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& Entomology

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INVESTIGATIONS INTO THE FATE OF SELECTED PESTICIDES IN AN EXPERIMENTAL SOIL-FILLED WASTE DISPOSAL FACILITY

BY

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ABSTRACT

INVESTIGATIONS INTO THE FATE OF SELECTED PESTICIDES IN AN EXPERIMENTAL SOIL-FILLED WASTE DISPOSAL FACILITY

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An experimental pesticides waste disposal facility at Michigan State University located in Fennvill, Michigan was used as a demonstration compartment for the study of the fate of the pesticides. The facility consisted of two inground compartments filled with muck soil (45.2% organic matter and pH 4.5). The inground compartments constructed with a concrete bottom liner and concrete walls. The parent pesticides, their major degradation products and the potential evaporation loss of the parent were monitored every week from June to October over a two-year period, 1990-1991. Three soil samples were taken from each compartment each week. Air samples were collected every week from above the compartments at two different heights 15 and 200 cm. Four pesticides have been selected for this study. endosulfan I and II (Thiodan), chlorpyrifos (Dursban), alachlor (Lasso), and simazine (Princep). HPLC and capillary GLC with electron capture (ECD) and nitrogen-phosphorus (NPD) detectors, were used to identify and quantify the pesticide residues and their degradation products.

Volatilization loss was the dominant dissipation route for all four of the pesticides in the soil. The average potential dissipation of the selected

pesticides were used in the study in 1990 and 1991 were 66.9 % and 67.3 % respectively for endosulfan I + II, 69.9 % and 81.5 % for chlorpyrifos, 84.7 % and 84.2 % for alachlor and 87.1 and 90.0 % for simazine. The pesticides waste disposal facility at Michigan State University was a good method for the dissipation of all four of the pesticides that were studied.

DEDICATION

TO THE MEMORY OF MY FATHER

ACKNOWLEDGEMENT

I would like to express my sincere appreciation to my major professor , Dr. Matthew zabik for his encouragement, guidance, support, friendship, patience and all he has done for me throughout the course of this investigation. He really has earned my highest level of respect and admiration.

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INTRODUCTION AND LITERATURE REVIEW

INTRODUCTION

Widespread use of pesticides has greatly benefited agriculture, but has also led to many problems. One of these problems is the effect of pesticides on the environment including environmental contamination by improper disposal of dilute pesticide wastes.

Handling and disposal of agrichemical wastes represents a potentially serious problem in Michigan and worldwide. Large volumes of dilute pesticide wastes result from livestock dipping operations, over estimating the amount needed for a spray operation, and cleaning and rinsing equipment. For such operations, safe facilities and procedures are essential to degrade the pesticides in proper way in the environment and protect human health and the environment. Degradation facilities must be developed which are simple to use, reliable and inexpensive.

Degradation is the most widespread phenomenon contributing to the disappearance of pesticides from soils. There the soil is an ideal medium for inducing transformation reactions of pesticides. Usually moist and aerated upper layer of soils provides the proper conditions for chemical changes, (mainly hydrolysis, oxidation reactions) responsible for biodegradation occurring in the soil solution. Under anaerobic conditions, such as those specific to flooded soils, reductive reactions prevail. Possessing a large and active surface area, soil colloids may induce surface-catalyzed degradation reactions of

adsorbed pesticides. At the same time, adsorption of pesticides to the soil particles strongly affects the availability of pesticides for transformation reactions. Sorption and desorption of a chemical by soil particles in soil-water system influence transport and transformation of the chemical in the environment (Bouchard 1989).

Soil is a complex and highly variable mixture of components containing many types of living organisms, i.e., bacteria, fungi, invertebrate and vertebrate animals. The soil microorganisms are most important because these metabolize or attenuate pesticide wastes. Under proper environmental conditions and with sufficient time, microbial degradation can play an important role in reducing pesticide concentrations in soil by degrading these compounds into simple compounds (Bingham 1973). Aromatic compounds are more resistant to biodegradation than aliphatic compounds. Compounds which have carbon in the skeletal chain or ring make the structure more susceptible to degradation (Atkins 1972). Halogens on an aromatic ring increase resistance to biodegradation, however, amino and hydroxy substitutions tend to increase biodegradability (Bingham 1973).

The most important soil characteristic related to pesticide degradation is rich microbial population capable of attacking a wide variety of chemical compounds. However, studies of pesticide degradation, carried out in the late 1960s, mainly with organophosphate and s-triazine, showed that in addition to microbiological processes, nonbiological processes such as the chemical and

physical properties of the soil plays an important role in the degradation of pesticides.

Oxidation and hydrolysis may degrade a pesticide into smaller components, or remove various functional groups. Hydrolysis occurs faster when pesticides are absorbed onto clay or silt particles (Baker 1972). Alkaline pH can also significantly influence degradation. Malathion was demonstrated to have hydrolysis half-lives at pH 7 and pH 9 of one month and ten hours, respectively (Paris 1975). Alkaline hydrolysis is not effective with every pesticide but has been shown to work with organophosphate, carbamate, imide and hydrazide (Ferguson 1975). Volatilization is an additional mechanism for pesticides transport from treated agricultural lands in the vapor phase into the atmosphere. Potential volatility of pesticides is related to their inherent vapor pressure, but the actual vaporization rates depend on the environmental conditions and other factors that control behavior of the chemical at the solid-air-water interface. Volatilization and air transport is a major pathway of pesticide movement. Some are transported long distances in the atmosphere and return to the soil and water surfaces contributing to widespread non-point environmental contamination. Moisture may become the critical factor in the control of volatilization (Glotfelty et al. 1984). The potential for pesticide volatilization is related to pesticide vapor pressure, but actual volatilization rate is dependent upon the environmental factors that modify or attenuate the effective vapor pressure of the pesticide. The two primary environmental

factors affecting volatilization from the soil surface are temperature, which influences the vapor pressure, and air movement (Nash 1983). It has only been recognized within the last decade that volatilization losses can contribute substantially to the removal of organic chemicals from soil. (Glotfelty et al. 1984). Trifluralin vapor pressure increases approximately five times for each 10-degree increase in temperature between 20 °C and 40 °C (Spencer 1974).

PHOTODECOMPOSITION OF PESTICIDES

Photochemical reactions may occur when a pesticide absorbs light energy of a particular wavelengths (Zabik 1983). In some cases, the energy involved is dissipated by the breaking of chemical bonds in the molecule. Photochemical reactions of pesticides are chemical processes that begin when radiation interacts with the pesticide molecule. The overall photochemical reaction can be divided into two parts: primary processes and secondary reactions. The primary photochemical processes involve a series of events that start with the absorption of a quantum of radiation by a molecule and ends with the disappearance of that molecule or its conversion back to its initial ground state or to different excited states. The secondary reactions are those nonphotochemical processes that lead to chemical products. The photochemical reaction of any pesticide involves two operations: (1) absorption of energy leading to excited states, and (2) the transformation of the various electronically excited states to chemical products. Light absorption by molecules involves transitions of electrons from one orbit to another, together with changes in the

rate of rotation and vibration of atoms within the molecules. Rotational changes rarely result in photochemical reactions in complex molecules.

The excitation of an electron, bonded or nonbonded, to an excited state requires that the exited electron arrives spinning in the same direction as it did in the ground state. The resulting excited state with retained electron-spin configuration is called an excited singlet state back to the singlet ground state is called fluorescence and occurs in approximately 10^{-7}s or less. Transition of the excited singlet state to the excited triplet state occurs by reversal of the spin of the electron that was excited. This process is called inter-system cross triplet excited state is always of lower energy than the excited singlet state and the direct transition from the singlet ground state to the excited triplet state which is also forbidden (of low probability). Consequently, the triplet state lives longer than the singlet state. This longer life allows most molecules in the triplet state to react before transition to the ground state occurs. Emission from the excited triplet state called phosphorescence and generally requires 10^{-4}s or longer.

A photochemical reaction can also be initiated through sensitization. In sensitized photochemical reaction a donor molecule absorbs the radiation and becomes electronically excited. This excited donor molecule, through energy transfer processes, imparts its energy to an acceptor molecule (i.e. pesticide) which then reacts chemically. Generally the donor molecule is excited to its triplet state. In order for triplet triplet energy transfer to occur, the triplet

excited state of the sensitizes (donor) must be energetically above the triplet excited state of the acceptor (pesticide).

$$D \xrightarrow{h\nu} D*$$

$$D^{*}+A \rightarrow A^{*}+D$$

$$A^{*} = products$$

Chemical products can, therefore, be produced from the excited singlet state and/or the excited triplet state. The products produced via the singlet may or may not be the same a those produced via the triplet.

$$S \xrightarrow{h\nu} S_1 \rightarrow products$$

$$T_1 \rightarrow products$$

The failure of a pesticide to react photochemically may be due to its inability to absorb the given wavelengths of light it is exposed to, or on absorption of light the excited states formed dissipate their energy through fluorescence, phosphorescence and/or other collisional processes. PCBs (polychlorobiphenyls) are thermally and biologically non-degradable. Photochemical degradation is shown to be a major, if not the only, degradation pathway since solar radiation of the wavelength required is present (Zabik

1983). PCP (pentachlorophenol), was found to decompose readily in sunlight whether in ionized form (Munakata and Kuwahara 1969) or not (Hamad, 1967). Methoxychlor in aqueous alcohol was converted to dimethoxybenzophenon, p-methoxyphenol and anisic acid (Fernandez, 1966).

ENVIRONMENTAL DYNAMICS OF PESTICIDES

Environmental dynamics of pesticides includes all processes that occur from the times of application into the environment until their degradation products or parent compound reach some steady state. The environmental dynamics includes irreversible binding to soil particles, mineralization or incorporation into biological material. This phenomena may be divided into three groups: distribution, movement, and attenuation. Distribution determines how pesticides or their degradation products can move from their original location to new locations by wind, erosion, volatilization from soil, plant, aqueous surfaces, and diffusion and/or mass flow in the soil air. Pesticides movement can occur with or in the soil water, leaching down and through the soil or back to the soil surface with evaporation. Water runoff and soil erosion can carry pesticides over land, either in solution, adsorbed on sediment, or in the crystalline state. Pesticide attenuation refers to all the processes that tend to reduced the amount of free pesticide and residue in the environment. These processes include: chemical, photochemical and biological degradation, irreversible soil adsorption, and plant and other organisms uptake. Volatilization may be considered an attenuation mechanism when a pesticide is dissipated by

this route.

BEHAVIOR OF PESTICIDES IN THE ENVIRONMENT

Behavior of pesticides in the environment is influenced by many factors: (1)- physical and chemical properties of pesticides which include chemical structural and configuration, molecular size, water solubility, lipophlicity, polarity, acidity or basicity, and vapor pressure. (2)- soil characteristics, which effect pesticides behavior include: soil type (percent silt, clay, organic matter, oxides, hydroxides) clay type, pH, soil structure (pore size, bulk density), cation exchange capacity and microbial population. (3)- environmental factors that influence pesticide behavior include: temperature, air movement (speed, direction, turbulence) rainfall (amount, intensity, duration, chronology of events), humidity, solar radiation, topography.

FATE OF PESTICIDES IN SOIL

The fate of pesticides in soil is ultimately connected with such expression as "disappearance" or dissipation and "persistence" or accumulation in the environment. The term disappearance of a pesticide from a certain substrate has been widely used in the past and was, in most cases, synonymous with the difficulty to detect the originally applied compound where it previously had been applied. Disappearance or loss through volatilization means, the parent compound or its metabolites really has not disappeared, but that they have been transported some where else (Lichtenstein 1970). On the other hand, persistence has to be regarded in relation to the area to which the pesticide has

been applied. This persistence depends on different factors: the physical and chemical properties of the pesticide itself, the formulation in which it has been applied and the mode of its application to the soil or other target area.

Overall the most important environmental factors effecting the fate of pesticides are: soil type, soil microorganisms, the presence of other chemicals, temperature, moisture, air movement, cover crops, soil cultivation, plant surfaces, etc. (Lichtenstein and Schultz 1962, 1964). Because these factors differ from place to place, it is impossible to attribute an absolute half life to any pesticide. Dependent on the environmental conditions, pesticides may have a relatively short persistence or may be detectable for a relatively long time.

VOLATILIZATION OF PESTICIDES

Volatility of several pesticides is found to be a function of the vapor pressures and water solubilities of each pesticides. This loss was also dependent on the substrate into which the pesticide had been incorporated. Pesticides bound to soil particles can volatilize, they are considerably more volatile when dissolved in water (Lichtenstein and Schultz 1961). Several researchers have reported higher rates of volatilization of insecticides and herbicides from wet than from dry soils (Bowman et al., 1965, Gray and Weierich1965 and Parochetti and Warren 1966). Increase volatility in wet soils is due to displacement or desorption of the pesticide from the soil surface, resulting in an increased vapor density or partial pressure of the pesticide (Spencer et al., 1969c; 1970b). Soil-water content affects volatilization losses

of organochlorine pesticide simply by competition for adsorption sites (Igue et al., 1970).

EFFECT OF SOIL MICROORGANISMS ON PESTICIDES

Soil microorganisms have a considerable effect on the stability of pesticide in the soil (Lichtenstein and Schultz 1960). The effect of moisture and soil microorganisms on parathion was reported by Lichtenstein and Schultz (1964). Parathion was most persistent in dry soil and least persistent in soil with a high moisture content. The role which soil microorganisms play can be seen by measuring the rate of decomposition in sterilized versus non-sterilized soils (Kanfman et al. 1986). A general review on the subject of microbial effect on pesticide degradation in the soil can be found by Wainwright (1978). In general, factors which effect microbial degradation are soil moisture, temperature, percent organic matter, pH and pesticide concentration.

CHEMICAL DEGRADATION OF PESTICIDES IN SOIL

Hydrolysis, oxidation and isomerization are the three most prevalent reactions in soil. Hydrolysis is faster in the moist soils than dry soils. Oxidation reaction of parathion to paraoxon was reported by Helling et al, (1971). Isomerization of parathion in soil can be demonstrated by conversion of the sulfur thion (=s) to thiol (-s-) as in s-methyl parathion.

PESTICIDE CHARACTERISTICS AND TOXICITY

Chlorinated hydrocarbons are more persistent in the environment than other classes of pesticides. Organophosphate are often more toxic to humans than chlorinated hydrocarbons; however they are deactivated in the environment much more rapidly. Carbamate are similar to organophosphate in their persistence and they are rapidly degraded in the environment. Organophosphate and carbamate toxicities vary widely some are less toxic than DDT while others have four or five times higher toxicity. The toxic action of organophosphate and carbamate pesticides is to deactivate the acetylcholinesterase enzyme. While the organochlorine pesticides can also be classed as neuropoisons. However, their mechanism of action is not the same as that of phosphates and carbamate.

Microbial metabolism, chemical reaction, and photodecomposition are the processes of great significance in degrading chlorinated hydrocarbon pesticides in soil. Strong adsorption to soil constituents limits the availability of these chemicals and their degradation products for more rapid degradation in soil. Although both anaerobic and aerobic degradation of chlorinated hydrocarbons have been observed in the environment, it is generally believed that anaerobic degradation is more rapid (Hill and McCarty, 1967).

