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THE FATE OF SELECTED PESTICIDES
I - POTENTIAL FOR LEACHING
II - EFFECT OF COMPOSTING ON RESIDUES

presented by

Christine Vandervoort

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THE FATE OF SELECTED PESTICIDES APPLIED TO TURFGRASS

PART I
POTENTIAL FOR LEACHING

PART II
EFFECT OF COMPOSTING ON RESIDUES

By

Christine Vandervoort

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

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1995

Dr. Matthew J. Zabik

ABSTRACT

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Applications of select pesticides to turfgrass were made and their fate in an intact soil monolith lysimeter and composted turfgrass system were studied. Detection of the parent molecule applied to each system was the end point for determination of the fate within the system.

In the lysimeter system chlorothalonil, triadimefon, dicamba, 2,4-D, isazofos, fenarimol, metalaxyl, and propiconazole were applied to turfgrass. The water collected from lysimeter was analyzed over 28 months time. Triadimefon was the only pesticide recovered from the lysimeter leachate.

The composted turfgrass had isoxaben, chlorpyrifos, 2,4-D, clopyralid, triclopyr, and flurprimidol sprayed on to established turfgrass. The grass was clipped one day after application and put in compost piles. The compost piles were sampled for 365 days after application of the pesticides and analyzed. The results showed declining residues of pesticides over time. The data suggest a biphasic rate of loss.

The lysimeter system showed the parent compound was not coming through the lysimeter at sufficient concentration to be detected by the method. The compost clearly showed signs of decline in the concentrations of the applied pesticides.

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INTRODUCTION

The objective of this research is to assess the potential for contamination of ground water, soil, and other non-target areas by pesticides used on turfgrass. The use of pesticides has become an integral part of man's desire to increase production of food and fiber. The entry of pesticides into the atmosphere, aquatic, and biological components of the environment provides the potential for chronic risk to the environment and human health. An understanding of the physio-chemical properties of the pesticide and the factors controlling them in the environment will permit assessment of possible risk. Groundwater is a finite and valuable resource that provides the United States with 51 % of its drinking water (Coutu, 1989) and 43 % of Michigan residents rely on groundwater for drinking. The rate at which pesticides disperse or degrade may impact surface water and aquatic life forms. Pesticides with high octanol-water partition coefficient tend to accumulate in hydrophobic compartments (biota and sediments) and may adversely impact the resulting organism (Wilcock, 1994). Aquatic organisms are immersed generally for their lifetime in water and their exposure may be acute to chronic depending on the contaminant level in the water. The reason for such studies is to assess non-target deposition of contaminants, as they may bioaccumulate in the food chain thus exposing humans

(Mathews, 1994). The insecticide DDT has a degradation product DDE which has been attributed to causing eggshell thinning in wild birds (Giesy, 1994) and bald eagles have had declining births and viable young which has been considered related to causal agent such as polychlorinated diaromatic hydrocarbons. A study conducted in 1989 in Turkey showed hexachlorobenzene (banned organochlorine pesticide) to be found in human fat tissue, even though it was banned in 1959 (Burgaz, 1994). To use chemical tools responsibly requires knowledge of how pesticides are disseminated, distributed, degraded, and accumulated in the environment, this will help to avoid similar situations in the future.

OBJECTIVES

The specific objectives of the research are to gain knowledge of the pesticides applied to turfgrass in respect to detection of the intact pesticide leaching through a soil filled monolith lysimeter and the effect composting of turfgrass has on parent pesticide residues.

The lysimeter study looks at the vertical transport of the intact pesticide through turf, thatch, and soil. Knowledge of the behavior of a pesticide in the soil will help in the understanding of the distribution of the pesticide in the environment. The lysimeter drainage will address the ability of a pesticide to travel with the water through the soil profile, under various rainfall and weather events, to show how pesicides behave under actual field conditions.

The composted turfgrass study evaluates the option of applying lawn and

garden wastes to growing gardens as a nutrient amendment and to help maintain the moisture in the soil. The compost must be applied safely without phytotoxicity or toxicity to non-target organisms due to residual pesticides. The fate of the intact applied pesticide is measured as a end point to evaluate the toxicity to the environment from the compost.

The population of the United States has had an extensive urban shift and this shift has brought an array of problems. The homeowner has yard wastes that are being placed in landfills and the landfills are of concern to the public. The State of Michigan Law PA 264 Section 18a (2) has now banned yard wastes being placed in landfills. The concerns include both the vast amount of material and the nature of the material being placed in the landfills. Large quantities of pesticides have been applied to turfgrass and ornamental shrubs to control pests in urban areas. Composting of yard waste brings the concern of chemical residues in the resulting plant material. The pesticides used may follow several paths after application to the target system. Pimental and Levitan (1986) believe less than 0.1 % of pesticides applied reach the target organism. Relatively small areas of the world are treated with pesticides, but universal distribution of small amounts are caused by water, wind, food, and feed movement. Golf courses are often a casualty of many pest problems. The average maintenance cost for a golf course is $151,000 with $13,000 being spent on pesticides and $7,300 spent on fertilizers (Shank, 1985). The goals of turfgrass maintenance is high quality turfgrass and reasonable economic return. Weed

pressures are a major concern for turfgrass systems due to the esthetic appeal being sought. Weeds compete for nutrients and can shade out the turfgrass which makes the turfgrass an unappealing place to golf. Turf managers make decisions to apply herbicides routinely but insecticides and fungicides application are done on assessment of the potential impact to the turfgrass (Commercial Turf Establishment and Pest Management, 1993). Insect and other disease vectors cause other control problems on the golf course. An example of an insect pest is the mole cricket, a tunneling insect, that causes major damage to grass. A golf course with a average infestation of mole cricket may spend up to $25,000 a year trying to hold them at a tolerable level (Reese, 1994). To help reduce the chemical control methods, which are only partially effective, biological controls have been used with success in North Carolina and Florida. The mole cricket is an immigrant from South America and when it came to North America it did not bring its natural predators. The IPM approach has introduced red-eyed flies and entomogenous nematodes as natural predators. The IPM program was able to show a increase in green revenues of $250,000 per year (Reese, 1994). The economic losses are a driving force for the need of chemical and biological control in turfgrass management. Table 1 (weed pests), Table 2 (insect pests), Table 3 (diseases),and Table 4 (nematode pests) show the common turfgrass pests found in lawns and golf courses. Weed control in turfgrass can be broken down into two categories, grasses and broadleaves. Postemergence herbicides such as 2,4-D, dicamba, clopyralid, triclopyr and isoxaben

are commonly used for broadleaf control. The grasses may be controlled with preemergent herbicides when germinating, but once established, the control of perennial grasses are most difficult. The mildew, rusts, smut, and other fungal diseases are controlled by chlorothalonil, propiconazole, fenarimol, triadiamefon, and metalaxyl. Chlorpyrifos and isazofos are used in control of bluegrass billbug, chinch bug, cutworms, June beetle, and sod webworm. The lawn care industry has an array of problems, one is the public perception of an industry which relies on toxic chemicals and a lack of concern of the environment.

Pesticides in the environment are dissipated by many mechanisms and biological processes, which do not necessarily lead to complete degradation of the chemical. The obvious choice would be for the pesticides to breakdown to innocuous products. Pesticides may degrade or bind to plant material or soil components. The compounds that bind are still of concern because of the possibility of future bioavailability to another organism. The release of an intact pesticide or a toxic pesticide metabolite is a real concern because of the potential damaging effects. The rate of release may be so slow, so as to be inoffensive to the environment, or may be rapid and cause damage.

Table 1. Weed pests that impact golf courses

Common Name	Scientific Name
clover	*Trifolium* spp.
prostrate knotweed	*Polyganum aviculare*
crabgrass	*Digitaria* spp.
dandelions	*Taraxacum officinale*
chickweed	*Stellaria media*
yellow nutsedge	*Cyperus esculentus*
annual bluegrass	*Poa annua*
goosegrass	*Eleusine indica*
barnyardgrass	*Echinochloa crusgalli*
foxtails	*Setaria* spp.
oxalis	*Oxalis stricta*
spurge	*Euphorbia supina*
ground ivy	*Glechoma hederacea*
creeping speedwell	*Veronica filliformis*
wild violets	*Viola* spp.

