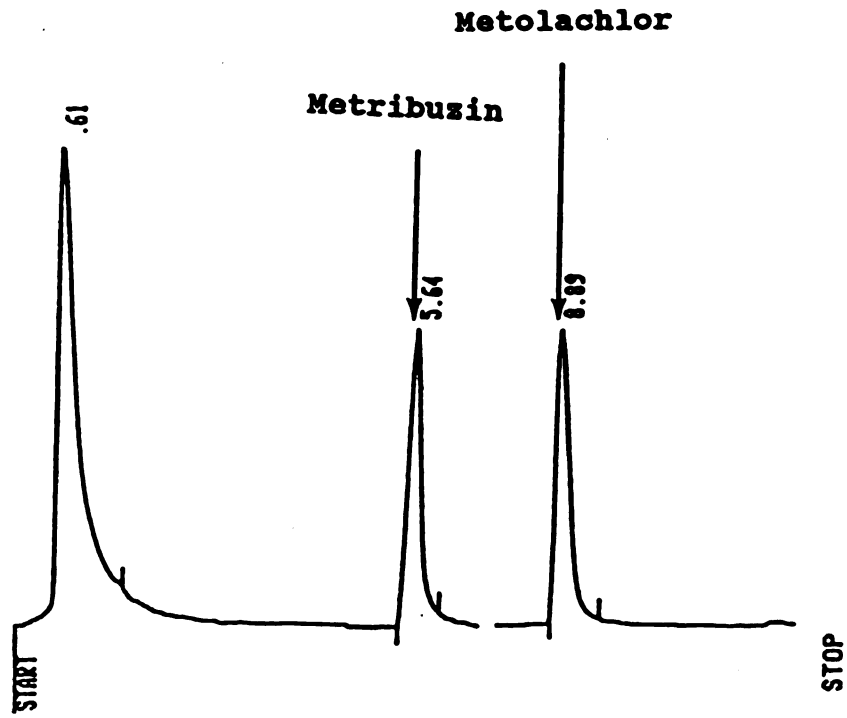
Figure D1. Chromatogram of 0.4 ppm standard solution of imidan (FPD, S mode).



01:27:58

FILE 0.	METHOD 0.	RUN 02	INDEX 02
PEAK#	AREAX	RT	AREA BC
1	5.59	0.18	34543 01
2	0.079	0.25	491 02
3	0.45	0.31	2780 02
4	0.132	0.34	815 02
5	0.171	0.35	1059 02
6	4.488	0.51	27733 02
7	12.301	0.67	76015 02
8	6.268	0.8	38733 02
9	1.773	1.16	10959 02
10	51.515	1.55	318329 03
11	0.198	2.62	1221 01
12	0.058	3.59	359 01
13	16.976	5.64	104903 01

Figure D2. Chromatogram of soil extract (FPD, S mode).

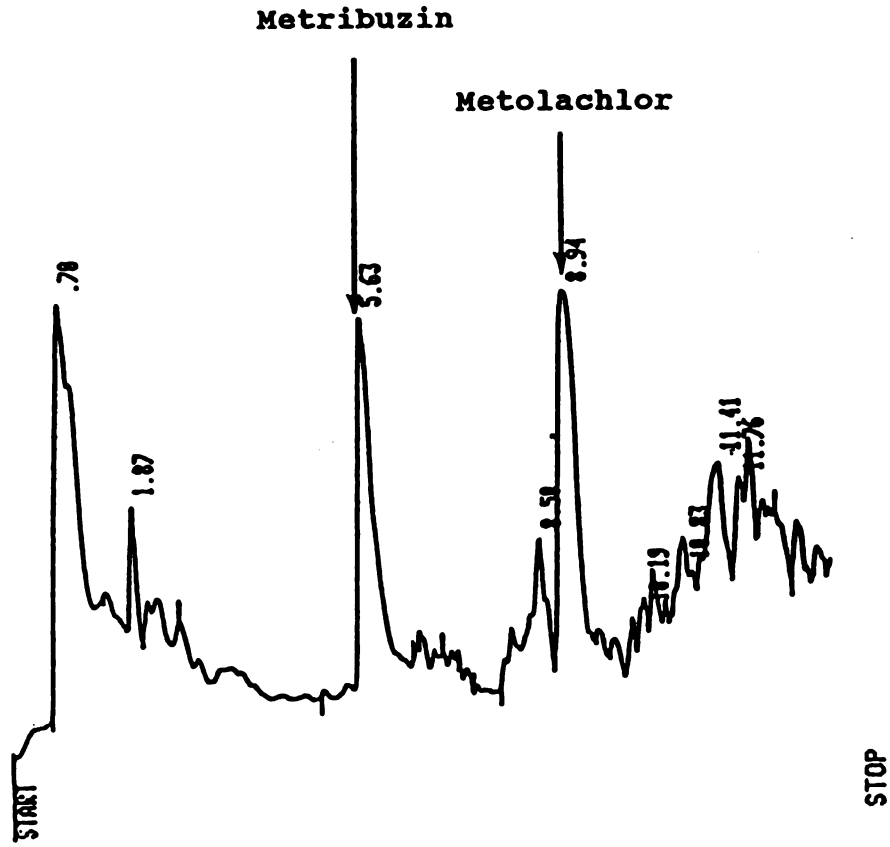


RUN # 17

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.61	558729	BB	0.321	25.939
5.64	242270	PB	0.225	18.064
8.89	277600	PB	0.260	20.367

Figure D3. Chromatogram of mixed Standard solution of metribuzin and metolachlor (ECD)



RUN # 48

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.70	571870	PV	0.387	29.474
1.87	51120	PP	0.111	2.635
5.63	352290	PB	0.264	18.157
8.58	156048	VV	0.287	8.042
8.94	507770	VV	0.348	26.170
10.19	49078	PV	0.220	2.530
10.83	71588	VV	0.245	3.689
11.41	140730	VP	0.317	7.253
11.76	39776	PV	0.130	2.050

TOTAL AREA= 1940200
MUL FACTOR= 1.0000E+00

Figure D4. Chromatogram of soil extract (ECD)

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