Organophosphate pesticides degrade fairly rapidly in soil. The rate of degradation increases with increased soil moisture content, temperature, and acidity (Harris and Lichtenstein, 1961). These factors enhance pesticides loss

by chemical degradation, volatilization, or microbial activity. Carbamate pesticides have a relatively short residual life in soil, and they are readily degraded by non target organisms.

DISPOSAL TECHNOLOGIES

The seriousness of the hazard to human health and the environment resulting from mismanagement of pesticide waste in particular and hazardous wastes in general became increasingly clear. As a part of this general awareness and as the use of pesticides continued to grow resulting in more and more pesticides wastes to be disposed of, the problem of pesticide waste disposal became a point of major concern. There are many disposal systems that might be candidates.

INCINERATION

A "pesticide incinerator" is defined as any installation capable of the controlled combustion of pesticides at a temperature of 1000 ^{o}C for two seconds dwell time in the combustion zone, or lower temperatures and related dwell times that will assure complete conversion of the specific pesticide to inorganic gases and solid ash residues (U. S. EPA 1974). In addition an incinerator must meet the performance standards promulgated under RCEA (40 CFR 264 Subpart 0) if pesticides regulated under RCRA are to be burned. This means an incinerator must be capable of destroying or removing 99.9% of the pesticide put into it.

Incineration of pesticides and/or containers requires special equipment

that is not widely available. Due to the highly specialized nature of an incinerator that can meet the specifications necessary to destroy complex pesticide formulations, plus the energy requirements, the process can be very expensive and not generally the method of choice for small quantities that may be generated by a farmer, for example. On the other hand, it can be a highly effective means of disposing of unwanted material (Ferguson 1975).

OPEN BURNING

Open burning is defined as combustion of a pesticide or pesticide container in any fashion other than incineration (U.S.E.P.A. 1974). Open burning is usually done by the simple act of piling up empty paper bags or plastic jugs and setting them on fire and is commonly used to dispose of combustible empty containers where local regulations permit the practice. It is sometimes prohibited by regional air quality regulations. Where it is permitted, open burning represents an inexpensive and convenient way of disposing of the combustible containers that are commonly used to package pesticides. The practice can present hazards to worker health and to other persons, plants and animals that may be in the vicinity. The impact upon the environment is mainly through dispersal of combustion gases, smoke and fumes into the atmosphere and through contamination of soils and waters by ashes and partially burned containers holding toxic residues.

PHYSICAL/CHEMICAL METHODS

Chemical deactivation/detoxification provides the opportunity to reduce a toxic chemical to a non-toxic state. It is a procedure that is not currently used to any significant degree in common disposal systems even thought there are many pesticides that can be successfully degraded when mixed with an alkali or acid solution or in some cases a specially prepared enzyme. The principal use would be in rinsing containers in situations where the reinstate cannot be added to the mix.

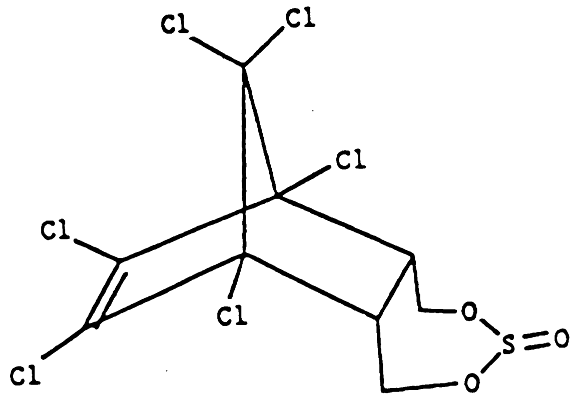
LAND DISPOSAL

Land disposal is the most widely used, least expensive, and most often available disposal system at the present time. The term "land disposal" includes sanitary landfills, surface impoundments, evaporation ponds and land farming. Land disposal in sanitary landfills, permitted to accept wastes can be expected to be the method of choice for the majority of the disposal system. Pesticides waste and other wastes are commonly disposed of in a sanitary landfill or buried at the site of use.

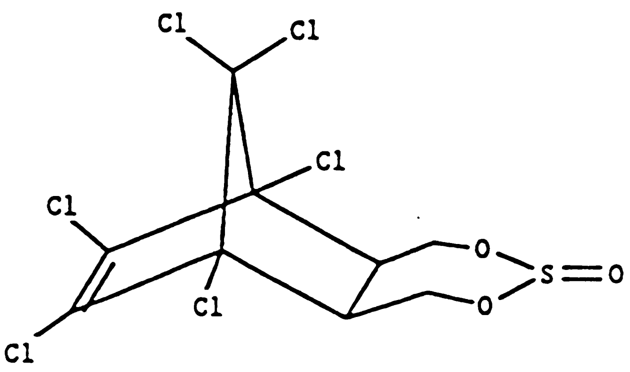
Research was conducted at Iowa State University on a concrete pit pesticides waste facility. The results revealed that the facility was safe from leakage, did not present a hazard of air pollution, and allowed chemical and microbial degradation of the deposited materials (Hall 1984).

CHARACTERISTICS OF THE PESTICIDES USED IN THIS STUDY

ENDOSULFAN (THIODAN)

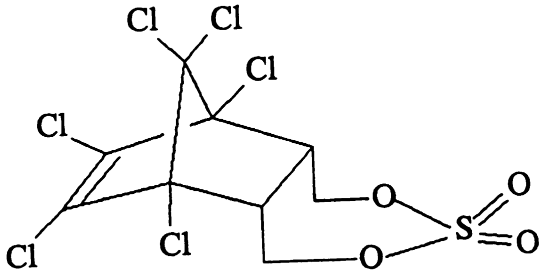


endosulfan I



endosulfan II

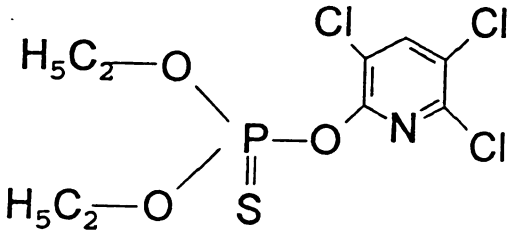
Endosulfan is a mixture of two stereoisomer, alpha-endosulfan, or endosulfan I, with a melting point of 108 to 110 °C, and accounts for 70% of technical endosulfan. Beta-endosulfan, or endosulfan II, with a melting point of 208 to 210 °C, and accounts for 30% of technical endosulfan. Endosulfan is a non-systemic contact and stomach insecticide. It is used for controls of aphids, trips, beetles, foliar feeding larvae, mites, cutworms and bugs. The acute oral LD_{50} for rates of the technical product in oil solution for rates is 80 to 110 mg/kg.



Endosulfan sulfate

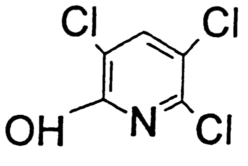
Soil pH has a great effect on the degradation of endosulfan, the higher the pH the higher the degradation rate (Guerin 1992). Endosulfan isomers can be dissipated in simple aqueous systems at neutral pH in the absence of biological material or chemical catalysts (Guerin 1992). In another study, incubations in lake water showed that the half-life of endosulfan I was 35 days at pH 7 and 105 days at pH 5.5 (Greve and Wit, 1971). The major oxidation product of endosulfan I and II, endosulfan sulfate, is less volatile and very stable and can persist longer than either of the parent compounds in the same system (Guerin 1992). Endosulfan sulfate is formed in many natural environments through biological oxidation and is only slowly chemically and/or biologically degraded (Miles and Moy 1978).

CHLORPYRIFOS (DURSBAN)



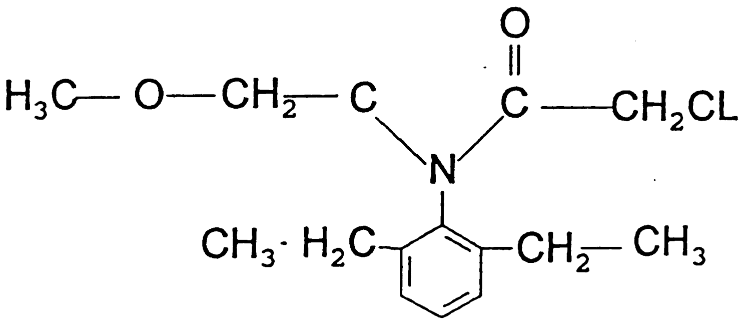
chlorpyrifos (Dursban)

The solubility of chlorpyrifos in water at 35 °C is 2 mg/l. It has a broad range of insecticidal activity and is effective by contact, ingestion and vapor action. It is non-systemically active. It is used for the control of mosquitoes (larvae and adults), flies, various soil and many foliar crop pests and household pests. It is used for ectoparasite control on cattle and sheep. The acute oral LD_{50} for male rats is 163 mg/kg, for female 135 mg/kg. Breakdown in soil is mostly by microbial metabolism. In leaching experiments, most of the chlorpyrifos remain in the upper 2" of soil having organic carbon content above 1 %. The major degradation metabolite of chlorpyrifos is 3,5,6-trichloro-2-pyridinol and used for this study.



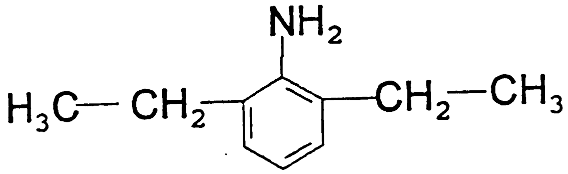
3, 5, 6 - trichloro-2-pyridinol

ALACHLOR (LASSO)



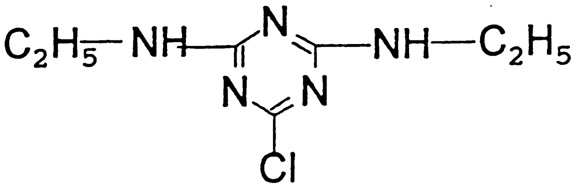
alachlor (Lasso)

groundwater at levels from 0.01 to 16.6 ppb in 3 states. Microbial degradation is the major mode of degradation (Beestman and Deming 1974) r mode below the root zones but slow. Alachlor reaches groundwater in cooler climates of Iowa and Indiana than in the southeast. It controls most annual grasses and certain broadleaf weeds in corn, dry beans, peanuts, soy beans (Farm chemicals handbook 1993). The major metabolites of alachlor is 2,6-diethylaniline and used for this study.



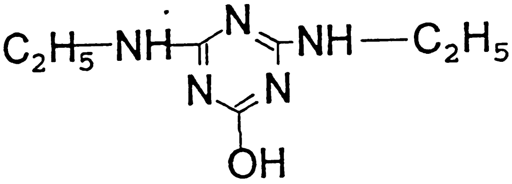
2,6-diethylaniline

SIMAZINE (PRINCEP)



simazine (Princep)

Simazine is a selective herbicide that controls most annual grasses and broadleaf weeds in corn. It is solubility in water 3.5 ppm at 20 °C. Simazine was detected in the groundwater over a half of the states in the United State of America. Some wells were found to contain atrazine and simazine in level above the EPA health advisory limit (Parsonsns and Witt 1989). The major metabolite is 2,6-diethylamine-4-hydroxy-s-triazine and used for this study.



2,6 diethylamine-4-hydroxy-s-triazine

TABLE 1. CHARACTERISTICS OF THE PESTICIDES USED FOR THIS STUDY

Pesticides	Vapor Presser Torr	Water Solubility ppm at 20°C	Log Kow	Henry's Calculated atm-m^3/mole	Molecular Weight
Endosulfan I + II	9.00E -3	0.6	3.8	1.12 E -5	404.88
Chlorpyrifos	1.87E -5	2.0	4.70	4.31E -6	350.58
Alachlor	2.20E -5	2.42	2.64	3.23E -8	269.77
Simazine	6.10E -9	3.50	2.51	4.62E -10	201.66

OBJECTIVE OF THE STUDY

The objective of this study was to determine the fate of selected pesticides in a soil-filled waste disposal facility by the determination of the following :

1- the major metabolic products for each pesticide.

2- the average evaporation loss for each parent pesticide at specified height and average wind speed.

3- the parent pesticides residues remaining in the soil compartments.

4- the percent of the degradation for each pesticide.

A pesticide waste disposal facility located at Michigan State University, Trevor Nichols Research Station, Fennville, Michigan was used for this study. A two-year study of pesticide residues and their major degradation products in the soil tank and evaporation loss of the parent pesticides above the compartments were conducted. This study focused on the fate of the selected pesticides in this waste disposal facility.

More than 20 different pesticides (including pyrethriod, organochlorine, organophosphate, carbamate pesticides, etc.) are used on the farm. Four pesticides were selected from all these pesticides for use in this study. These pesticides were selected because they represent different groups of pesticides family (Table 2). The pesticides residues and their major degradation products

(Table 3) were monitored from June to October over a two-year period 1990-1991 in two soil compartments. The five pesticides were used for the study are:

- endosulfan I and II (Thiodan) as chlorinated hydrocarbon insecticide.
- chlorpyrifos (Dursban) as an organophosphate insecticide.
- alachlor (Lasso) as an acid amide herbicide.
- simazine (Princep) as a triazine herbicide.

TABLE 2. THE PESTICIDES USED IN THE STUDY

COMMON NAME	FAMILY	ACTION
endosulfan I & II (Thiodan)	chlorinated bicycled sulfite	insecticide & acaricide
chlorpyrifos (Dursban)	phosphorothioate	insecticide
alachlor (Lasso)	acid amides (acetanilide)	herbicide
simazine (Princep)	triazine	herbicide

TABLE 3. THE PARENT PESTICIDES AND THEIR METABOLITES

PARENT PESTICIDES	**METABOLITES**
edosulfan (Thiodan) 6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahyro-6-9-methano 2,4,3-benzodioxa-thiepin-3-oxide	***(1) edosulfan sulfate** (2) endosulfan ether (3) endosulfandiol
chlorpyrifos (Dursban) o,o-diethyl o-(3,5,6-trichloro-2-pyridyl) phosphorothioate	***(1) 3,5,6-trichloro-2-pyridinol** (2) chlorpyrifos-oxon
alachlor (Lasso) 2-chloro-2′,6′-diethyl-N-(methoxymethyl) acetanilide	***(1) 2,6-diethylaniline** (2) 2′,6′-diethylacetanilide (3) 2,6-diethyl-N-(methoxymethyl) anailin
simazine (Princep) 2-chloro-4-6-bis (ethylamino)-s-triazine	***(1) 2,6 diethylamine-4-hydroxy-s-triazine** (2) 2,4-diamino-6-chloro-s-triazine (3) 2-amino-4-chloro-6-ethylamino -s-triazine

*** The major metabolites used in the study**

CHAPTER 2

MATERIALS AND METHODS

MATERIALS AND METHODS

MATERIALS

The pesticide waste disposal facility at Michigan State University was utilized as an experimental site for a single inground compartment. The facility had been modified to give a better distribution pattern of the dilute wastes over the entire soil surface.

The pesticide waste disposal facility consisted of two compartments each one filled with muck soil. These two plots (compartments) separate from each other and each one has concrete wall and a concrete liner (Figure 1). Three known inputs of selected pesticides were applied to plots 1 and 2 from June to October in 1990 and 1991. These selected pesticides were monitored for the parent compounds and their major degradation products in each plot. Air samples were collecting from above the two plots at two different heights; 15 and 200 cm.