Table 2. Insect pests that impact golf courses

Common/Scientific Name	impact
black turfgrass ataenius/*Ataenius spretulus*. . . .	larva feed on roots
cutworms/*Agriotis ipsilon*.	worms feed on foliage
may or june beetles/*Phyllophaga* spp..	larva attack roots
sod webworm/ *Fissicrambus mutabilis*.	1st & 2nd generation feed on foliage
european chafer/*Rhizotropus majalis*.	larva feed on roots
japanese beetle/*Popillia japonica*.	larva feed on roots
ants/*Formica* spp.	
greenbugs/*Schizaphis graminumants*	
chinch bug/*Blissus leucopterus*	
bluegrass billbug/*Schenohporus parvulus*	

Table 3. Disease/Pathogens that impact golf courses

disease/pathogen	impact
dollar spot */Sclerotinia hemcocarpa*	attack cool season grasses
brown patch/*Rhizoctonia solani*	attack cool season grasses
fusarium patch/*Fusarium nivale*	attack cool season grasses
helminithosporium leaf spot/*Bipolaris sorokiniana*	attack cool season grasses
melting out/*Drechslera poae*	attack cool season grasses
pythium blight/*Pythium aphanidermatum*	attack cool season grasses
typhula blight/*Tuphula incarnata*	attack cool season grasses
take all patch/*Gaeaumannomyces gaminis*	attack bentgrasses

Table 4. Nematodes that impact golf courses

disease/pathogen	impact
pinewood nematode/*Bursathelenchus xylophilus*.	attack the genus pinus

LITERATURE REVIEW

To evaluate the fate of toxic chemicals, the nature of the chemical and the environment it finds itself in must be examined. Pesticides are applied in various ways to reach the target organism. The journey from the application equipment to the target must be controlled as much as possible to minimize loss to nontarget organisms and the environment. Pesticides usually breakdown or degrade via three methods, photodecomposition by sunlight, biological decomposition, and/or chemical decomposition. The rate of degradation is influenced by volatilization, surface runoff, leaching, capillary action (moving upward in the soil profile), sorption (includes adsorption, partitioning, and absorption), and storage in biological organisms. A discussion of leaching potential and effect of composting on pesticides will follow, with a look at the mechanisms effecting these fate, such as adsorption and partitioning to the environmental media, volatility, diffusion and flow, photochemistry, biochemical, and chemical degradation will follow.

PART I - POTENTIAL FOR LEACHING

The potential for leaching can be assessed using monolith soil filled lysimter. Outdoor lysimeters offer a range of climatic conditions that effect the movement of the applied pesticide. The soil in undisturbed lysimeters maintain the macro- and micro- pores, fissures, and channels which effect the flow. Benazolin-ethyl (ring labelled with ^{14}C) (Leake, 1991) was applied to a lysimeter with bare soil on top, over a 18 month period. The majority of the recovered radioactivity was in the top

10 cm of the soil column. The presumed loss of radioactivity was to mineralization of the parent pesticide. In one lysimeter no radioactivity above background was detected and in the other less than 1 % of the total applied was detected in the leachate. In Germany a undisturbed soil lysimeter leachate (Kordel, 1991) was collected over one year and then the soil cores were removed and analyzed. Cloethocarb was applied as a radio-labeled compound and the radioactivity was measured. The results showed less than 0.02 ug/l total radioactivity were recovered in the leachate throughout the year. Cloethocarb was detected down to 40 cm in the soil profile. Bentazone (Kordel, 1991) was also applied to a young pea crop with winter wheat as a rotational crop and less than 0.1 ug/l of total radioactivity was recovered in two years. Betazones metabolites were detected in the leachate but never exceeded 0.02 ug/l. The trend of minimal residues in the leachate occurs commonly with lysimeters that have undisturbed soil profile where as the ones that are laboratory filled show different results. The design facilitates leaching in that it does not have a vegetative cover, OM from plant debris in the upper layers of soil are missing, and the soil chosen is sand and gravel. Since the middle 1960s, soil scientists have noticed that the extent of soil uptake for nonionic organic compounds (contaminants and pesticides) is closely related to the OM content in soil (Sun, 1992).

PART II - EFFECT OF COMPOSTING ON RESIDUES

Composting is the biotransformation of complex polysaccharides and other organic compounds to CO_2 and humic substances by microorganisms. In controlled laboratory composting studies percent loss of carbon averaged 28.9 % +/- 9.2 (Michel, 1993) in 32 days. The same study showed 71 % loss in cellulose and 73 % loss of hemicellulose after 43 days of composting. In another study, a leaf and grass compost amended with ^{14}C ring labelled 2,4-D was analyzed for evolved CO_2 (unpublished by Michel at Michigan State University). After 10 days 27 % of the ^{14}C ring labelled 2,4-D was mineralized to CO_2 and 50 days after composting 47 +/-6 % was mineralized.

PESTICIDE FATE IN THE ENVIRONMENT

ADSORPTION AND PARTITIONING TO THE ENVIRONMENTAL MEDIA

The rate of pesticide application to obtain adequate control often depends upon the amount of organic material (OM) found in the soil. The OM has the ability to form strong chemical bonds with some pesticides, but interacts with other compounds only by van der Waals forces (weak forces). The binding of the chemical residues may contribute to their persistence in the soil and render them harmless to the environment (Stevenson, 1975). The nature of the pesticide binding to the OM in soil is obscure due to the many forms of OM and its non-precise structural formula. The humic acid and fulvic acid portion of OM is negatively charge, with high molecular weights and diverse functional groups. They have several oxygen-containing groups

such as carboxyl, aliphatic, alcohols, phenolic, enolic-hydroxyls, and carbonyls. Sulfur and nitrogen functional groups are also found in OM. OM may interact with pesticides through several attachment schemes. The attachment mechanisms include van der Waals force, ligand exchange, H-bonding, and hydrophobic bonding. Sorption of pesticides to soils is correlated to the rapid increase in sorption with decreasing pH.

Ion exchange can occur with some pesticides to the negative sites in OM or clay, if the pesticide is positively charged or protonated. The cation exchange capacity of soil (the concentration of negatively charged sites) will always be greater than the pesticide concentration, except perhaps in very sandy soils. The ability of the soil to ion exchange is pH-dependent and becomes greater for neutral and basic soils. Anionic pesticides will generally not be attracted to the negatively charged OM or clay unless a divalent cation is bridging between the soil and the pesticide. OM and clay are often found bound together in a clay-metal-OM complex and the absorbed species are found on both the clay and OM surfaces. Most pesticides have a greater affinity to OM than the clay surfaces. When the ratio of clay to OM is the same but different clays are involved a general rule is to have greater adsorption to montmorillonite, illite than kaolinite clay types. Clay surfaces have several adsorption mechanisms such as ion exchange, coordination complexes, van der Waals forces and H-bonding. These mechanisms are specific for the chemical and clay mineral involved. Clay minerals generally have a high surface area and high charge

density thus readily react with any molecule that has a charge or dipole (Bollag, 1990). Water will compete with chemicals for adsorption sites on clay minerals and adsorption of a chemical may not be as great in moist soils as in dry soils (White, 1975). Multivalent adsorbed cations in clay can polarize water so that it can donate H atoms and absorb basic pesticides. A pesticide that becomes bonded to a clay mineral may become biologically unavailable both to organism and to degradation. In some cases, however, adsorption can promote abiotic degradation.

Hydrolysis of sorbed molecules is slower than in the aqueous phase (Macalady, 1983). Abiotic hydrolysis products in sediment systems were found to be, in many cases, the same as the products of hydrolysis in clear water (Macalady, 1983).

VOLATILITY

Volatilization is a function of the vapor pressure of the pesticide and is affected by pesticide concentration, soil-water content, adsorptivity of the soil, diffusion rate in soil, temperature, and air movement. Volatilization is most rapid immediately following application, although it will continue over an extended period of time, especially in a dry environment. Air currents provide for movement of pesticides from the site of application. Particulate matter and pesticide vapors are carried to high altitudes and for long distances. Volatilization may be minimized with adjuvants added to the spray mixture and care in selection of weather conditions that limit dispersal. The droplet size in spray applications must be sufficiently small as to arrive at the target and large enough to provide enough mass to hit the target and

not tumult from the path. The rate of evaporation is related to pressure and temperature by

$$\lambda_E = \frac{kP}{T}$$

where P is pressure, T is temperature, k is constant which is unit specific, and λ_E is the rate of evaporation (Hartley and Graham-Bryce, 1980). The rate of evaporation increases as temperature increases due to increased kinetic energy. Evaporation will occur as the number of molecules with sufficiently high energy to overcome the attractive forces of the surrounding molecules escape the liquid phase into the gaseous phase.

DIFFUSION AND FLOW

The chemicals that do hit the target organism must then make their way to the site of action within the organism. To transverse the various membranes to the site of action requires molecules to pass through lipid bilayers which are generally nonpolar. The chemical will be driven by the chemical concentration gradient to its partition concentration ratios appropriate for the two chemicals (layers) it is partitioning into. Adsorption of pesticides on to plant material, soils, clay, and OM may be reversible or irreversible, although in a heterogeneous compost system the distinction may not be clear. A compost system also, has a dynamic concentration gradient. As the compost material is broken down, it may release a chemical of

interest or bind it as the chemical composition is always changing. Molecular diffusion is a spontaneous process which occurs continuously while a concentration gradient exists. Molecular diffusion is constrained only by the matter forming the medium. Diffusion may be measured by using a principle known as Fick's (Tchobanoglous, 1985) law or the rate of diffusion in a given direction at a point normal to the cross sectional area. Fick's law is given by:

$$\frac{F}{A} = -D \frac{dC}{dx}$$

where F is the amount of chemical diffusing per unit time across area A and dC/dx is the concentration gradient in the same direction. The proportionality constant is the diffusion coefficient, D. Although these theoretical equations exist for calculating concentrations of chemicals in steady-state they provide limited value in natural systems where the concentration gradients are always changing. Diffusion in a porous medium is orders of magnitude slower than in solutions. The pathways in soil, plant material, and other organic systems is complicated by membranes, fats, organelles, and various other components that make up the medium. As pesticides move throughout the environment they encounter varying degrees of tortuosity of pathway. Blind pores (dead end) may exist in natural porous media and these contribute to micro rates of diffusion that deviates from the expected rate from Fick's law. The blind pores may also become traps and allow for increased chemical load

to the medium. The standard method of measuring adsorption is to apply several concentrations of a chemical in a solution to the adsorbate and measure the remaining chemical after a known time. In a compost system the reliability of creating a uniform system to test adsorption is in question. The compost and the lysimeter system both have intrinsic properties that can not be reduced to allow for accurate measurements of adsorption over time. The interplay between solute, solvent, and adsorbate may be generalized and measured at the expense of evading the specific factors controlling the movement of the pesticides.

Molecular diffusion will occur as long as there is a concentration gradient. The process is not energy dependent and will occur instantaneously and continuously. Diffusion can not dissociate from other forces such as flow. Though flow does not effect diffusion, it does change the concentration of solutes that are subject to the concentration gradients.

PHOTOCHEMISTRY

Many organic compounds undergo a chemical change when exposed to visible and/or ultraviolet radiation and occurs more often when atmospheric oxygen is present. A molecule that absorbs a quanta of radiation between 200 to 600 nm becomes electronically excited. The excited species can be expected to differ from the ground-state atom in reactivity. Not only does it possess a new electron configuration but it has extra energy. The relationship between energy, E and wavelength, λ is given by:

$$E = \frac{119627}{\lambda} \; kJ \; mol^{-1}$$

The photochemical wavelength range given above has energies similar to chemical bond energies found in organic compounds. Table 5 shows some average bond energies of organic compounds. The bond energy range is 140-800 kJ/mole and the ultraviolet-visible energy range has similar energies of 200-600 kJ/mole. If the electronic excitation energy can in some way be available for bond rupture, then chemical change may occur. If the electronic excitation is sufficient to overcome the energy of activation, then the excited species will react more rapidly than the ground state species.

Thermal energy may also be distributed in a molecule by translation, rotational, and vibrational excitation. The fate of the electronically excited species can be illustrated by Figure 1. Chemical change can occur as in pathway (i) of Figure 1 by dissociation, a result of direct reaction with the electronically excited species (process ii), isomerization (process iii), intermolecular energy transfer (process iv), intramolecular energy transfer (process v), luminescence (process vi), quenching (process vii), or ionization (process viii).

Photochemistry involves two processes, the process of absorption and the fate of the electronically excited species formed. The process of absorption involves a loss of intensity of electromagnetic radiation and the gain in energy of the absorbing molecule. The difference in energy of the ground state molecule and the excited is

equivalent to one photon of radiation. The converse process occurs when an excited state molecule gives up energy to electromagnetic radiation to increase the intensity of the radiation field.

Spontaneous emission is the major concern in photochemistry, which includes fluorescence and phosphorescence. Fluorescence is the emission of energy corresponding to a transition between states of the same multiplicity (singlet-singlet or triplet-triplet transition). In a singlet state all electrons are paired, where in a triplet two electrons are unpaired with parallel spins. Phosphorescence occurs after a singlet excited species releases energy via an intersystem crossing to a triplet state and the subsequent excited triplet emits radiation down to the ground singlet state.

As indicated in Figure 1 process (i) photodissociation can further be divided into optical dissociation, predissociation, and induced predissociation. Optical dissociation occurs when a electronically excited species has absorbed sufficient energy to dissociate into fragments, were predissociation occurs when an excited state is populated below its dissociation energy limit and a radiationless intramolecular energy transfer occurs which then puts the excited species into another electronic level above its dissociation limit and with this will dissociate to its fragments. The new state may also be less than the dissociate energy state and not result in dissociation. Induced predissociation becomes significant in species similar to the predissociation but they have added perturbation such as collisions, magnetic fields, or electric fields. These added perturbations contribute to the energy needed for

dissociation.

There exist two significant problems with descriptive photochemistry in large organic molecules. The absorption spectra are complex and may not be resolvable to determine the occurrence of optical, pre, and induced dissociation because of the close spacing of vibrational and rotational levels and the increased number of electronic states. The second obstacle is the multiple fragmentation pathways that exist for an excited polyatomic molecule. Although absorption is wavelength specific, in complex molecules fragment products may occur simultaneously.

Excited species which lead to chemical reaction include reactions such as isomerization, intermolecular reaction, and ionization. The intrinsic reactivity of the specific electronic arrangement, the effect of the excitation energy and the lifetime of the particular excited state contribute to the reactivity of the excited chemical. The intrinsic reactivity of excited state molecules have alterations in their geometry, dipole moment, electron donating and accepting characteristic which changes their acid-base properties. Ethene shows a geometric change from a planar molecule to a perpendicular molecule on excitation, this occurs due to the higher energy electron leaving the pi bond and only the sigma bond left. Perpendicular configuration allows for minimal electrostatic repulsion of the non-bonded electrons. Dipole changes are seen with absorption of electromagnetic radiation due to changes in distribution of electrons.

TABLE 5 Average Bond Energies (kJ/mole)

Organic Bond	Bond Energy	Organic Bond	Bond Energy
H-H	435	N-Cl	201
H-F	565	C-C	347
H-Cl	431	C=C	812
H-Br	364	C-H	414
F-F	155	C-O	351
Cl-Cl	243	C=O	707
O-O	138	C-Cl	326
O-H	464	C-N	293
O-F	184	S-S	264
O-Cl	205	S-H	339
N-N	159	P-H	318
N-H	389	P-Cl	

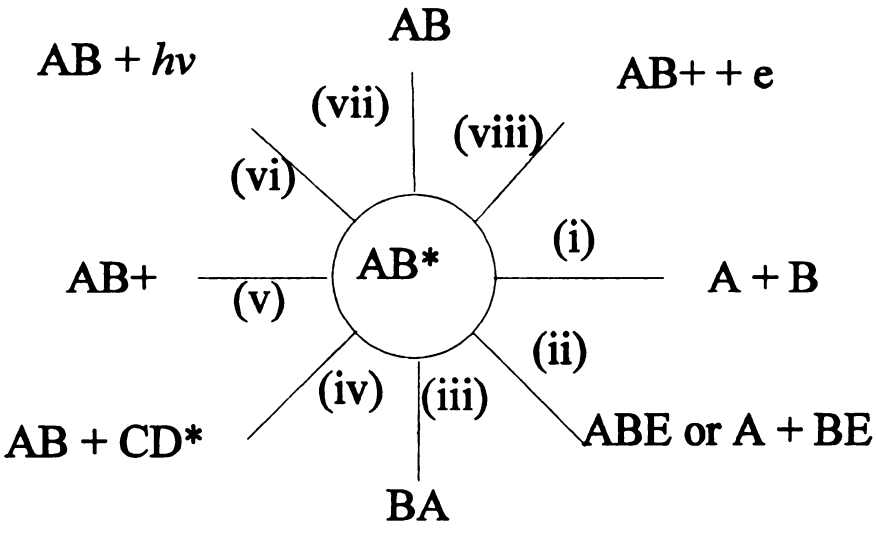


Figure 1 Photochemical Pathways

BIOCHEMICAL DEGRADATION

Chemicals are attacked by various anaerobic and aerobic bacteria, fungi, and other microbes. For a chemical to be degraded it must provide an energy resource to the attacking organism, otherwise the chemical may be enzymatically attacked as a mechanism to detoxify the chemical from harming the microbes environment. Though degrading organisms are ubiquitous, they may not occur in sufficient quantity as to need to compete for the anthropogenic chemical and never use them as a energy source, if this is the case the chemical will remain unchanged.