I- Complete meteorological data were collected at the time of sampling which included measurement of

a) Air temperature.

b) Wind speed.

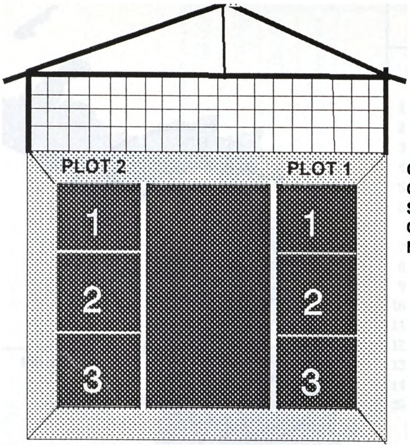
c) Soil temperature.

d) Relative humidity.

e) Rain fall.

In 1990 and 1991 a mixture of the selected pesticides were applied at three separate intervals, early, mid and late summer (June 7, July 13 and August 30 of 1990 and June 14, August 10th and September 17 of the 1991)

The following amounts of the formulated pesticides were used for the application. 1) 454 g of 80 WP wettable powder simazine (Princep), has 80% active ingredient of simazine (363.2 g), 2) 375 g of 50 WP wettable powder chlorpyrifos (Dursban), has 50% active ingredient of dursban (187.5 g), 3) 227 g of 50 WP wettable powder endosulfan (Thiodan), has 50% active ingredient of endosulfan (113.5 g), 4) 300 g (emulsifiable herbicide) of alachlor (Lasso), has 45.1% of alachlor (135.3 g) were added to 1900 L (500 gallons) of water and mixed well. A volume of 760 L (200 gallons) of the solution of the pesticides were applied to each plot (plot 1 and plot 2). Weight of the pesticides in each plot is shown in (Table 4).



Organic matter	45.2%
Organic carbon	26.2%
Soil pH	4.5
CEC	71.7meq/100 g
Muck soil	

Figure 1. Digram of the top view of the pesticide waste facilitity at Michigan State University

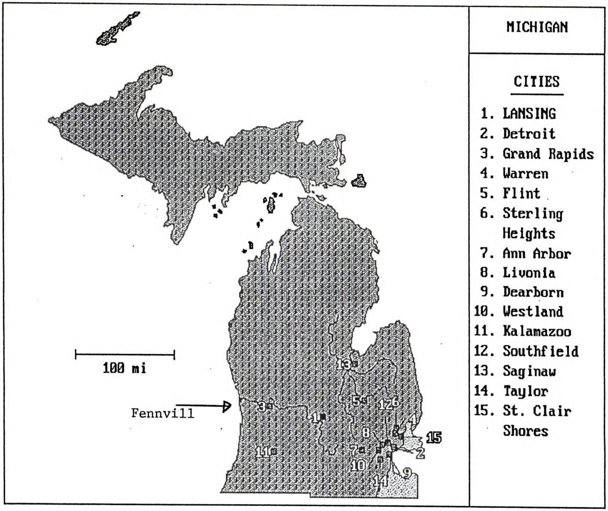


Figure 1A. The location of the waste disposal facility used for the study

TABLE 4. WEIGHT OF PESTICIDES USED FOR THE STUDY

PESTICIDES	Weight of pesticides in plot 1	Weight of pesticides in plot 2	Total weight of pesticides applied in plots 1 & 2 in 1990 & 1991
Endosulfan I + II	45.2 X 3 = 135.6 g	45 .2 X 3 = 135.6 g	135.6 X 2 X 2 = 542.4 g
Chlorpyrifos	75 X 3 = 225 g	75 X 3 = 225 g	225 X 2 X 2 = 900 g
Alachlor	54.1 X 3 = 162.4 g	54.1 X 3 = 162.4 g	162.4 X 2 X 2 = 649 g
Simazine	145.3 X 3 = 435.9.g	145.3 X 3 = 435.9 g	145.3 X 2 X 2 = 1743.6 g

A. SAMPLES

1. Soil Samples

The pesticide waste disposal facility consisted of two plots. Each plot was divided into three sections. Soil sample from each section was collected using a stainless steel cylinder 40 cm long X 4.1 cm id. Each core soil sample weighed about 100-200 g was collected through the total depth 80 cm of the soil bed. Three soil samples were collected from each plot (plot 1 and plot 2) each week. The day 0 soil samples were taken within 24 hr after the completion of the application process. Each soil sample was mixed thoroughly and a subsample was taken for analysis of the pesticides and their degradation products. The soil in the degradation compartments were monitored for the residue concentrations at weekly intervals for the pesticides and their degradation products.

2. Air Samples

Samples of air were taken from the center of each plot (compartment) at two different heights 15 cm and 200 cm every week for monitoring the parent pesticides. Four air samples were collected each time. Two samples from each plot. The air was monitored for the same pesticides as indicated. The method was employed the use of polyurethane foam plugs (PUF) as described by Glotfelty et al. (1989). Air samples were taken on the day of application and for the next 24 hr and then every week. The air was drawn with an electric vacuum pump equipped with four port manifold. The air-flow rate which was measured by a flowmeter and controlled at 20 L/min. Each sampling cup was connected to a sampling pump via tygon tubing. The air was sampling by 4.5 cm diameter X 5 cm in length plug of porous polyurethane foam (PUF) as the sampling trap. The air-flow rates were measured at the beginning and at the end of each sampling period. Total air volumes were calculated from the flow rate and the duration of the sampling period. The PUF were position in glass cylinders (cups) tapered at one end. The sampling probes were located at two different heights above the soil surface 15 and 200 cm. Exposed plugs were sealed in glass bottles with Teflon-lined caps and stored at -20°C prior to analysis. The pesticides were recovered from the PUF plugs by 6-hr Soxhlet extraction (30-40 cycles) using a 1:1 mixture of hexane and acetone.

B. GLASSWARE PREPARATION

Glassware (round-bottomed flasks, separatory funnels, beakers, funnels and chromatographic columns) were thoroughly washed with detergent and hot water, and then rinsed with distilled water followed by acetone. The glassware were placed in a furnace and heated overnight at 350 °C before use.

C. REAGENT

1. Solvents

Acetone, acetonitrile, petroleum ether, hexane, methanol and ethyl acetate were pesticides grade solvents (HPLC grade) and used as received.

2. Chemicals

- Sodium sulfate (granular, anhydrous) was reagent grade, and shown to be free of interference to an electron capture detector.
- Florisil- PR grade, 60-100 mesh was activated at 135 °C for 48 hr before use.
- Endosulfan I (Thiodan) (99.8%), Endosulfan II (Thiodan) (97.9%), chlorpyrifos (Dursban) (99.7%), alachlor (Lasso) (99.1%) and Simazine (99.6%). All reference chemical standards were obtained from U.S. Environmental Protection Agency (EPA), Pesticides and Industrial Chemicals.

3. Miscellaneous items.

- Glass wool (pyrex)- free of interference to an electron capture detector.
- Whatman extraction thimbles were single thickness free of interference, 33 mm X 94 mm.

D. EQUIPMENT

- Hewlett-Packard gas chromatography (GC) model 5890 series II equipped with dual detectors ^{63}Ni electron capture detector (ECD) and nitrogen-phosphorus detector (NPD).
- Waters model 490 E, High Performance Liquid Chromatography (HPLC)

equipped with a variable wavelength detector (190-700 nm). Waters HPLC pump model 501. - Zymark TurboVap evaporator.

METHODS

A. Air analysis

The PUF plugs were rinsed with distilled, deionized water in a Nalgen pipet washer for six hours followed by soxhlet extraction with 500 ml acetone for six hours and then 500 ml hexane for six hours prior to use (Turner and Glotfelty 1977).

Air samples were taken on the day of application and for 24 hr, and then every week. Air was drawn at about 20 L/min through 4.5 cm diameter X 5 cm in length plug of PUF. The polyurethane foam plug was transferred into an extraction thimble, and subjected to soxhlet extraction. Lindane was used as internal standard by spiking 1 ml of 20 ppm in the PUF. The pesticides were recovered from the PUF plugs by 6-hr Soxhlet extraction (30-40 cycles) using a 1:1 mixture of hexane and acetone. Then the solvent extract was run through 3 g of sodium sulfate anhydrous (400 ^{o}C overnight before used). The solvent extract was then concentrated to 20 ml by a rotary evaporator and transferred into a vial. No clean up was made.

Recovery study

The recovery study was carried out by spiking 2 ml of 1 ppm of the pesticides mixture alachlor, chlorpyrifos, simazine, endosulfan I and endosulfan II to three polyurethane foam plugs. The PUF plugs were left at room temperature until dry. The extraction method described above was followed. The average recoveries ranged between 82% to 96.3%. (Table 5).

TABLE 5. RECOVERY % OF THE SELECTED PESTICIDES

PESTICIDES	Sample I Recovery %	Sample II Recovery %	Sample II Recovery %	AVERAGE Recovery %
Endosulfan I	106	88	95	96.3
Endosulfan II	99.5	85	98	94.2
Chlorpyrifos	93	95	89	92.4
Alachlor	95	97	82	91.3
Simazine	82	79	85	82

Freezer study

The freezer study was carried out by spiking 20 ml of 1 ppm of the pesticides mixture (alachlor chlorpyrifos, simazine, endosulfan I and endosulfan II) to three polyurethane foam plugs (PUF). The PUF plugs were left in the room temperature until dry. The plugs were kept in the freezer at -20 ^{o}C for 6 months. The extraction method described above was followed. The average recoveries ranged between 79% to 90% (Table 6).

TABLE 6 . RECOVERY % OF THE SELECTED PESTICIDES AFTER STORING FOR 6 MONTHS

PESTICIDES	Sample I Recovery %	Sample II Recovery %	Sample III Recovery %	AVERAGE Recovery %
Endosulfan I	90	88	92	90
Endosulfan II	87	86	89	87.3
Chlorpyrifos	85	90	84	86.30
Alachlor	88	78	90.5	85.5
Simazine	75	83	79	79

B. Soil analysis

1. Extraction

Two soil subsamples of 10 g each were taken. One soil subsample was left at the room temperature until dryness and then weighted. The second soil subsample was used for analysis before dryness. The reason for that is to avoid the adsorption of pesticides to the soil particles and the evaporation of pesticides from the soil subsample. The concentration of pesticides was calculated based on the dry soil samples weight taken from the weight of the first soil sample. The soil sample was spiked with lindane as an surrogate standard. The soil sample was transferred into an extraction thimble and subjected to soxhlet extraction for 8 hr. The solvent extraction was 50 ml hexane, 50 ml acetone and 50 ml methanol. Then after extraction 50 ml of deionized water was added to the solvent extraction. The solvent extraction was partitioned with 50 ml of petroleum ether for three times. The extract was then combined. A 2.2 cm i.d. chromatographic column was packed with 10 g of activated Florisil (130 °C overnight before used) and 3 g of anhydrous sodium sulfate on the top of the column. The column was then washed with 50 ml of petroleum ether. The combined extract was run through the Florisil column and collected. Then the column was washed with 50 ml of petroleum ether was run after. The extract was concentrated to 20 ml as a final volume.

Recovery study

The recovery study was carried out by spiking 20 ml of 1 ppm of the pesticides mixture alachlor, chlorpyrifos, simazine, endosulfan I, endosulfan II, endosulfan sulfate, 2,6 diethylamine-4-hydroxy-s-triazine, 3,5,6-trichloro-2-pyridinol and 2,6-diethylanailine to three soil samples weighing 6 g each. The soil samples were left at the room temperature until dry. The analysis method described above was followed. The average recovery ranged between 71% to 97% (table 7).

TABLE 7. RECOVERY % OF THE PARENT PESTICIDES AND THEIR METABOLITES FROM SOIL SAMPLES

CHEMICALS NAMES	Sample I Recovery %	Sample II Recovers %	Sample III Recovers %	AVERAGE Recovery %
Edosulfan I	88	90	95	91
Endosulfan II	85	88	83	85.3
Endosulfan sulfate	90	98	103	97
Chlorpyrifos	88	86	91	88.3
3,5,6-trichloro-2-pyridinol	79	75	72	75.3
Alachlor	92	89	84	88.3
2,6-diethylaniline	89	87	81	86.7
Simazine	79	76	80	78.3
2,6 diethylamine-4-hydroxy-s-triazine	71	69	73	71

Freezer study

The freezer study was followed as the recovery study method. The soil samples were kept in the freezer -20 °C for six months. The analysis method above was followed. The average recovery ranged between 69.3% to 92.3% (Table 8).

TABLE 8. RECOVERY % OF THE PARENT PESTICIDES AND THEIR METABOLITES FROM SOIL AFTER STORED FOR 6 MONTHS

CHEMICALS NAME	Sample I Recovery %	Sample II Recovery %	Sample III Recovery %	AVERAGE Recovery %
Endosulfan I	85	88	83	85.3
Endosulfan II	87	80	79	82
Endosulfan sulfate	95	92	90	92.3
Chlorpyrifos	90	85	83	87
3,5,6-trichloro-2-pridinol	75	79	70	74.7
Alachlor	91	86	81	86
2,6-diethylanaline	88	83	84	85
Simazine	88	77	80	81.7
2,6 diethylamine-4-hydroxy-s-triazine	70	65	73	69.3

Detection of air and soil samples

The pesticides and their degradation products were quantified by using HPLC and capillary GLC with a variety of detectors depends on the chemical structure of the pesticide or the degradation products. A gas chromatograph equipped with ^{63}Ni electron capture detector was used for detection of chlorpyrifos, alachlor, endosulfan I, edosulfan II and endosulfan sulfate. A gas chromatograph equipped with nitrogen phosphorus detector was used for detection of simazine and 2,6 diethylanalyine the breakdown product of alachlor. Peak area were calculated using a Hewlett Packard Chemstation. HPLC was used for detection and quantification of 2,6 diethylamine-4-hydroxy-s-triazine and 3,5,6 trichlorpyridinol the breakdown products of simazine and chlorpyrifos respectively.

Calculation of the pesticides concentrations

Quantitation of the pesticides was based on peak area. A standard curve was constructed for each pesticide from external standard at different concentrations (0.5, 1 and 4 ppm). The amount of each pesticide in the soil and air samples was determined from its standard curve. The following equation was used to calculate the concentration of the pesticide in soil samples ppm (ug/g) or in air samples ug/m^3 .

$$\text{ug/g or ug/m}^3 = \frac{X^* \times Vf}{Ws}$$

Where:-
X = amount of pesticide from a standard curve*.
Vf = the final extract sample volume (ml).
Ws = weight of soil sample (g) or air volume.
* Linear regression was used for quantitation of the amount of the pesticides.

CHROMATOGRAPHIC CONDITIONS

Gas chromatography-ECD

Hewlett-Packard model 5890 series II gas chromatograph was used for analysis. The following conditions were employed for the analysis.

Column : DB-5 fused silica capillary column (60 m X 0.25 mm i.d) with 0.25 micron phase thickness (J & W Scientific).
Oven Temperature : Programmed from an initial
Injector temperature : 220 °C.
Detector temperature : 300 °C.
Carrier gas : Helium at a flow rate of 30 psi.
Make up gas : Nitrogen at flow rate of 20 psi
Integrator :Hewlett-Packard Chemstation was used for collecting the data.

Gas chromatograph-NPD

Hewlett-Packard model 5890 series II gas chromatograph was used for analysis. The following conditions were employed for the analysis.

Column :DB-5 fused silica capillary column (30 m X 0.25 mm i.d.)
Oven temperature :Programmed from an initial of 140 °C to a final 180 °C at a rate of 2 °C/min

Injector temperature :240 ^{o}C

Detector temperature :250 ^{o}C

Carrier gas :Helium at a flow rate of 20 psi

Gas flows :Air at 60 ml/min and hydrogen 30 ml/min.

Integrator :Hewlett-Packard Chemstation was used for collecting data.

HPLC condition

High performance liquid chromatography (HPLC) reverse phase with UV detector was used for the separation and identifying the 2,6 diethylamine-4-hydroxy-s-triazine and 3,5,6 trichloropyridinol the metabolites of simazine and chlorpyrifos. This instrument has a two-solvent system with gradient programming capability and data processor (Maxima). The analyses were performed at the following conditions:-

Column :Cyano column, 22 cm Length X 4.6 mm ID

Mobil phase :Solvent A: ethyl acetate with 10 % methanol

Solvent B: hexane

The solvent gradient starts at 2% A, increases to 10% A in 10 min. Then it drops back to 2% A in 5 min. Finally, the system is stabilized for 5 min at 2% A before the next injection.

Flow rate :1 ml/min

Detector :UV absorbance detector at 310 nm (model 490 E) .

Pump :Waters model 501

PH DETERMINATION

pH was determined by following the method of Smith and Atkinson (1975). Distilled water (50 ml) was added to 20 g of dry soil and thoroughly mixed. pH determination were recorded by using pH meter model PHH-80 (AE Company).

ORGANIC MATTER

Organic matter was determined by the method of Miller and Keeney (1982). A sample of 10 g of soil was taken, then dried in oven (95 °C) for 2 to 3 hours and then the weight was recorded as W_1. The soil sample was placed in an another oven for 24 hr at 420 °C. The sample was taken from the oven and cooled in a desiccator and the weight was recorded as W_2. The percentage organic matter was calculated according to this formula.

$$\% \text{ organic matter} = \frac{W2}{W1} \times 100$$

CATION EXCHANGE CAPACITY (CEC)

The method of Warncke (1988) was followed for the analysis of CEC. A sample of 2 g of soil was weighed and transferred to a 50 ml centrifuge tube. Twenty ml of 1 N neutral ammonium acetate was added and mixed for 15 sec with a Vortex mixer. The sample was allowed to stand for two hours. The sample was mixed and centrifuged for 5 minutes at 2500 rpm. The supernant liquid was decanted. These steps were repeated two more times. Ethyl alcohol (95%) was then added, and mixed for 15 sec. This mixture was centrifuged and the supernant liquid was the decanted. These last two steps were repeated two more times. Five ml of an acidified sodium chloride solution (10% NaCl + 0.3 ml conc. HCL per liter) was added and mixed. The sample was transferred quantitatively to a steam distillation flask using deionized distilled water. Six drops of 10 N NaOH was added just prior to distillation. The steam was distilled into boric acid collecting 30 ml (Blank for distillation = 5 ml NaCl solution + 10 ml distilled water).

$$\text{CEC} = \frac{[\text{ ml (s) - ml (b)}]\ N}{S}$$

Where:

ml (s) = ml acid to titrate sample

ml (b) = ml acid to titrate blank

N = normality of acid

S = sample weight

TABLE 9. CHARACTERISTICS OF THE SOIL USED IN THE WASTE DISPOSAL FACILITY AT MICHIGAN STATE UNIVERSITY

Soil Type	Muck soil
Organic Matter	45.2 %
Organic Carbon	26.2 %
Soil pH	4.5
Cation Exchange Capacity	71.7 meq/100g

CHAPTER 3

RESULTS AND DISCUSSIONS

RESULTS AND DISCUSSIONS

The total weight of the pesticides residues, evaporation losses and the major degradation products for Endosulfan I, Endosulfan II, Chlorpyrifos, Alachlor, and Simazine were monitored weekly from June to October in 1990 and 1991 in two soil degradation compartments. These compartments were soil-filled, concrete-lined and used as an experimental pesticides waste disposal facility. This facility is located at the Michigan State University, Trevor Nichols Research Station in Fennville, Michigan. A known weight of each pesticides was used (Table 4). The formulated pesticides were dissolved in water and applied to the two soil degradation compartments. The application of the pesticides was done three times each year for each compartment (plot) for two years in 1990 and 1991 as multiple inputs each year. The data showed a fluctuation in the concentration of the parent pesticides remaining in the soil each week which may be due to the movement of pesticides upward and downward in the soil column or dissipation of the pesticides. Also the major degradation products showed an increase each week until a steady state was reached after which they started decrease. Weekly analysis of soil samples gave a good picture of the fate of each pesticide in the soil for the preceding time period, as will as at the end of the first and second year. One major metabolite from each pesticide and evaporation loss of each pesticide was determined. Also the pesticides residues remaining in the two soil compartments were determined. The potential average volatilization loss was determined from the average of the two sampling heights and the average of the wind speed for the week calculated from the average daily wind speed. The effect of wind speed on the evaporation loss for all the four pesticides was determined (Figures 3,7,11 and 15). The minimum volatilization loss was calculated from the minimum wind speed which was 1 kph at the average height 107.5 cm (average of 15 cm and 200 cm). The maximum volatilization loss was calculated from the maximum wind speed each day then the average of the week at the average height at 107.5 cm. The effect of wind speed on the potential distribution for each pesticide was determined at the average height in 1990 and 1991 (Figures 4,5,10,11,14,15,18 and 19).

In addition the effect of the height on the evaporation loss was studied for all the four pesticides (Figures 11,13,15 and 17). The air sampling height greatly affected the calculated values for pesticide evaporation losses.

The average mass balance relationship for endosulfan, chlorpyrifos, alachlor and simazine in 1990 and 1991 was calculated (Figures 18 and 19). Also the average potential dissipation of the selected pesticides used in the Fennvill, MI waste disposal facility in 1990 and 1991 was calculated (Table 19).

ENDOSULFAN I + II (THIODAN)

Endosulfan (45.2 g) which contain a mixture of endosulfan I + II was applied to each soil degradation compartment (plot 1 and plot 2) three times a year for two years. A total weight of 135.6 g (0.34 mole) was applied in the first year and 271.1 g total (0.67 mole) for two years in each plot. The percent distribution of endosulfan I + II in 1990 in the soil compartments (plot 1 and plot 2) was determined by calculating the percent of the residues remaining in the soil, the percent of endosulfan sulfate which is the major metabolites of endosulfan I + II, and the percent of average evaporation loss of endosulfan I + II at the average wind speed and average height (Table 10). After the first year in 1990, 30.17 % of endosulfan I + II remained in soil plot 1 and 33.03% in soil plot 2. The percentages for endosulfan sulfate were 2.14 % in soil plot 1 and 1.77 % in soil plot 2. The percentage from average evaporation loss of endosulfan I + II was 70.22 % from plot 1 and 53.58 % from plot 2. After the second year in 1991, 56.11% of endosulfan I + II remained in soil plot 1 and 48.35 % in the soil plot 2. The percentages for endosulfan sulfate were 0.85 % in soil plot 1 and 2.94 % in soil plot 2. The average percent evaporation loss were 92.91 % from plot 1 and 59.36 % from plot 2. The average potential distribution of endosulfan I + II was calculated at the average wind speed and height in 1990 and 1991 (Figure 2).

Using the minimum wind speed (1 kph) assumption, the average evaporation loss from the two plots was 12.27% in 1990 and 12.29% in 1991 at the average height. The effect of wind speed on the evaporation loss of endosulfan I +II is shown in table 10. The evaporation loss was also calculated at the maximum wind speed and the average height. The evaporation loss was higher in the second year than the first year which may be due the higher concentration in the compartment due to the carry over from the first year or due to the different weather conditions such as the wind speed, temperature, or humidity. The effect of height had a large effect on the evaporation loss was a major factor in the calculation of total loss (Table 11). The volatilization loss measured at 15 cm was higher than at 200 cm. For average calculation, a column of air from the soil surface up to 200 cm which was close to the roof of the facility, was taken into consideration. Therefore average evaporation loss at 107.5 cm (average of 15 cm and 200 cm) was employed for the calculations.

For endosulfan I and II loss due to volatilization was the highest route of dissipation from the soil degradation compartments. The high volatilization of endosulfan I + II was due to its low water solubility and relatively high vapor pressure which is indicated by its Henry's law constant (1.12X 10^{-5}). On the other hand, the oxidation product, endosulfan sulfate, showed the lowest route of dissipation which may be due to the pH of the soil (4.5) or the low population of the microorganisms which are responsible for the oxidation of endosulfan. Soil pH has a great effect on the degradation of endosulfan, the heigher the pH the heigher the degradation rate (Guerin 1992).

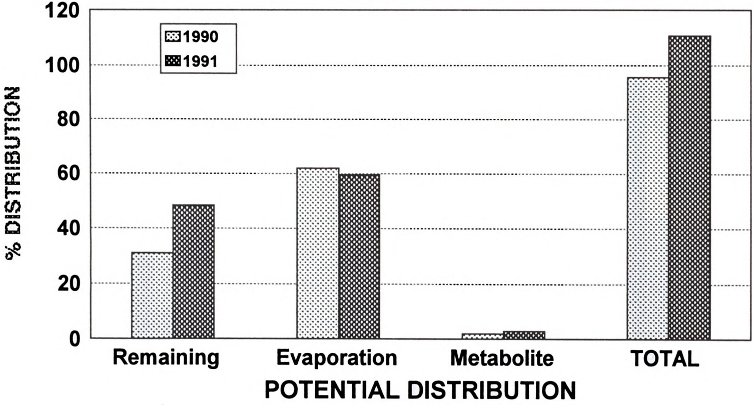
The average mass balance relationship for endosulfan I + II in 1990 was 64.89 % as the average evaporation loss, 2.1 % as endosulfan sulfate and 33.1 % as a remaining of the parent in the soil (Figure 18). Also in 1991 the relationship of the average mass balance was calculated and the average evaporation loss from the two plots was 58.4 %, endosulfan sulfate 1.5 % and the remaining of the parent 40.1 % (Figure 9). Over all the dissipation of endosulfan I + II in 1990 was 66.99 % and 59.9 % in 1991.

Table (10) The effect of the wind speed on the distribution of Endosulfan I + II							
Distribution of Endosulfan I + II at the average wind speed and the average height							
	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	30.17%	33.02%	31.60%	56.11%	48.35%	52.23%	41.91%
Evaporation loss	70.22%	53.58%	61.90%	92.91%	59.36%	76.14%	69.02%
Endosulfan sulfate	2.14%	1.77%	1.96%	0.85%	2.94%	1.90%	1.93%
Total percent	102.53%	88.37%	95.45%	149.87%	110.65%	130.26%	112.86%
Distribution of Endosulfan I + II at the minimum wind speed and the average height							
	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	30.17%	33.02%	31.60%	56.11%	48.35%	52.23%	41.91%
Evaporation loss	13.93%	10.60%	12.27%	19.13%	19%	12.29%	12.28%
Endosulfan sulfate	2.14%	1.77%	1.96%	0.85%	2.94%	1.90%	1.93%
Total percent	46.24%	45.39%	45.82%	76.09%	70.42%	73.26%	59.54%
Distribution of Endosulfan I + II at the maximum wind speed and the average height							
	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	30.17%	33.02%	31.60%	56.11%	48.35%	52.23%	41.91%
Evaporation loss	139.23%	106.12%	122.68%	178.22%	121%	149.57%	136.12%
Endosulfan sulfate	2.14%	1.77%	1.96%	0.85%	2.94%	1.90%	1.93%
Total percent	171.54%	140.91%	156.23%	235.18%	172.20%	203.69%	179.96%

Table (11) The effect of the height and the wind speed on the evaporaton loss of Endosulfan I +

Year 1990	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1+ 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	101.74%	38.70%	70.22%	86.91%	20.25%	53.58%	61.90%
Minimum	20.78%	7.80%	14.29%	18.47%	4.21%	11.34%	12.82%
Maximum	207.83%	78.05%	142.94%	183.54%	42.15%	112.85%	127.89%
Year 1991	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1+ 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	123.64%	60.38%	92.01%	84.00%	34.71%	59.36%	75.68%
Minimum	23.98%	11.76%	17.87%	18.87%	6.51%	12.69%	15.28%
Maximum	280.53%	103.47%	192.00%	165.62%	97.57%	131.60%	161.80%

FIGURE 2. THE AVERAGE POTENTIAL DISTRIBUTION OF ENDOSULFAN I + II AT THE AVERAGE WIND SPEED AND HEIGHT IN THE WASTE DISPOSAL FACILITY IN 1990 AND 1991