The composted grass is also attached by the degrading organisms, cellulose is hydrolyzed to smaller celludextrins subunits and the major degraders of lignin are higher fungi such as ascintcetes and basidiomycetes. There are four primary ligninases implicated in lignin breakdown. Ligninase the primary enzyme, catalyzes extensive oxidation of non-phenolic as well as phenolic unit in lignin. Laccase is a extracellular enzyme produced by white-rot fungi. This oxidizes the phenol to the phenoxy radical and transfers 4 electrons to O_2. Manganese Peroxidase functions similar to laccase in oxidation of the phenol. Lignin degradation also requires H_2O_2, this is provided by several different oxidases.

CHEMICAL DEGRADATION

The fate and persistence of chemicals is affected by such interrelated processes as solubility, photochemistry, volatility, sorption to OM and soil components, hydrolysis, and the combined actions of weathering such as wind, humidity, and

temperature so as to expose the chemical to breakdown. Oxidation, hydrolysis, reduction, and conjugation precipitate molecular changes. Chemical transformation and degradation may result in metabolites that are more toxic then the parent compound.

The major metabolite of phosphorothioates (general structure in Figure 2) are a hydrolysis product, 2,5,6-trichloro-2-pyridinol. The thio group is oxidized to oxon and reduction of the chlorine and replacement with SCH_3 is seen in chlorpyrifos. The fate of phenoxyalkanoic acids (general structure in Figure 3) degradation is by beta oxidation to remove two of the carbon fragments from the functional end of the alkanoic acid until only a hydroxyl is left. The ring structure is metabolized to CO_2.

Figure 2 General Structure of Phosphorothioate (Similar to Chlorpyrifos)

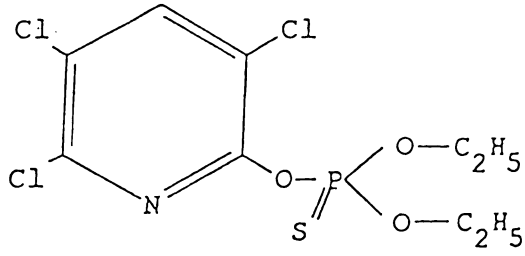
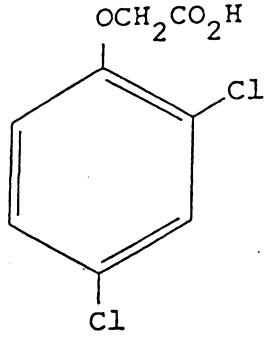


Figure 3 General Structure of Phenoxyalkanoic Acids (Similar to 2,4-D)



EXPERIMENTAL DESIGN

PART I - POTENTIAL FOR LEACHING

The objective of this study was to collect leachate from four lysimeters for analysis of applied pesticides. Installation of two lysimeters was completed in April of 1990 at Hancock Turfgrass Research Center (HTRC) in E. Lansing, MI. These lysimeters are termed soil monolith lysimters to mean that they are soil filled with a undisturbed soil core. Many researchers use soil packed lysimeters such as a study conducted at University of Georgia Agricultural Experimental Station in early 1991. The lysimeters constructed had gravel on the bottom, followed by sand, and then a soil mix with turfgrass about one year old. Soil OM and plant litter is largely responsible for the immobility of organic compounds in agronomic areas (Boyd et al., 1990). Sand and gravel are known leachers of organic chemicals. To make the lysimeters, a stainless steel cylinder 45 inches in diameter and 4 feet deep was driven into the soil, using a backhoe until the cylinder was completely filled with soil. The cylinder was then removed from the ground and a bottom with a drain was welded on and then placed back in the ground. The soil in the lysimeters is a Owosso sandy loam soil and Kentucky bluegrass turf was established on the surface. The second two lysimeters were installed in 1991 and constructed in the same manner as the earlier ones, except for the top 18-20 inches was removed and pea gravel and sand was put on. This was to simulate United States Golf Association greens mix as seen on the golf

course.

The pesticides were selected based on their use and leaching potential. Leaching potential was evaluated by water solubility, strength of adsorption to soil components, and half-life in soil. Pesticides with water solubilities below 10 ppm were not expected to leach and half-lives less than 30 days were not thought to be a problem but rather to degrade before reaching groundwater. The pesticides were first applied to the turfgrass August 12, 1991 and the application continued until September 4, 1992. The Application schedule is in Table 6 and it shows the time and rate of the applications. The the water leachate samples were collected from the lysimeter about every two weeks. If the volume of water coming through the lysimeters was large then the samples were obtained more often, to avoid loss. Method validation studies were conducted on each chemical and taken through the entire analytical method in triplicate. This was done by taking 100 g of distilled water and adding a known amount (spike) of pesticide to it. The results are isazophos 100 %, chlorothalonil 94 %, dicamba 129 %, 2,4-D 107 %, rubigan 95 %, propiconazole 86 %, triadimefon 71%, and metalaxyl 76 %. The recoveries greater than 100 % represent both analytical error and matrix enhancement of the residues. An acceptable analytical recovery would be 70 to 120 % (Leavitt, 1989). Storage recovery studies were done for each pesticides by storing spiked solutions for 6 months under the same conditions as the water samples. Storage recoveries assess the potential for losses occurring during storage (EPA, 1992). The results

are isazophos 95 %, chlorothalonil 68 %, dicamba 114 %, 2,4-D 92 %, fenarimol 120 %, propiconazole 93 %, triadimefon 120%, and metalaxyl 70 %.

Table 6 Pesticide Application Schedule to the Lysimeters for 1991 & 1992 Lysimeter 1 & 2 were constructed in 1990 & lysimeter 3 & 4 in 1991.

Application Date	Pesticide	kg ai/A	Lysimeter
8/21/91	isazophos	1.02	1 & 2
8/21/91	chlorothalonil	4.34	1 & 2
9/17/91	dicamba	0.05	1 & 2
9/17/91	2,4-D	0.52	1 & 2
5/3/92	rubigan	0.35	1 & 2
6/18/92	propiconazole	0.38	1 & 2
7/21/92	triadimefon	0.69	1 & 2
7/21/92	metalaxyl	0.69	1 & 2
7/21/92	chlorothalonil	4.34	3 & 4
8/5/92	metalaxyl	0.69	3 & 4
8/5/92	chlorothalonil	4.34	1 & 2
8/13/92	metalaxyl	0.69	3 & 4
8/20/92	chlorothalonil	4.34	3 & 4
9/4/92	chlorothalonil	4.34	3 & 4
9/4/92	metalaxyl	0.69	3 & 4

PART II - EFFECT OF COMPOSTING ON RESIDUES

This study was designed to determine the fate of triclopyr and 2,4-D (Turflon II Amine), chlorpyrifos (Dursban), triclopyr and clopyralid (Confront), isoxaben (Gallery), and flurprimidol (Cutless) in composted grass. June 12, 1991 the pesticides were applied to 0.23 acres of a mixed stand of Kentucky bluegrass (*Poa pratensis* L.), perennial ryegrass (*Lolium perenne*), and fine fescue (*Festuca* sp.). These were old stands of turf and varietal identification was not known. The pesticides were applied at 0.64 kg ai/A chlorpyrifos (Dursban 4E), 1.2 kg ai/A triclopyr plus 2,4-D (Turflon II amine), 0.91 kg ai/A triclopyr plus clopyralid (Confront), 0.34 kg ai/A isoxaben (Gallery 75 DF) and 0.34 kg ai/A flurprimidol (Cutless). Water was applied to plots that had isoxaben applied to move the chemical into the grass and thatch layer, to avoid volatilization or photodegradation. On June 13, 1991 the grass was clipped with a rotary mower set at 3.8 cm. The inner 0.17 acres were collected for the compost piles. The clippings were collected and brought to the Hancock Turfgrass Research Center (Michigan State University, E. Lansing, MI) to establish the compost piles. Each pesticide had two separate piles, one was left unturned for the duration of the study and another that was turned weekly for the first 8 weeks of the study. A control piles without any pesticide applied were made for use in background studies. Samples were collected at 1, 14, 28, 56, 128, and 365 days after treatment (DAT). The interior and exterior of each pile was sampled and placed in

a one quart mason jar and transported to the laboratory (Pesticide Research Center, Michigan State University, E. Lansing, MI), were they were stored at -10° C until extraction. The interior of the pile was 15 cm from the surface of the compost pile. This distinction became less apparent as the volume of the pile was reduced and essentially not distinct after about 6 months. Method validation recovery studies were conducted on each chemical and taken through the entire analytical method in triplicate. The results were triclopyr, 72.0 %; isoxaben, 66.4 %; flurprimidol, 143.5 %; clopyralid, 132.0 %; chlorpyrifos, 83.1 % ; and 2,4-D, 107.4 %. The nature of the sample from one sample to another and within a sample period was variable. The samples could be dry, wet, contain fungal growths, and various other debris with this great difference between samples, the analysis was unique with each sample. To account for some on the variation dry weight was reported for each sample. A 10 g sample was dried in a 104 ° C oven over night and put in a dessicator and weighed after cooling. Pertinent physio-chemical properties of each chemical are given in Table 7.