Metabolite = Endosulfan sulfate

FIGURE 3. THE EFFECT OF HEIGHT AND WIND SPEED ON THE POTENTIAL EVAPORATION LOSS OF ENDOSULFAN I + II IN 1990 and 1991

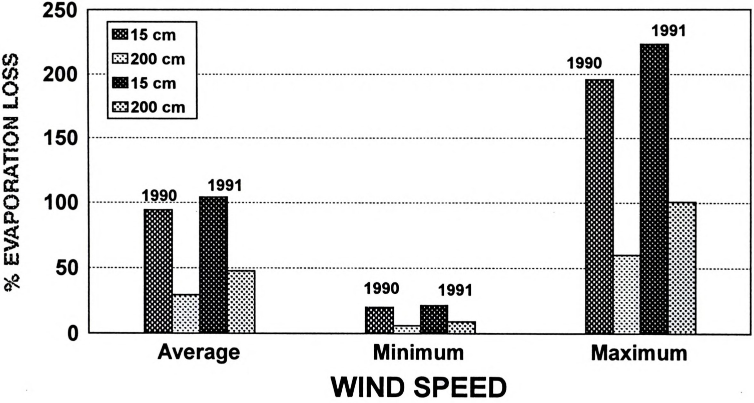
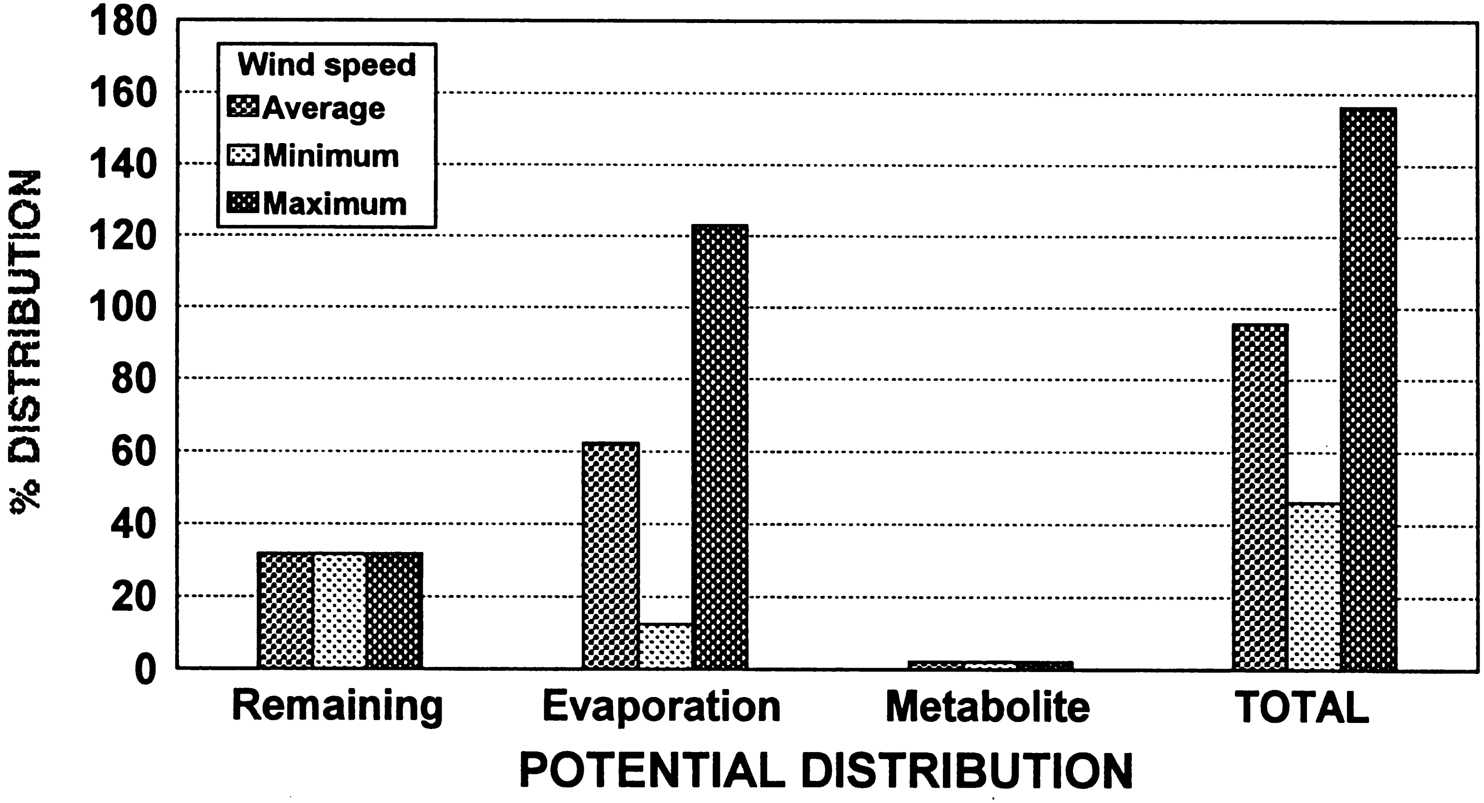
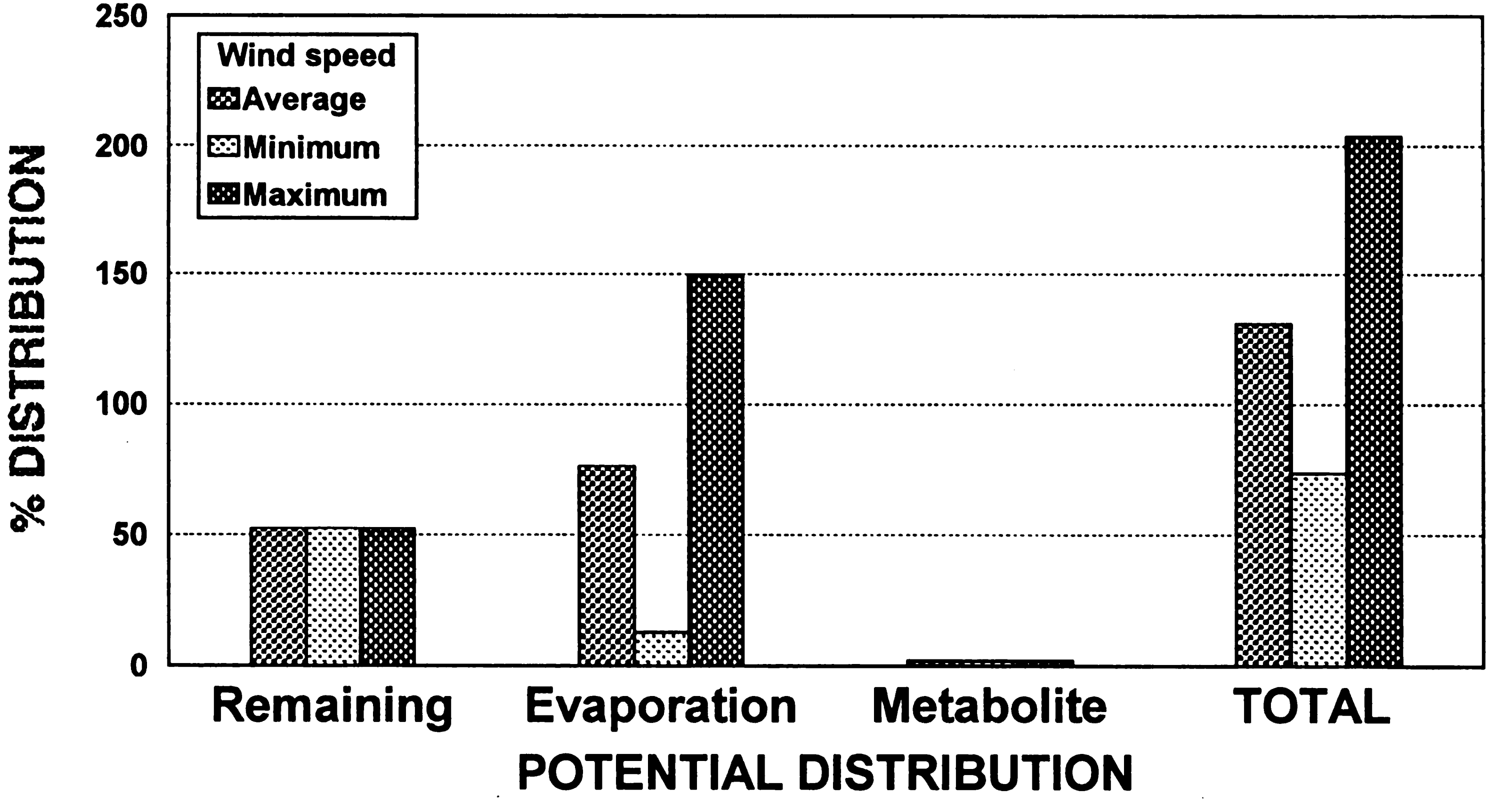


FIGURE 4. THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OF ENDOSULFAN I + II AT THE AVERAGE HEIGHT IN 1990



Metabolite = Endosulfan sulfate

FIGURE 5.THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OF ENDOSULFAN I + II AT THE AVERAGE HEIGHT IN 1991



Metabolite = Endosulfan sulfate

CHLORPYRIFOS (DURSBAN)

Chlorpyrifos (75 g) was applied to each soil degradation compartment (plot 1 and plot 2) three times a year for two years. A total weight of 225 g was applied in the first year and 450 g total for two years in each plot. The percent distribution of chlorpyrifos in 1990 in the soil compartments (plot 1 and plot 2) was determined by calculating the percent of the residues remaining in the soil, the percent of 3,5,6 trichloropyridinol which is the major metabolites of chlorpyrifos, and the percent of average evaporation loss of chlorpyrifos at the average wind speed and average height (Table 12). After the first year in 1990, 21.9 % of chlorpyrifos remained in soil plot 1 and 34.4 % in soil plot 2. The percentages for 3,5,6 trichloropyridinol were 4.7 % in soil plot 1 and 7.8 % in soil plot 2. The percentage from average evaporation loss of chlorpyrifos was 59.2 % from plot 1 and 58.2 % from plot 2. After the second year in 1991, 17.2 % remained in soil plot 1 and 15.6 % in the soil plot 2. The percentages for 3,5,6 trichloropyridinol were 6.3 % in soil plot 1 and 4.7 % in soil plot 2. The average percent evaporation loss were 69.3 % from plot 1 and 57.0 % from plot 2. The average potential distribution of chlorpyrifos was calculated at the average wind speed and height in 1990 and 1991 (Figure 6).

Using the minimum wind speed (1 kph) assumption, the average evaporation loss from the two plots was 13.0 % in 1990 and 13.8 % in 1991 at the average height. The effect of wind speed on the evaporation loss of chlorpyrifos is shown in table 13. The evaporation loss was also calculated at the maximum wind speed and the average height. The evaporation loss was higher in the second year than the first year which may be due the higher concentration in the compartment due to the carry over from the first year or due to the different weather conditions such as the wind speed, temperature, or humidity. The effect of height had a large effect on the evaporation loss was a major factor in the calculation of total loss (Table 13). The volatilization loss measured at 15 cm was higher than at 200 cm. For average calculation, a column of air from the soil surface up to 200 cm which was close to the roof of the facility, was taken into consideration. Therefore average evaporation loss at 107.5 cm (average of 15 cm and 200cm) was employed for the calculations.

The loss due to volatilization of chlorpyrifos was the highest route of dissipation from the soil degradation compartments.The high volatilization loss was due to its high water solubility. Henry's law constant for any pesticide of less than 2.5×10^{-5} is nondimensional Henry's law and therefore evaporation loss control by water evaporation and vapor movement across the laminar layer at the soil/air boundary (Glotfelty et al 1989). Chlorpyrifos Henry's law constant is 4.2×10^{-6} and therefore dose not obey Henery's law . On the other hand the hydrolysis product 3,5,6-trichloropyridinol (TAP) gave the lowest route of dissipation and may be, due to the fact that, the soil pH was low or a low population of microorganisms was present. The pathway of chlorpyrifos degradation in soil involves both chemical and microbial processes. The major products of degradation have been identified as the hydrolysis product 3,5,6-trichloropyridinol (TAP), the secondary metabolite 3,5,6-trichloro-2-methoxypyridine (TCMP) (Racke and Coats 1990) and eventually CO_2 resulting from mineralization of the aromatic ring (Racke and Coats 1988). The rapid hydrolysis of chlorpyrifos in the problem soils may be partially attributed to the high pH of these soils (8.0-8.1) (Racke 1990). Chlorpyrifos is strongly sorbed in soil, especially from solution to the sorbed phase which is much less susceptible to microbial uptake and degradation (Racke and Coats 1990).

Table (12) The effect of the wind speed on the distribution of Chlorpyrifos

Distribution of Chlorpyrifos at the average wind speed and average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	21.88%	34.40%	28.14%	17.19%	15.60%	16.40%	22.27%
Evaporation loss	59.24%	58.16%	58.70%	73.94%	59%	66.66%	62.68%
3,5,,6-trichloropyridinol	4.69%	7.81%	6.25%	6.25%	4.69%	5.47%	5.86%
Total percent	85.81%	100.37%	93.09%	97.38%	79.66%	88.52%	90.81%

Distribution of Chlorpyrifos at the minimum wind speed and average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	21.88%	34.40%	28.14%	17.19%	15.60%	16.40%	22.27%
Evaporation loss	14.53%	11.41%	12.97%	15.88%	11.65%	12.29%	12.63%
3,5,,6-trichloropyridinol	4.69%	7.81%	6.25%	6.25%	4.69%	5.47%	5.86%
Total percent	41.10%	53.62%	47.36%	39.32%	31.94%	35.63%	41.50%

Distribution of Chlorpyrifos at the maximum wind speed and average height

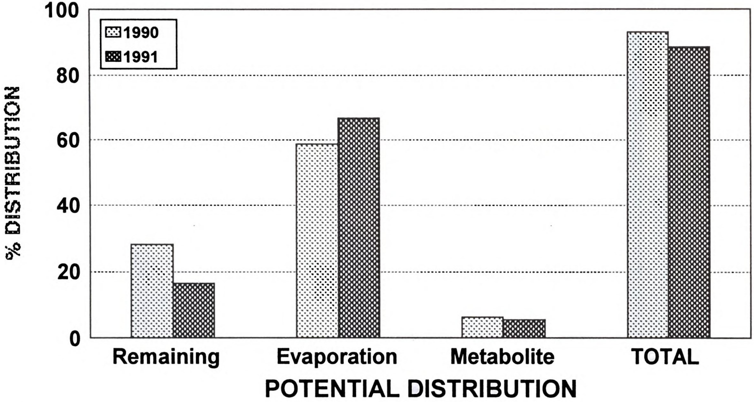
	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	21.88%	34.40%	28.14%	17.19%	15.60%	16.40%	22.27%
Evaporation loss	145.28%	131.40%	138.34%	167.42%	128%	132.89%	135.62%
3,5,,6-trichloropyridinol	4.69%	7.81%	6.25%	6.25%	4.69%	5.47%	5.86%
Total percent	171.85%	173.61%	172.73%	190.86%	148.10%	169.48%	171.11%

Table (13) The effect of the height and the wind speed on the evaporaton loss of Chlorpyrifos

Year 1990	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1+ 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	77.44%	41.05%	59.25%	79.71%	36.60%	58.16%	58.70%
Minimum	18.84%	10.22%	14.53%	15.76%	7.06%	11.41%	12.97%
Maximum	188.37%	102.18%	145.28%	179.94%	82.85%	131.40%	138.34%

Year 1991	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1+ 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	98.80%	49.07%	73.94%	79.27%	39.46%	59.37%	66.65%
Minimum	21.07%	10.69%	15.88%	15.29%	8.01%	11.65%	13.77%
Maximum	220.52%	114.32%	167.42%	164.10%	91.51%	127.81%	147.61%

FIGURE 6. THE AVERAGE POTENTIAL DISTRIBUTION OF CHLORPYRIFOS AT THE AVERAGE WIND SPEED AND HEIGHT IN THE WASTE DISPOSAL FACILITY IN 1990 AND 1991