Table 7 Physio-Chemical Properties of the Test Chemicals

Chemical	Vapor P (mm Hg)	Water Solubility (mg/l)	Log K_{ow}	K_{oc}
2,4-D	$< 7.5 \times 10^{-8}$	715	2.74	60
Flurprimidol	1.53×10^{-7}	130	2.96	
Tricolpyr	1.26×10^{-6}	440	-0.69	
Clopyralid	1.2×10^{-5}	1000		
Isoxaben	3.9×10^{-7}	1-2	2.64	
Chlorpyrifos	1.87×10^{-5}	2	4.70	6070
Dicamba	3.40×10^{-5}	4500	2.46	0
Metalaxyl	2.20×10^{-6}	7100		16
Chlorothalonil	2.00×10^{-6}	0.6	2.88	
Propiconazole	4.20×10^{-7}	110		~100
Triademefon	1.5×10^{-7}	70	3.18	300
Fenarimol	2.20×10^{-7}	13.7	3.40	2000
Isazofos	1.30×10^{-4}	250	3.80	100

1 torr = 1 mm Hg = 75 bar = .075 mbar

ANALYTICAL METHODS

STANDARD PURITY

All standards were purchased from Chem Service or directly from the manufacturer. The purity of the standards is given in Table 8. Standards were prepared from the dry powder and diluted with a solvent appropriate for the solubility of the chemical and compatible with the GC analysis. The chemical structure of all pesticides used in the two studies are given in Figure 4 and 5.

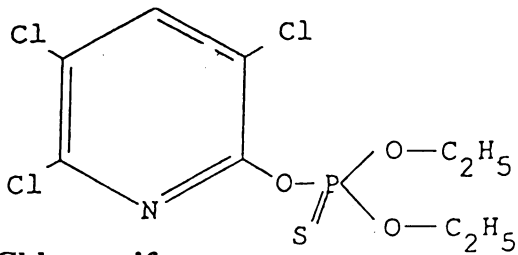
TABLE 8 Standard Purity

STANDARD	PURITY
2,4-D	98.0
2,4-D Methyl ester	99
Triadimefon	97.6
Chlorothalonil	99.8
Chlorpyrifos	99.7
Clopyralid	> 95
Dicamba	99.0
Flurprimidol	99.8
Isazophos	98
Isoxaben	92.5
Metalaxyl	99
Fenarimol	99.70
Propiconazole	97
Triclopyr	99.7

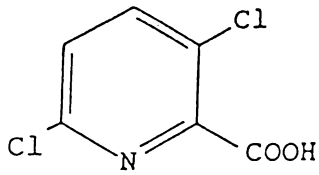
PART 1 - POTENTIAL FOR LEACHING

All samples were analyzed with High Performance Liquid Chromatography (HPLC), antibody assay kits, or Gas Chromatography (GC) to determine the amount of pesticide in the sample. Quantitation was performed by running a

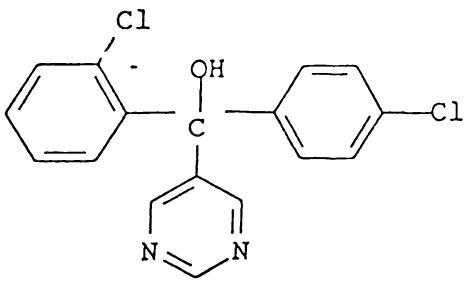
Figure 4 Pesticide Structures



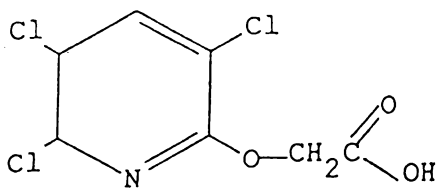
Chlorpyrifos



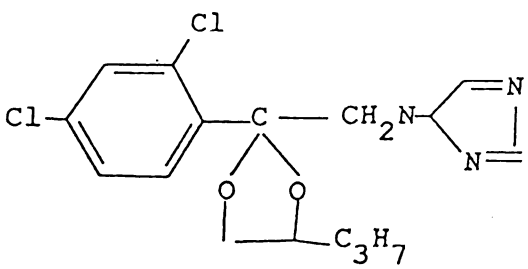
Clopyralid



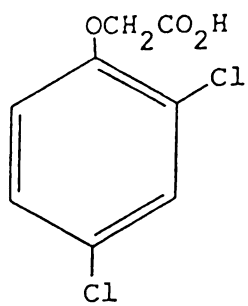
Fenarimol



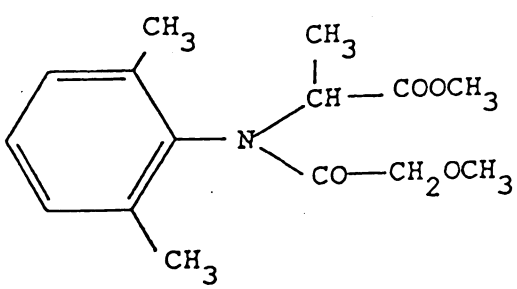
Triclopyr



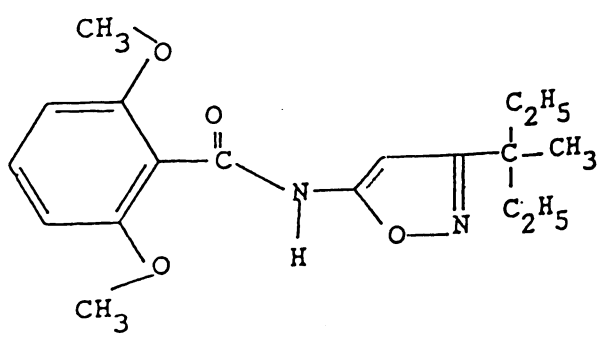
Propiconazole



2,4-D

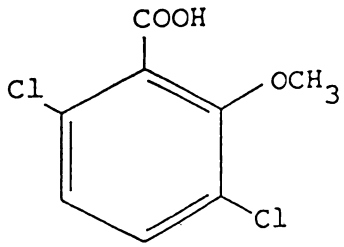


Metalaxyl

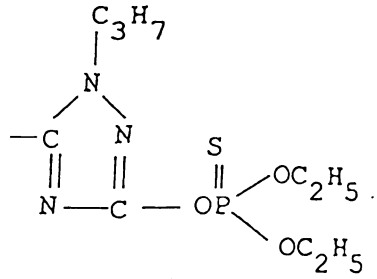


Isoxaben

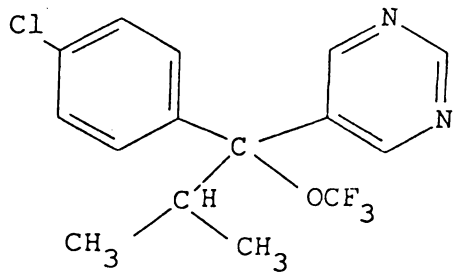
Figure 5 Pesticide Structures



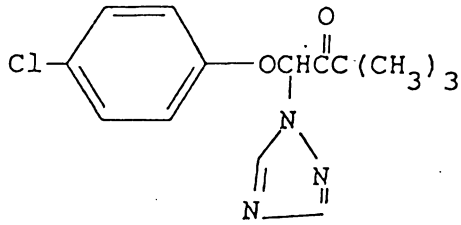
Dicamba



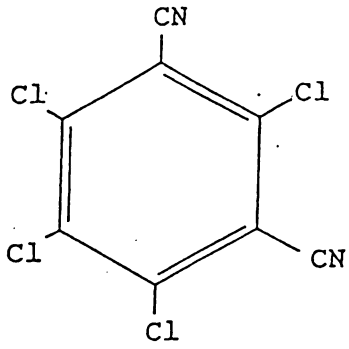
Isazofos



Fluriprimidol



Triadimefon



Chlorothalonil

standard curve for the pesticide in question to determine linearity of the range being quantified. The sample was concentrated or diluted to bring it into the linear range of the instrument for the pesticide of concern. A single point calibration standard was used to quantify the amount of pesticide in the sample. The calibration standard used to quantify the sample was one used to obtain the linear range of the standard curve.

To determine chlorothalonil (Tetrachloroisophthalonitrile) in water a 100 g sample (PAM-FDA, 1970) was placed in a 250 ml separatory funnel with 20 g of NaCl to increase the polarity of the aqueous solution. The water was extracted with 20 ml of hexane three times and the hexane portions were combined and reduced to about 1 ml for ECD-GC analysis.