Metabolite = 3,5,6-trichloropyridinol

FIGURE 7. THE EFFECT OF HEIGHT AND WIND SPEED ON THE POTENTIAL EVAPORATION LOSS OF CHLORPYRIFOS IN 1990 and 1991

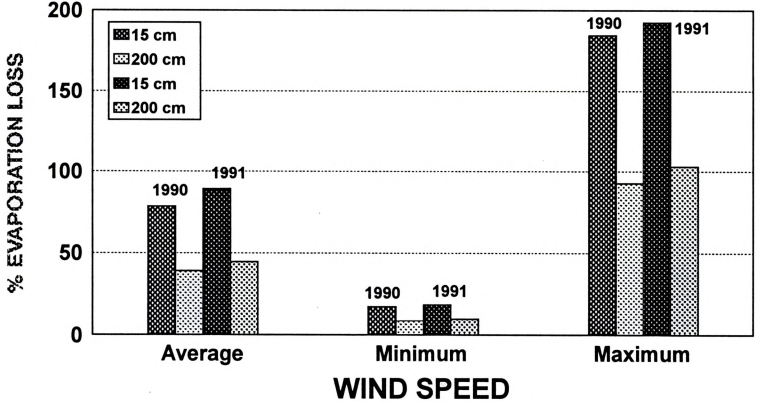
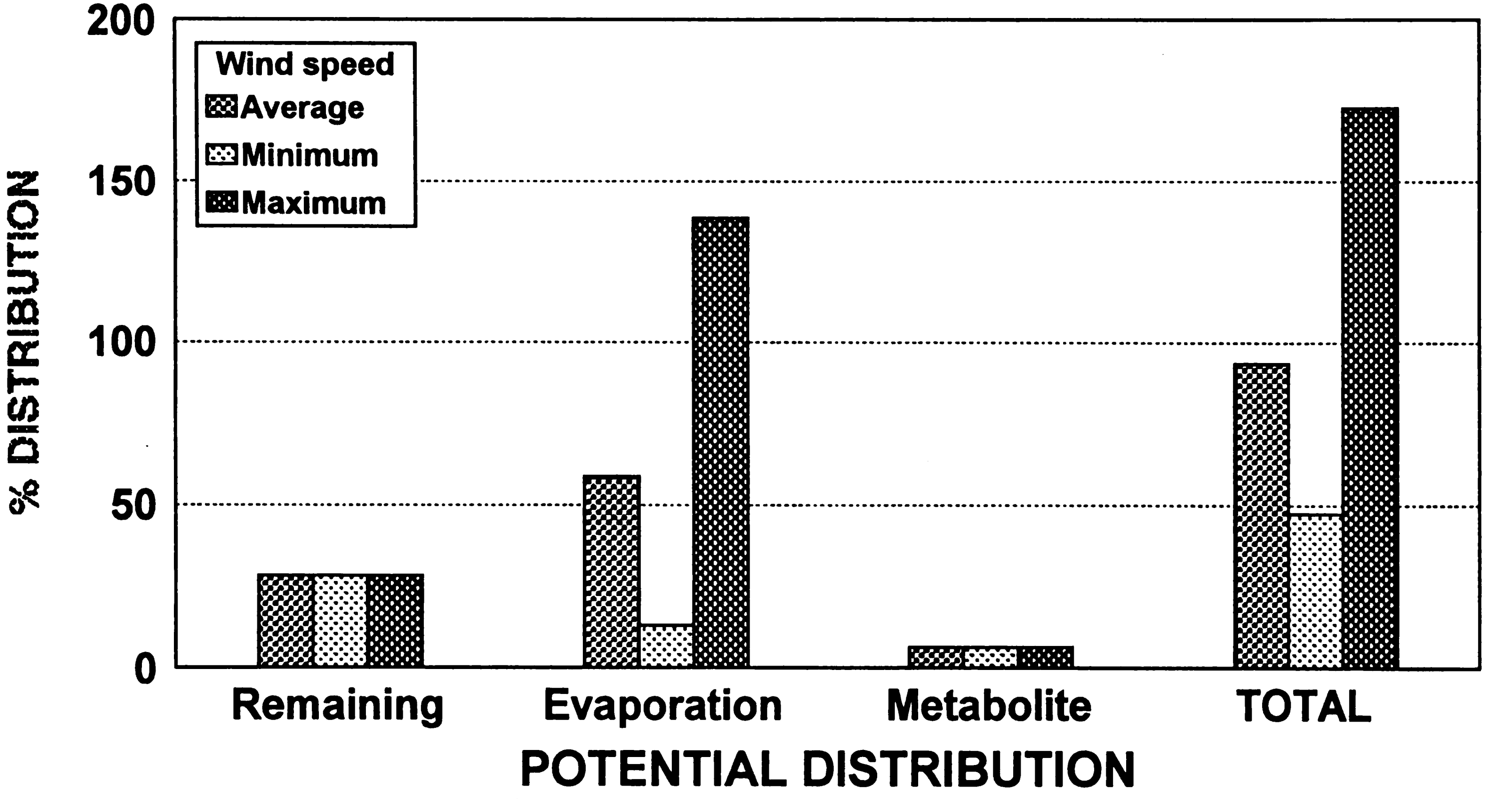
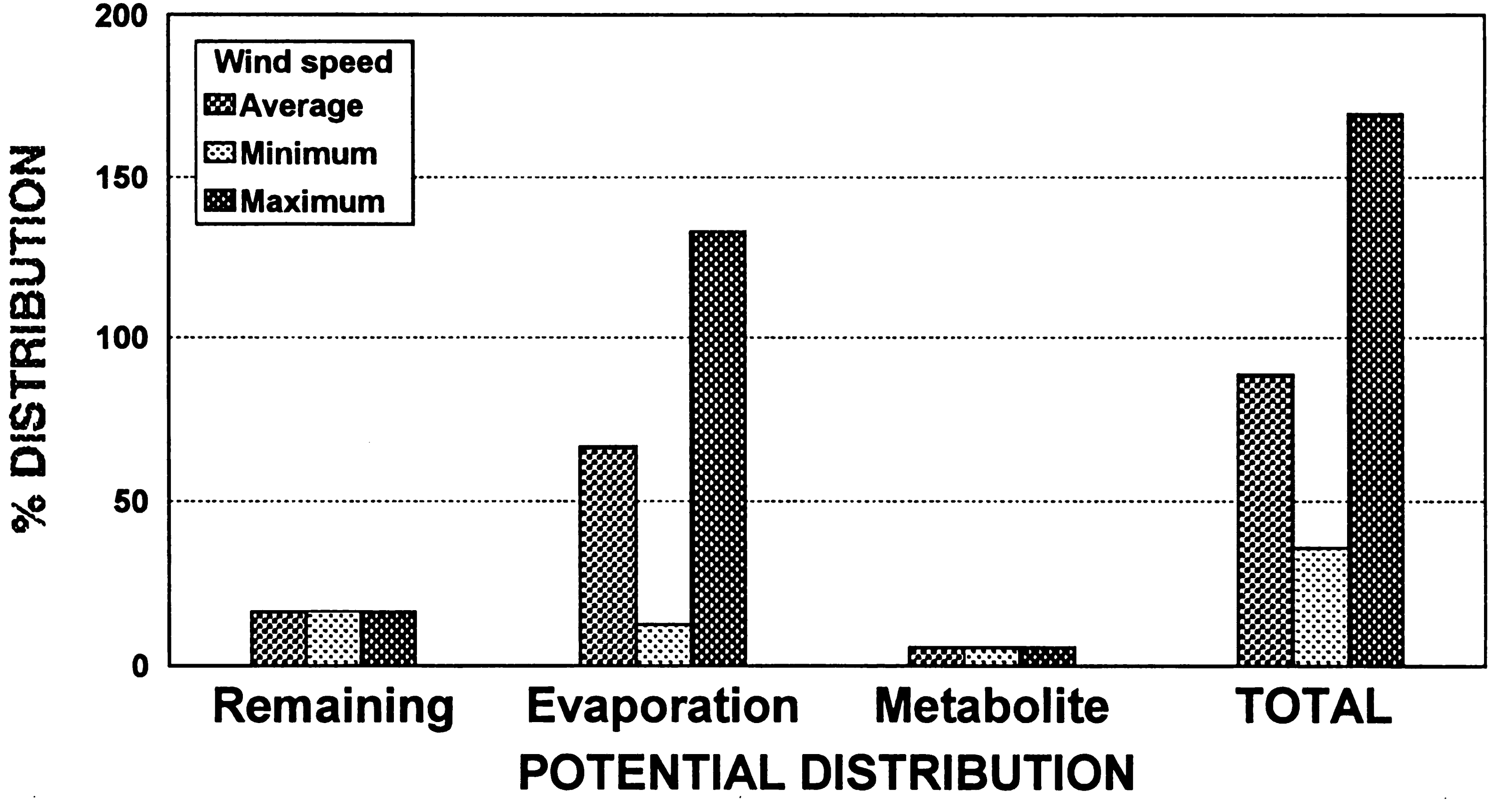


FIGURE 8. THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OFCHLORPYRIFOS AT THE AVERAGE HEIGHT IN 1990



Metabolite = 3,5,6-trichloropyridinol

FIGURE 9. THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OF CHLORPYRIFOS AT THE AVERAGE HEIGHT IN 1991



Metabolite = 3,5,6-trichloropyridinol

ALACHLOR (LASSO)

Alachlor (54.1 g) was applied to each soil degradation compartment (plot 1 and plot 2) three times a year for two years. A total weight of 162.3 g was applied in the first year and 324.6 g total for two years in each plot. The percent distribution of alachlor in 1990 in the soil compartments (plot 1 and plot 2) was determined by calculating the percent of the residues remaining in the soil, the percent of 2,6 diethylaniline which is the major metabolites of alachlor, and the percent of average evaporation loss of alachlor at the average wind speed and average height (Table 14). After the first year in 1990, 23.3 % of alachlor remained in soil plot 1 and 13.3 % in soil plot 2. The percentages for 2,6 diethylaniline were 20.3 % in soil plot 1 and 15.0 % in soil plot 2. The percentage from average evaporation loss of alachlor was 86.4 % from plot 1 and 79.8 % from plot 2. After the second year in 1991, 20.8 % remained in soil plot 1 and 25.0 % in the soil plot 2 (Table 14). The percentages for 2,6 diethylaniline were 9.2 % in soil plot 1 and 9.6 % in soil plot 2. The average percent evaporation loss were 109.0 % from plot 1 and 116.2% from plot 2. The average potential distribution of alachlor was calculated at the average wind speed and height in 1990 and 1991 (Table 15).

Using the minimum wind speed (1 kph) assumption, the average evaporation loss from the two plots was 24.2 % in 1990 and 18.4 % in 1991 at the average height. The effect of wind speed on the evaporation loss of alachlor is shown in table 15. The evaporation loss was also calculated at the maximum wind speed and the average height (Table 15). The evaporation loss was higher in the second year than the first year which may be due the higher concentration in the compartment due to the carry over from the first year or due to the different weather conditions such as the wind speed, temperature, or humidity. The effect of height had a large effect on the evaporation loss was a major factor in the calculation of total loss (Table 14). The volatilization loss measured at 15 cm was higher than at 200 cm. For average calculation, a column of air from the soil surface up to 200 cm which was close to the roof of the facility, was taken into consideration. Therefore average evaporation loss at 107.5 cm (average of 15 cm and 200cm) was employed for the calculations.

The volatilization loss of alachlor was the primary route of dissipation in the soil degradation compartments. The high volatilization loss was due to its high water solubility and is reflected in the nondimensional Henry's law constant. The Henry's law coefficient for alachlor is 3.23×10^{-8} and, therefore, evaporation loss is control by water evaporation and vapor movement across the laminar layer at the soil/air boundary (Glotfelty et al 1989). On the other hand the major metabolite 2,6-diethylaniline gave the lowest route of dissipation because. Microbial degradation has been reported to be the major means of destruction of chloroacetanilide pesticides in soils (Beestman and Deming, 1974). The degradation of alachlor by the soil fungus *Chaetomium globosum* has been extensively studied and a number of metabolites have been identified

(Tiedje and Hagedorn 1975). Chou (1977) found that 2-chloro-2′,6′-diethylaniline and 1-(chloroacetyl)-2,3-dihydro-7-ethylindole was produced in soil from alachlor. Mineralization in soil suspension was tested on soils that had received alachlor in the field and 7.3% of the alachlor at a lower concentration was mineralized in Lima-Kendaia silt loam (Novick 1986). A small percentage of the ring carbons of alachlor was converted to CO_2 under aerobic conditions during the 30-day period. 2,6-diethylaniline accumulated in relatively small amounts during alachlor degradation probably due to its subsequent metabolism and these findings are consistent with 2,6-diethylaniline being a major intermediate in the alachlor degradation pathway (Tiedje and Hagedorn 1975).

Table (14) The efffect of the wind speed on the distribution of Alachlor

Distribution of Alachlor at the average wind speed and the average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	23.33%	13.33%	18.33%	20.83%	25.00%	22.92%	20.62%
Evaporation loss	86.39%	79.78%	83.09%	109.37%	116%	112.78%	97.93%
2,6-diethylaniline	20.26%	15.00%	17.63%	10.00%	9.17%	9.59%	13.61%
Total percent	129.98%	108.11%	119.05%	140.20%	150.36%	145.28%	132.16%

Distribution of Alachlor at the minimum wind speed and the average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	23.33%	13.33%	18.33%	20.83%	25.00%	22.92%	20.62%
Evaporation loss	24.56%	17.36%	20.96%	28.82%	20%	12.29%	16.63%
2,6-diethylaniline	20.26%	15.00%	17.63%	10.00%	9.17%	9.59%	13.61%
Total percent	68.15%	45.69%	56.92%	59.65%	54.26%	56.96%	56.94%

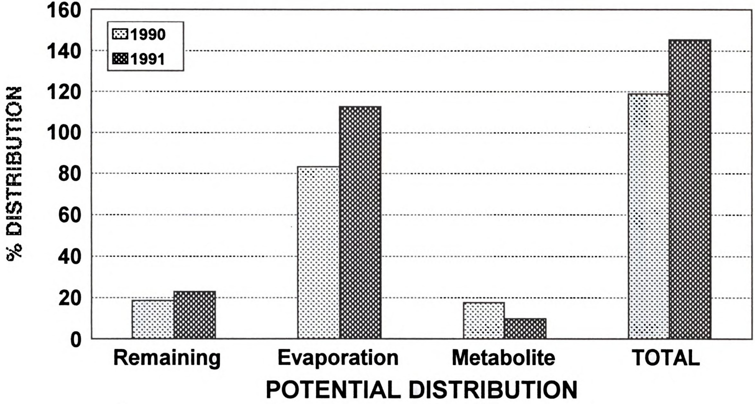
Distributionof Alachlor at the maximum wind speed and the average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	23.33%	13.33%	18.33%	20.83%	25.00%	22.92%	20.62%
Evaporation loss	218.51%	95.73%	157.12%	241.61%	171%	132.89%	145.01%
2,6-diethylaniline	20.26%	15.00%	17.63%	10.00%	9.17%	9.59%	13.61%
Total percent	262.10%	124.06%	193.08%	272.44%	205.19%	238.82%	215.95%

Table (15) The effect of the height and the wind speed on the evaporaton loss of Alachlor

Year 1990	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1+ 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	110.10%	62.67%	86.39%	97.84%	61.71%	79.78%	83.08%
Minimum	32.71%	15.67%	24.19%	23.29%	13.41%	18.35%	21.27%
Maximum	220.21%	102.76%	161.49%	216.49%	79.37%	147.93%	154.71%
Year 1991	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1+ 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	149.43%	69.31%	109.37%	169.70%	62.68%	116.19%	112.78%
Minimum	40.12%	17.39%	28.76%	26.38%	14.66%	20.52%	24.64%
Maximum	298.85%	127.34%	213.10%	227.34%	129.80%	178.57%	195.83%

FIGURE 10. THE AVERAGE POTENTIAL DISTRIBUTION OF ALACHLOR AT THE AVERAGE WIND SPEED AND HEIGHT IN THE WASTE DISPOSAL FACILITY IN 1990 AND 1991