Fenarimol (El-Hadidi,1993) (3-(2-chlorophenyl)-3-(4-chlorophenyl)-5-pyrimidinemethanol) was determined by extraction of 100 g of water with 50 ml of 10% w/w NaCl solution and extracted twice with 40 ml of methylene chloride. The methylene chloride portions were taken to dryness with a Turbo-Vap at 40-45 °C. An alumina column was prepared with a solvent extracted glass wool pledget with about 13 g of alumina and 1.7 cm of Na_2SO_4. The column was rinsed with 10 ml of methylene chloride. The methylene chloride rinse is followed with 40 ml of 9:1 v/v methylene chloride:ethyl acetate solution and this was discarded. The fenarimol was eluted with 99:1 v/v methylene chloride: methanol v/v solvent mixture. The eluant was taken to dryness and brought to volume with hexane for

ECD-GC analysis.

Dicamba (2-Methoxy-3,6-dichlorobenzoic acid) (PAM-FDA, 1970) was determined by acidifying a 100 g sample to pH 1 with 10 % H_2SO_4. The acidic solution was extracted with 50 ml of diethyl ether 3 times and the ether extracts are combined and reduced to about 10 ml. A Celite column was prepared with 100 g of Celite and washed with 40 ml of equal volumes of 2 M NaH_2PO_4 and 2 M K_2HPO_4. Equilibrate 1.5 l of diethyl ether with 100 ml of the phosphate buffer and remove the aqueous portion after layers have separated. Add 15 g of the washed Celite to a 1 cm i.d. column with equilibrated ether to keep packing covered. The extract was added to the column and eluted with 265 ml of phosphate buffered ether. The volume of eluant was reduced to about 2 ml for deriviatization with diazomethane. The volume was reduced and brought to volume for ECD-GC analysis.

Triadimefon (1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-(butanone) was extracted from 100 g water with 50 ml of chloroform 3 times and the extracts are combined. The extracts are taken to dryness and a Florisil column was prepared with a glass wool pledget placed in the bottom, 10 g of 2.5 % deactivated Florisil and topped with 5 g of anhydrous Na_2SO_4 to a 20 mm i.d. column. The column was rinsed with 6:4 v/v hexane:ethyl acetate mixture. The residue was dissolve in 10 ml of the hexane:ethyl acetate mixture and transferred to the column. A flow rate of 2-3 drops per second was maintained of 150 ml of

hexane:ethyl acetate and all eluant was collected. Take the extract volume to dryness to remove the hexane:ethyl acetate and bring up in hexane for compatibility with the GC for analysis.

Isazofos (0-(5-chloro-1-{methylethyl}-1H 1,2,4-triazol-3-yl)O,O-diethyl phosphorothioate) was extracted with 20 ml of chloroform 3 times. The NaCl was added to the water to increase the polarity so as to favor partitioning isazofos into the organic phase. The chloroform extracts were combined and reduced to about 1 ml in the Turbo-Vap. Analysis of isazofos was with the nitrogen/phosphorus sensitive detector equipped with a DB-5 capillary column.

Millipore Corporation's immunoassay test kits were used to determine 2,4-D in water samples obtained from the lysimeters. The samples detected on the basis of polyclonal antibodies which compete for 2,4-D residues (in the sample) and 2,4-D enzyme conjugate (in the kits). The 2,4-D in the sample competes with the 2,4-D enzyme conjugate for a limited number of antibody binding sites. Solutions of substrate and chromogen were added to the test tubes. The 2,4-D enzyme conjugate causes the chromogen to turn blue. The quantity of 2,4-D was determined by the intensity of the color. The greater the amount of 2,4-D the lesser color development because of the competition with the enzyme conjugate. The amount was quantified by visible spectroscopy at 450 nm.

Metalaxyl (N-(2,6-Dimethylphenyl)-N-(methoxyacetyl)-alanine methyl ester) was extracted from 100 ml of water with two 25 ml portions of toluene and

put through 0.5 g of anhydrous Na_2SO_4 to remove the aqueous residue. The toluene extract was reduced to dryness and brought up to 4 ml with methanol and was ready for HPLC analysis. The HPLC column was a Speri-5 RP-18, 5 micron which was 220 X 4.6 mm i.d. A 50:50 v/v acetonitrile and water was applied with a flow rate of 1.5 ml / min. A 50 ul injection loop was used for sample injection. A UV detector at 220 nm is used to detect Metalaxyl.

Propiconazole(1-{2-(2,4-dichlorophenyl)4-propyl-1,3-dioxolan-2-ylm-ethyl]-1H-1,2,4-triazole) was extracted from water by adding 20 g NaCl to move the organic compounds out of the water and into dichloromethane. Three 20 ml portions of dichloromethane were used to extract propiconazole from the aqueous phase. The three portions of dichloromethane were combined and reduced to 1 ml by adding 1ml of isooctane as a keeper solvent. The extract was now ready for GC injection. A N/P flame ionization detector was used for detection.

PART II - EFFECT OF COMPOSTINGS ON RESIDUES

All samples were analyzed with High Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC) to determine the amount of pesticide in the sample. Quantitation was performed by running a standard curve for the pesticide in question to determine linearity of the range being quantified. A single point calibration standard was use to quantify the amount of pesticide in the sample.

Determination of chlorpyrifos (O,O-Diethyl-O-[3,5,6-trichloro-2-pyridyl]-phosphorothioate) in grass was with an Electron Capture Detector (ECD) GC. Approximately 10 g of grass was extracted for each analysis. The grass was homogenized with 100 ml of acetone for 5 to 10 minutes and then filtered with 0.5 cm of HyFlo Super Cel (Johns-Manville) in 150 ml sintered glass funnel on a vacuum filtering assembly. The Hyflo Super Cel (diamtomaceous earth) is an extremely weak adsorbent and was used for very polar contaminants (Heftmann 1967). The extraction was repeated with a fresh 100 ml of acetone. The filtrates are combined and taken to dryness.

The extract was transferred with 20 ml of hexane to a prewashed column for cleanup. The extract was placed in a column with 1.5 g of 60 to 100 mesh silica gel (oven dried at 110° C for 4 hours) with a glass wool (solvent extracted) pledget in the bottom of a 1 cm internal diameter glass column. Silica gel has a slightly acidic adsorbent character. The surface hydroxyls attached to silicon atoms are responsible for the adsorptive properties which are adsorption of polar

or unsaturated molecules (Heftmann 1967). Three 20 ml portions of hexane was used to elute the sample through the column. The combined eluted hexane was taken to dryness with a Turbo-Vap and brought to volume with acetone for the GC injection.

Gas chromatography was performed by Perkin-Elmer 8500 instrument equipped with Ni^{63} ECD. The oven temperature was held at 200° C, the injector temperature was 250° C, and the detector was 345° C. The carrier gas (helium) flow rate was 15 psig and the makeup gas is N_2. A DB-5 capillary column 0.25-um film thickness 30m long with and internal diameter of 0.32 mm. The chlorpyrifos standards were obtained from Chem Service, Inc. with a purity of greater than 99 %.

Determination of clopyralid (3,6-Dichloro-2-pyridinecarboxylic acid) (Galoux, 1982) in grass was done with a ECD GC. About 10 g of grass was homogenized for 5 minutes with 150 ml of 0.25 M KOH. The extract was transferred to a 500 ml separatory funnel via a Whatman # 1 filter. One hundred ml of diethyl ether, 5 g of NaCl and 20 ml of H_2SO_4 were added to the separatory funnel. The diethyl ether layer was collected and the extraction was repeated with fresh diethyl ether. The combined extracts were put through a anhydrous Na_2SO_4 bed to remove any water and the volume was reduced to about 1 ml.

The clopyralid extract was then esterified with diazomethane, the volume was reduced to < 0.5 ml and then brought to volume for GC analysis. The

clopyralid samples were run with the same GC conditions as the chlorpyrifos samples. The clopyralid standards were obtained from Chem Service, Inc.

Determination of triclopyr (3,5,6-Trichloro-2-pyridinooxyacetic acid) in grass was done with a ECD GC. The 10 g sample was shaken for 10 minutes with 6 g of NaCl, 1 ml of 9 M H_2SO_4, 50 ml of diethyl ether and 50 to 100 ml of H_2O. The extract was filtered through a Whatman # 1 with a vacuum applied. The filtrate was then transferred to a separatory funnel and the ether portion was retained. The aqueous portion and filter paper was then shaken with 50 ml of diethyl ether for 10 minutes. The ether portion was separated and combined with the other ether portion. The extract was washed twice with 20 ml of 10 % NaCl w/v, and dried over anhydrous Na_2SO_4. The volume was then reduced to almost dryness.

A silica gel column was prepared by adding 3 g of silica gel to a 1 cm internal diameter glass column in a hexane slurry. The column was washed with 100 ml of toluene and hexane (10 % : 90 %) v/v. The extract was added and then eluted with 100 ml toluene and hexane (35 % : 65 %) v/v. The volume was reduce to < 0.5 ml and esterified with BF_3 in methanol. The extract was held at 80 °C for 1 hour. The sample was then transferred with hexane to a separatory funnel, washed twice with 20 ml of 10 % NaCl w/v, and dried over anhydrous Na_2SO_4. The sample was reduced in volume for the GC. The GC used was the same as was used for the chlorpyrifos samples.

Flurprimidol (alpha-(1-methylethyl)-alpha-[4-(trifluromethoxy)phenyl]-5-pyrimidinemethanol) in grass was done on the ECD GC using solid phase extraction with an basic alumina column (Alltech 500 mg). The basic alumina has a hydrophilic polar surface character capable of adsorbing the hydrophilic species from the nonaqueous solutions. The grass was refluxed for 1 hour in 4:1 methanol:water v/v in a boiling flask with water cooled reflux condensing tube. After cooling, the extract was filtered through a Whatman # 7 filter into a separatory funnel with 30 ml of 5 % NaCl w/v. The flurprimidol solution is extracted three times with 50 ml of hexane and the hexane extract was then passed through anhydrous Na_2SO_4. The hexane extract was then evaporated to dryness and brought to 3 ml with dichloromethane and put on to the Alumina Sep-Pak cartridge. The flurprimidol was eluted off of the Sep-Pak with 3:1 dichloromethane:methanol v/v solution. The Perkin-Elmer GC with the same conditions is used for the flurprimidol as was used for the Chlorpyrifos samples.

Determination of isoxben (N-[3-(1-Ethyl-1-methylpropyl)-5-isoxazolyl]-2,6-dimethoxybenzamide) in grass was done with HPLC. The grass was ground and extracted with 150 ml of methanol by shaking for one hour on a gyratory shaker. The sample was then filtered through a Whatman # 1 filter paper in a Buchner funnel with the aid of vacuum. The plant material and filter paper were returned to a pint jar and shook for half an hour with 100 ml of methanol. Again the extract was filtered as above in a Buchner funnel and the filtered extracts were

combined and transferred to a 1000-ml separatory funnel. Seventy-five milliliters of a 5 % NaCl solution and 200 ml of water were added to the separatory funnel. The solution was extracted with two 125 ml portions of n-Hexane and the n-Hexane was discarded. This was followed with three 70 ml extractions with dichloromethane. The dichloromethane was passed through anhydrous sodium sulfate bed to remove the water. The dichloromethane extract was evaporated to dryness and transfer through a alumina/florisil column with dichloromethane. The column was washed with 50 ml of 4:1 dichloromethane/ethyl acetate v/v and 25 ml of 99:1v/v dichloromethane/methanol and the eluate was discarded. Fifty ml of 99:1v/v dichloromethane/methanol was put on the column and the eluate was collected. The solvent volumes used in the alumina/florisil column should be verified with each new batch of alumina and florisil. Evaporate the eluate to dryness and add 2 ml of 2 % $KMnO_4$ w/v and swirl. Then add 2 ml of 2 M KOH, followed by 4 ml of dichloromethane and shake vigorously. Let the solution stand for 5 minutes and remove the dichloromethane layer and dry though anhydrous sodium sulfate. Repeat the addition of dichloromethane step twice and combine dichloromethane washes. Evaporate the dichloromethane to dryness and bring to volume for HPLC analysis in the mobile phase of 60:40 methanol/water.

Determination of 2,4-D (2,4 dichlorophenoxy acetic acid) was done by extraction of 10 g of grass with 5 ml of H_2O, 8 ml of H_2SO_4, and 50 ml of methanol by shaking for 20 minutes. The extract was filtered through a Whatman

#1 Filter. The process was repeated with fresh solvents on the filter paper. The combined filtrates are reduced to the H_2O. The aqueous extracts are extracted with two portions of 50 ml of methylene chloride and reduced to about 1 ml with N_2. A 1 cm i.d. Florisil column was prepared with 3 g of Florisil and about 2-4 mm of Na_2SO_4 and 30 ml of petroleum ether was rinsed through and discarded. The sample extract was placed on the column, followed by 15 ml of petroleum ether and the eluate was discarded. Elution of 2,4-D was accomplished by adding 25 ml of 1:1 v/v petroleum ether and ethyl ether. The eluant was reduced to less than 0.5 ml.

The acidic group on 2,4-D was esterified to a methyl ester by reaction with diazomethane. The extract was reduced to less than 0.5 ml and brought up to volume for ECD-GC analysis.

RESULTS AND CONCLUSIONS

PART I - POTENTIAL FOR LEACHING

The pesticides generally did not make it through the lysimeters to the collection point or were not of sufficient concentration to be detected. Each pesticide has a finite capacity for sorption to the soil in the lysimeter due to the finite amount of soil available. The concentration of the residues from the leachate analysis are given in Appendix B. The rate of accumulation in the soil is influenced by the rate of the pesticide addition to the soil and the rate it is moved out of the soil. The rate of addition is dependent on the sources and application schedule, while the rate of disappearance is related to the concentration, volatilization, degradation, photolysis, runoff, and leaching, all of which occurs continuously.

Immediately after spraying, the chemical will partition between air, water, soil, and biota. The tendency of a persistent chemical to partition to a specific phase in the environment, determines were in the environment it will be found and the relative concentration in these environmental phases. If any of the phases has a sink or essentially infinite capacity as compared to the other phase then the chemical will go to infinite dilution and detection will not be achieved in the lysimeter. Of course if the chemical is hydrophilic it will stay within the water and if of sufficient concentration will be detected during analysis. K_{ow} is a good indicator of hydrophobicity and would predict the favored partition phase a

chemical would be found. Soil sorption is often shown to have a correlation to K_{ow}, the partitioning of a solute between two immiscible solvents, water and octanol (Chiou and Schmedding, 1982 and 1983). This relationship would imply if a compound has a high K_{ow} then a high sorption to soil, especially if the soil has high organic content. K_{ow} can be used to predict the potential for sorption to nonpolar or polar compounds. If a chemical tends to favor sorption to OM and the soil is of high OM then the chemical will not be seen in the lysimeter drainage in sufficient quantity to be above instrumental detection levels. Volatilization, chemical degradation, runoff, and sorption both in soil and thatch remove the intact pesticide from moving down through the lysimeter. Degradation by microbes is affected by the amount of moisture and sorption of the pesticide to the soil or thatch. In a study conducted at Kentucky State University (KSU) it was shown that landscape features such as living turf mulch between crop rows prevents surface water pollution from pesticides but increases infiltration of pesticides into the soil profile (Byers, 1995). The treated turf in the KSUstudy though it did have greater infiltration depths , down to 1.5 m, within 3 months it was only at trace concentrations, which was similar to the conventional tillage. Transport of pesticides by runoff is a function of rainfall, hydration of the soil, and vegetative characteristics. If there is a lag between application and rainfall, the probability of runoff is decreased due to plant uptake, degradation, and volatilization. Each chemical will volatilize at a different rate due to its vapor

pressure, sorption to soil or plants, hydration of the soil, temperature, and pesticide concentration. If the water solubility of a chemical is sufficiently high as to facilitate transport with water as it moves up and down the soil horizon in response to moisture levels, it will not be seen in the lysimeter drainage until the lysimeter has been sufficiently hydrated to drain past the vadose layer of soil.

The soil column will be composed of solid soil particles, water, air, and organic oils from breakdown of organisms and plants. The pesticide will partition between the different phases of hydrogeological environment according to its chemical properties. The lateral movement in the lysimeter is reduced due to the sides of the lysimeter so disregarding this movement or assuming it to be negligible will be appropriate for this discussion. The potentially highest concentration of a chemical to go through the lysimeter was chlorothalonil at 1.4 mg/ml (1400 ppm) and the lowest dicamba 0.3 ppm. This concentration assumes the mass to move at constant velocity through the soil profile but this will not occur. The chemical may travel as a vapor or liquid dissolved in the water or as a oil at the junction of the water. The pathway of transport will have different porosity and constituents to retard the velocity which will cause the chemicals to dilute along the path.

Chlorothalonil was not detected in the lysimeter drainage and that can be supported by its insolubility in water (0.6 mg/l) and high affinity for silty and clay loam soils. The half-life in aerobic soils is from one to three months but combined

with its hydrophobic character it is unlikely to find its way to groundwater. In laboratory studies Chlorothalonil has been shown to hydrolyze to 2,3,5-trichloro-4-hydroxyisophthalonitrile, with half-lives as short as four hours (Lawruk, 1995).