Metabolite = 2,6-diethylaniline

FIGURE 11. THE EFFECT OF HEIGHT AND WIND SPEED ON THE POTENTIAL EVAPORATION LOSS OF ALACHLOR IN 1990 and 1991

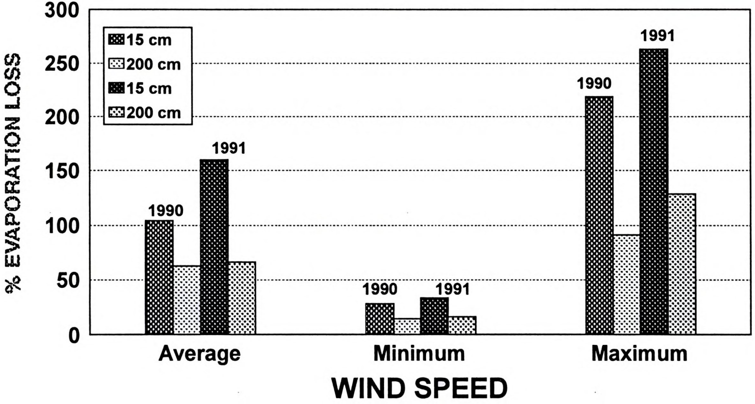
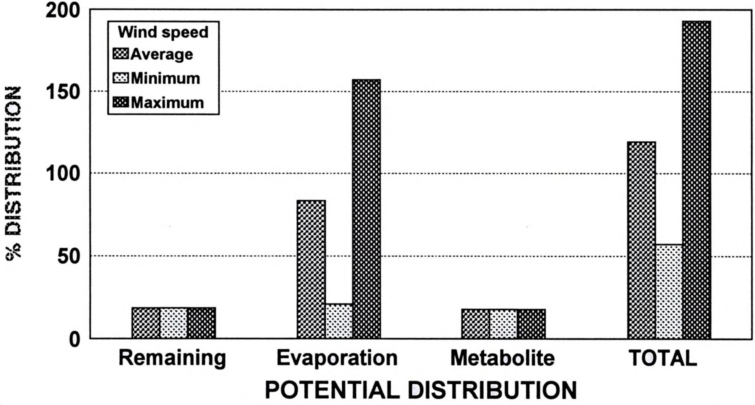
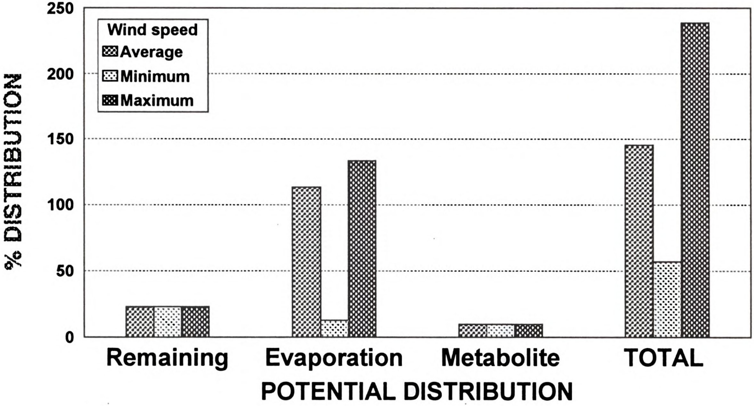


FIGURE 12. THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OF ALACHLOR AT THE AVERAGE HEIGHT IN 1990



Metabolite = 2,6-diethylaniline

FIGURE 13. THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OF ALACHLOR AT THE AVERAGE HEIGHT IN 1991



Metabolite = 2,6-diethylaniline

SIMAZINE (PRINCEP)

Simazine (145.3 g) was applied to each soil degradation compartment (plot 1 and plot 2) three times a year for two years. A total weight of 435.9 g was applied in the first year and 871.8 g total for two years in each plot. The percent distribution of simazine in 1990 in the soil compartments (plot 1 and plot 2) was determined by calculating the percent of the residues remaining in the soil, the percent of 2,6 diethylamine-4-hydroxy-s-triazine which is the major metabolites of simazine, and the percent of average evaporation loss of simazine at the average wind speed and average height (Table 16). After the first year in 1990, 23.7% of simazine remained in soil plot 1 and 22.7 % in soil plot 2. The percentages for 2,6 diethylamine-4-hydroxy-s-triazine were 0.46 % in soil plot 1 and 0.46% in soil plot 2. The percentage from average evaporation loss of simazine was 139.4 % from plot 1 and 171.3 % from plot 2 (Table 17). After the second year in 1991, 15.7 % remained in soil plot 1 and 17.6 % in the soil plot 2 (Table 16). The percentages for 2,6 diethylamine-4-hydroxy-s-triazine were 0.01 % in soil plot 1 and 0.01 % in soil plot 2. The average percent evaporation loss were 153.6 % from plot 1 and 148.7 % from plot 2. The average potential distribution of simazine was calculated at the average wind speed and height in 1990 and 1991 (Table 17).

Using the minimum wind speed (1 kph) assumption, the average evaporation loss from the two plots was 44.4 % in 1990 and 40.2 % in 1991

at the average height. The effect of wind speed on the evaporation loss of simazine is shown in table 16. The evaporation loss was also calculated at the maximum wind speed and the average height (Table 17). The evaporation loss was higher in the second year than the first year which may be due the higher concentration in the compartment due to the carry over from the first year or due to the different weather conditions such as the wind speed, temperature, or humidity. The effect of height had a large effect on the evaporation loss was a major factor in the calculation of total loss (Table 16). The volatilization loss measured at 15 cm was higher than at 200 cm. For average calculation, a column of air from the soil surface up to 200 cm which was close to the roof of the facility, was taken into consideration. Therefore average evaporation loss at 107.5 cm (average of 15 cm and 200cm) was employed for the calculations.

The volatilization loss of simazine gave the highest dissipation loss of all the pesticides studied in the soil degradation compartments. The high volatilization loss was due to its high water solubility and reflected in the nondimensional Henry's law constant. The Henry's law coefficient for simazine is 4.62×10^{-10} and therefore evaporation loss is controlled by water evaporation and vapor movement across the laminar layer at the soil/air boundary (Glotfelty et al 1989).

Table (16) The effect of the wind speed on the distribution of Simazine

Distribution of Simazine at the average wind speed and the average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAG
Remaining in the soil	23.73%	22.69%	23.21%	15.74%	17.59%	16.67%	19.94%
Evaporation loss	139.42%	171.31%	155.37%	153.58%	149%	151.12%	153.24%
2,6--diethylamin-4-hydroxy s-triazine	0.46%	0.46%	0.46%	0.01%	0.01%	0.01%	0.24%
Total percent	163.61%	194.46%	179.04%	169.33%	166.25%	167.79%	173.41%

Distribution of Simazine at the minimum wind speed and the average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	23.73%	22.69%	23.21%	15.74%	17.59%	16.67%	19.94%
Evaporation loss	34.86%	34.15%	34.51%	38.00%	36%	12.29%	23.40%
2,6--diethylamin-4-hydroxy s-triazine	0.46%	0.46%	0.46%	0.01%	0.01%	0.01%	0.24%
Total percent	59.05%	57.30%	58.18%	53.75%	53.26%	53.51%	55.84%

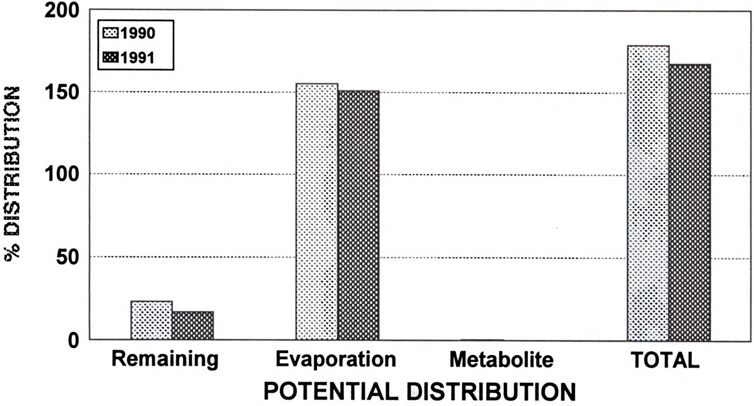
Distribution of Simazine at the maximum wind speed and the average height

	Year of 1990			Year of 1991			1990 + 1991
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	AVERAGE
Remaining in the soil	23.73%	22.69%	23.21%	15.74%	17.59%	16.67%	19.94%
Evaporation loss	263.58%	250.78%	257.18%	299.54%	274%	132.89%	195.04%
2,6--diethylamin-4-hydroxy s-triazine	0.46%	0.46%	0.46%	0.01%	0.01%	0.01%	0.24%
Total percent	287.77%	273.93%	280.85%	315.29%	291.70%	303.50%	292.17%

Table (17) The effect of the height and the wind speed on the evaporaton loss of Simazine

Year 1990	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1 + 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	153.58%	125.26%	139.42%	174.98%	167.64%	171.31%	155.37%
Minimum	47.97%	40.84%	44.41%	46.35%	42.55%	44.45%	44.43%
Maximum	404.70%	359.13%	381.92%	402.72%	377.05%	389.89%	385.90%
Year 1991	Plot 1	Plot1	Plot 1	Plot 2	Plot 2	Plot 2	Plot 1 + 2
Wind speed	Height	Height	Height	Height	Height	Height	Height
	15cm	200cm	Average	15cm	200cm	Average	Average
Average	188.87%	118.30%	153.59%	175.22%	122.07%	148.65%	151.12%
Minimum	49.74%	33.22%	41.48%	46.54%	31.35%	38.95%	40.21%
Maximum	444.96%	288.97%	366.97%	388.25%	269.08%	328.67%	347.82%

FIGURE 14. THE AVERAGE POTENTIAL DISTRIBUTION OF SIMAZINE AT THE AVERAGE WIND SPEED AND HEIGHT IN THE WASTE DISPOSAL FACILITY IN 1990 AND 1991



Metabolite = 2,6-diethylamin-4-hydroxy-s-triazine

FIGURE 15. THE EFFECT OF HEIGHT AND WIND SPEED ON THE POTENTIAL EVAPORATION LOSS OF SIMAZINE IN 1990 and 1991

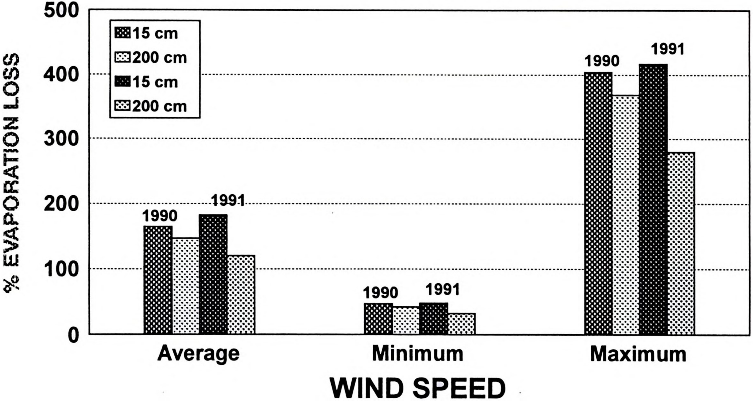
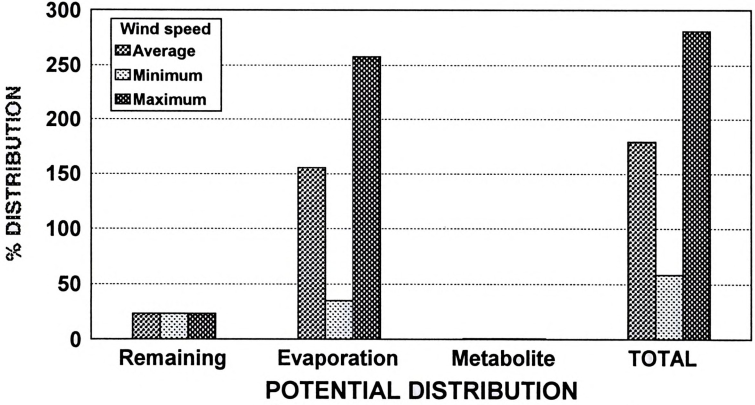
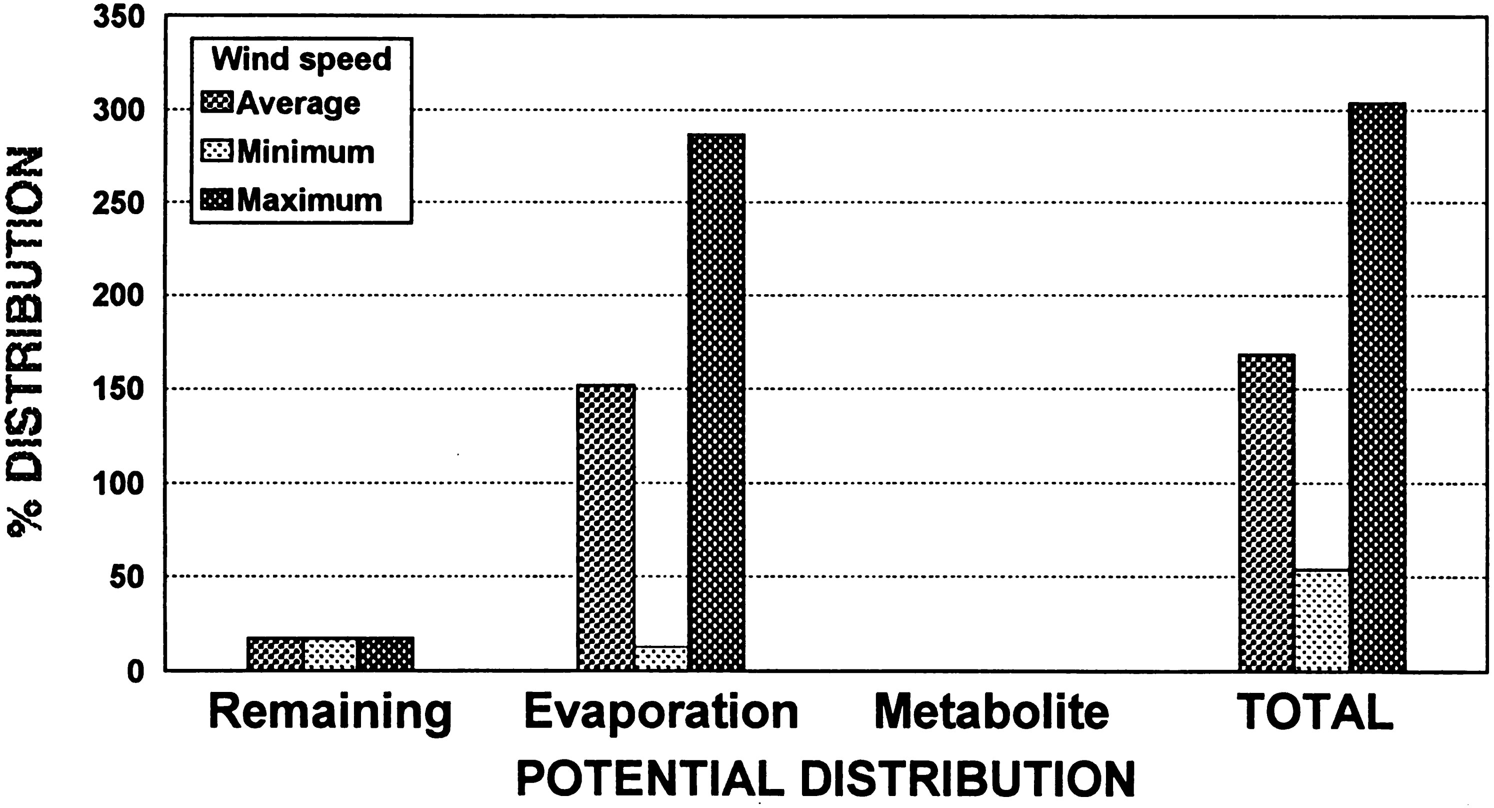


FIGURE 16. THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OF SIMAZINE AT THE AVERAGE HEIGHT IN 1990



Metabolite = 2,6-diethylamin-4-hydroxy-s-triazine

FIGURE 17. THE EFFECT OF WIND SPEED ON THE POTENTIAL DISTRIBUTION OF SIMAZINE AT THE AVERAGE HEIGHT IN 1991



Metabolite = 2,6-diethylamin-4-hydroxy-s-triazine

The field data showed that the evaporation loss was the dominant dissipation route for all four of the pesticides. Volatilization was the most an important route of pesticides loss from the waste disposal facility and far exceeded any other degradation loss such as hydrolysis, oxidation or metabolism. Field-measured volatilization losses were not precise because of the wide fluctuation in wind speed, temperature and humidity during the week and even during any given day. At best one can only approximate the volatilization losses over long time periods and the amount of the potential error is not known. It is very hard to get the exact evaporation loss because of the wind speed and the air sampling height. To help eliminate variation in the wind speed and the other factors, sampling the air every day would be the best way but would lead to an exceeding large number of samples. A complex model such as that proposed by Jury et al (1983) would be needed to adequately take into account all the factors that influence pesticides volatilization from soil. The presence of formulation components in water complicates the estimation of pesticides volatilization from the compartments. As the soil-water increased the volatilization rate of pesticides increased (Woodrow 1991). The volatilization rates of the pesticides in wet soils are higher than in dry soil. On days when the soil surface became dry, the volatilization of the pesticides was greatly reduced by increased adsorption of the pesticides onto the dry soil particles. Vapor

pressure, water solubility and soil organic carbon adsorption coefficient are important factors in determining the magnitude of the evaporation loss. The volatilization losses of a number of volatile, non polar pesticides were measured by Glotfelty in 1984, after their surface application to fallow soil. The volatilization rates were more rapid from moist soil than from dry soil (Glotfelty et al 1984). The rate of volatilization of pesticides from soil is controlled by a number of intrinsic factors that depend upon properties of the chemical and of the soil (Glotfelty et al 1989). Pesticides in the soil solution obey Henry's law (Spencer 1970). Spencer therefore concluded that a knowledge of Henry's law coefficients and soil-water adsorption isotherms could be used to predict pesticides volatility from soil. An empirical rate expression developed by Swann et al 1982 which is appropriate to soil surface applications. The volatilization rate K_v is given by this equation:

$$K_v = Q\ (P/K_{oc}\ S)$$

Where

P = Vapor pressure (mmHg)
K_{oc} = the soil adsorption coefficient (organic basis)
S = the water solubility
Q = the empirically determined coefficient = $4.4\text{X}10^7$.

Volatilization of compounds for which the nondimensional Henry's law coefficient is much less than $2.5\text{X}10^{-5}$ is controlled by water evaporation and by vapor movement across the laminar layer at the soil-air boundary (Jury et al

1983). This occurs because the rate of movement of these compounds to the soil surface with evaporating water exceeds their rate of volatilization from the surface. After a period of time, volatilization of these more soluble, less volatile, chemicals should become constant because they accumulate at the surface.

The data showed a relationship between evaporation loss and water solubility for the nondimensional Henry's law pesticides (Figure 20). Chlorpyrifos, alachlor and simazine have Henry's law constant lower than 2.5 X 10^{-5} (Table 18) and the lower the number of Henry's law constant the higher evaporation loss due to the higher water solubility (Figure 21). The chlorpyrifos showed a lower value of evaporation loss than alachlor. Simazine exhibited the highest value for evaporation loss. The vapor pressure of chlorpyrifos is higher than alachlor and simazine, however, simazine showed the highest evaporation loss due to the higher water solubility. However, simazine has the lowest vapor pressure. The data showed that the higher of the pesticides water solubility, the higher the evaporation loss (Table 18).

The average potential dissipation of the selected pesticides were used in study in 1990 and 1991 were 66.9 % and 67.3 % respectively for endosulfan I + II, 69.9 % and 81.5 % for chlorpyrifos, 84.7 % and 84.2 % for alachlor and 87.1 and 90.0 % for simazine. The pesticides wastes disposal facilityat Michigan State University was a good method for the dissipation of all four of the pesticides that were studied.

Table (18) Evaporation loss of the selected pesticides at the average height and wind speed

Evaporation loss	Year of 1990			Year of 1991				
	Plot (1)	Plot (2)	Average	Plot (1)	Plot (2)	Average	water solubility	Henry's constant
Endosulfan I + II	70.27%	53.58%	61.93%	92.01%	59%	75.69%	0.60 ppm	1.12 E-5
Chlorpyrifos	59.24%	58.16%	58.70%	73.94%	59%	66.66%	2.00 ppm	4.31 E-6
Alachlor	86.30%	79.78%	83.04%	109.37%	116%	112.78%	2.42 ppm	3.23 E-8
Simazine	139.42%	171.31%	155.37%	153.58%	149%	151.29%	3.50 ppm	4.62 E-10

FIGURE 18. THE RELATIONSHIP BETWEEN WATER SOLUBILITY AND EVAPORATION LOSS OF THE PESTICIDES

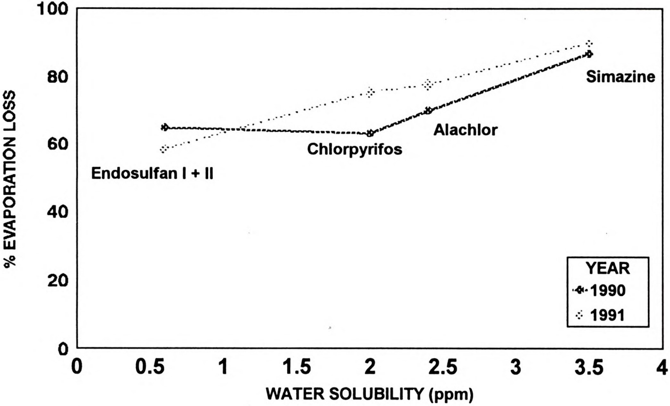


FIGURE 19. THE RELATIONSHIP BETWEEN HENRY'S LAW CONSTANT AND EVAPORATION LOSS OF THE PESTICIDES

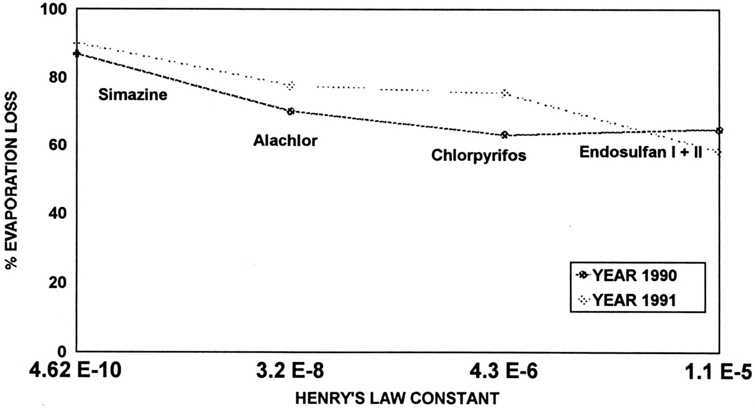


Figure 20. THE AVERAGE MASS BALANCE RELATIONSHIP FOR THE PESTICIDES USED IN THE STUDY OF THE MICHIGNA STATE UNIVERSITY WASTE DISPOSAL FACILITY IN 1990

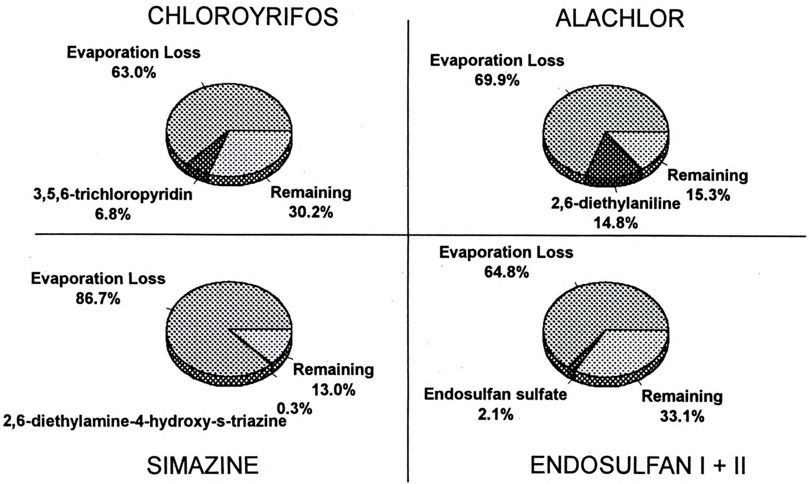


FIGURE 21. THE AVERAGE MASS BALANCE RELATIONSHIP FOR THE PESTICIDES USED IN THE STUDY OF THE MICHIGNA STATE UNIVERSITY WASTE DISPOSAL FACILITY IN 1991

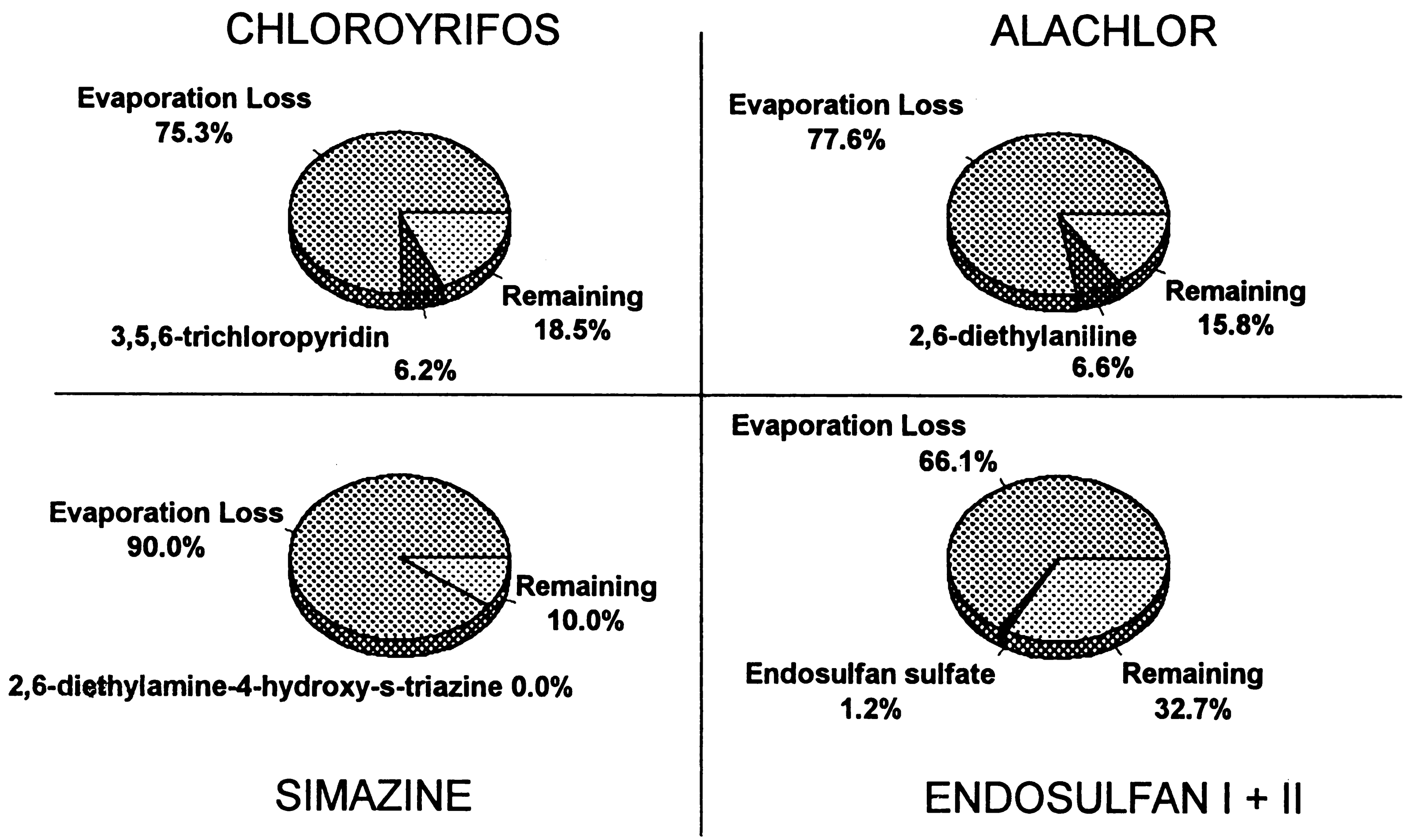


TABLE 19. THE AVERAGE POTENTIAL DISSIPATION OF THE SELECTED PESTICIDE USED IN THE STUDY OF THE FENNVILL, MICHIGAN WASTE DISPOSAL FACILITY IN 1990 AND 1991

Pesticides	% dissipation	
	1990	1991
Endosulfan I + II	66.9	67.3
Chlorpyrifos	69.9	81.5
Alachlor	84.7	84.2
Simazine	87.1	90.0

CHAPTER 4

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Dilute pesticide wastes resulting from cleaning and rinsing of used containers, spray tanks, equipment used for pesticide applications and overestimating the amount needed for a spray operation. For such operations, safe facilities and procedures are essential to degrade the wastes and protect human health and the environment . The waste disposal facility at Michigan State University was an adequate method for the dissipation of dilute pesticide wastes. Also the inground soil degradation compartment is environmentally safe because it has a concrete bottom liner and concrete walls. In addition, no pesticides residues were detected in the drainage tile under the facility after the two years study.

Volatilization loss was the dominant dissipation route for endosulfan I and II, chlorpyrifos, alachlor, and simazine. The average potential dissipation of the selected pesticides used in the study in 1990 was between 66.9 % and 87.1 % for endosulfan and simazine respectively. In 1991 the dissipation was between 67.3 % for endosulfan and 90.0 % for simazine. water in a soil is essential for effective pesticides dissipation in a waste disposal system. Water is important for volatilization and hydrolysis of pesticides.

The pesticides waste disposal facility at Michigan State University was a good method for the dissipation of all four of the pesticides used in the study.

Degradation facilities should be developed which are simple to use, reliable and inexpensive.

In order to maintain a reasonable level of safety, any pesticides waste disposal facility should be monitored the groundwater under and around the facility at least twice every year for any pesticides contamination. Moreover, minimizing the pesticide wastes input should be consider by calculating the exact amount of pesticides needed. Also the contamination of groundwater from any waste facility can be avoided by improved design, construction, operation, and maintenance. Design considerations should always include the hydrogeology of the location, area to be served, and types of wastes. The use of liners and covers, as well as collection and treatment of leachate further reduce the potential for groundwater contamination. Therefore disposal of pesticide wastes must be in accordance with the Federal Resource Conservation and Recovery act, state and local regulations.

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