Dicamba was not detected in the lysimeter over the course of the study. Dicamba is highly water soluble (500,000 mg/l) and with this it would seem likely to make into the water before break down. Leaching from the soil should occur in 3-12 weeks but the typical half-life is one to four weeks so if the chemical does not immediately move to the water phase then degradation may further reduce concentrations in the soil and thatch layer.

Metalaxyl has a one to eight week half-life in soil under typical field conditions and degradation may be accelerated by photodegradation to about 2 weeks. Metalaxyl was not detected in the lysimeter and degradation and binding to plant material may account for this.

Triadimefon was detected twice in one lysimeter and three times in another, at essentially the same time in each lysimeter. The first detection was 56 days after application of triadimefon to the site in lysimeter 2, 86 days in lysimeter 1, 131 days again in both lysimeters, and a final detection at 146 days in lysimeter 2. The compound is very stable in water at pH 3.0, 6.0, and 9.0 up to 28 weeks. If the chemical moved into the water soon after application this may account for the detection on the various days because the soil half-life is about eighteen days. The rainfall and irrigation data for the period from 1 day before to 9 days after

triadimefon application showed 8.01 cm of precipitation. The large amount of precipitation could facilitate the travel through the turf and thatch layer, directly to the water in the soil profile.

All the remaining compounds were not detected and this would be due to an array of causes. A similar study was conducted at the University of Georgia College of Agriculture Experimental Station (unpublished data conducted by A. E. Smith and D. C. Bridges) with lysimeters 20 % (about 2.2 X 10^{-4} m^3)of the size used in the studies conducted at MSU. Dicamba was applied at 0.07 kg/ha and 2,4-D at 0.28 kg/ha and the leachate was having positive detection of 2,4-D at 21 days and dicamba at 7 days after treatment. The leachate was collected for 70 days and positive detection occurred throughout that time. The lysimeters were constructed with 10 cm gravel, 7.5 cm coarse sand, and 35 cm of sterilized rooting mix. The sand and gravel are natural leachers which contrasts to the lysimeters used at MSU, being of undisturbed sandy loam soil. The sterilization eliminates microbes for degradation of the pesticides. Even with this system that favors leaching over the MSU lysimeters less than 1.0 % of the applied pesticides were recovered in the lysimeter leachate.

Although the intact pesticides were not detected in the leachate, it supports the idea of degradation, sorption to thatch or turf, or moving away from the lysimeter by volatilization or photodegradation on the surface to be occurring. If the pesticide remains in the turfgrass system, then assessing the use of composting

to degrade pesticide as a means of decreasing residue levels would be appropriate.

PART II - EFFECT OF COMPOSTING ON RESIDUES

Patterns of chemical loss in the compost piles was similar in all of the pesticide treatments. Isoxaben (Figure 10 and 11), flurprimidol (Figure 12 and 13), triclopyr (Figure 8 and 9), and chlorpyrifos (Figure 6 and 7) all were below the detection limit of the methods used after 365 days. Clopyralid (Figure 16 and 17) and 2,4-D (Figure 14 and 15) were reduced to 1.4 ppm and 1.3 ppm respectively after 365 days. The chemicals tend to show a biphasic degradation. There was generally an initial rapid dissipation rate followed by a slower process. The first phase of chemical loss may be related to volatilization and photolysis while the second phase chemical loss by microbial degradation. The reasoning being that the microbial population was not there or other energy sources were available at the earlier times for the microbes to consume. Table 9 shows the first-order decay constants, k (day^{-1}) (Frederick, 1994), for each pesticide at various times. The values are calculated between the first detection (initial concentration or A) and the next interval with a detected concentration (X) sample interval. The initial recovery for each chemical is A, where X equals the concentration at time t. These values were determined by the equation:

$$X = Ae^{(-kt)}$$

The variation in the k value would not lend itself as a good parameter to predict chemical loss from the compost pile. If the k value was used for the entire study

you would predict all chemicals to leave the pile either by loss to environment or metabolic changes.

The sampling in the field had inherent difficulties. The compost piles were not homogeneous masses. Within the piles there could be aggregate population of degrading organisms and this produced unequal rates of decline of the chemicals within the piles. The sampling suffered from aggregate distribution of chemical and microbes and may account for a portion of the variation seen in the results. If the sampling occurred in an area were the population of degrading organisms was high, then the chemical may be absent or at a low concentration and conversely if sampling took place at an area of low population of degrading organisms then the chemical concentration may be high.

The pesticide concentrations of each chemical in each is given in Appendix A (pp 60- 62) and the graph that accompany the text are normalized to the highest value, with the highest normalized value being one. This allows for comparison between chemicals of the relative changes without comparing absolute concentrations, ie. allows evaluation of the timing of the changes. All of the values given for the pesticide concentrations are given in dry grass weight. The reason for choosing dry weight was that the variation in the composition of the samples appeared to be great. The determination of percent water confirmed the variation in physical appearance. The percent water ranged from < 1 % to greater than 70 %.

Figure 6 Chlorpyrifos Inside the Pile

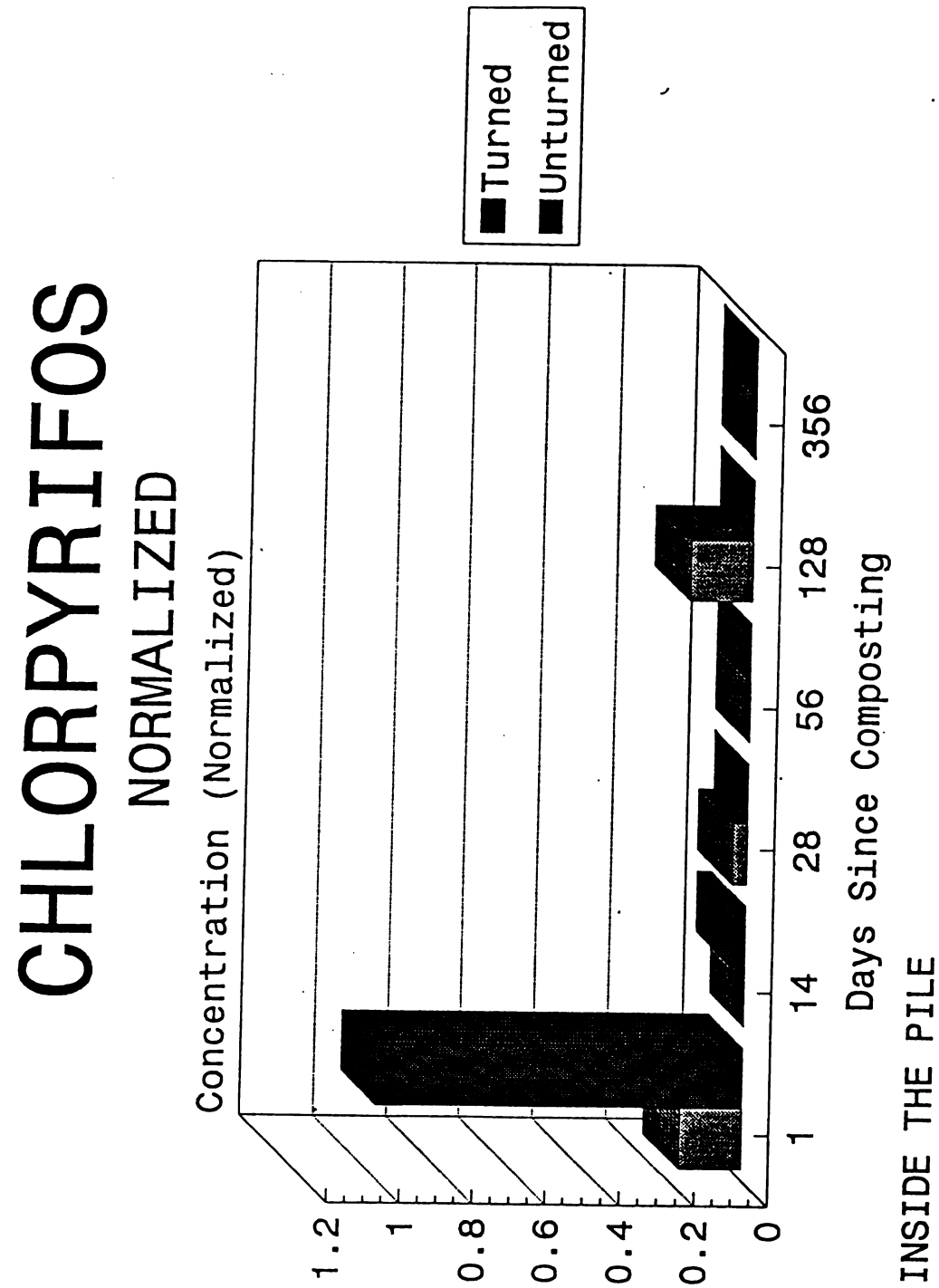


Figure 7 Chlorpyrifos Outside the Pile

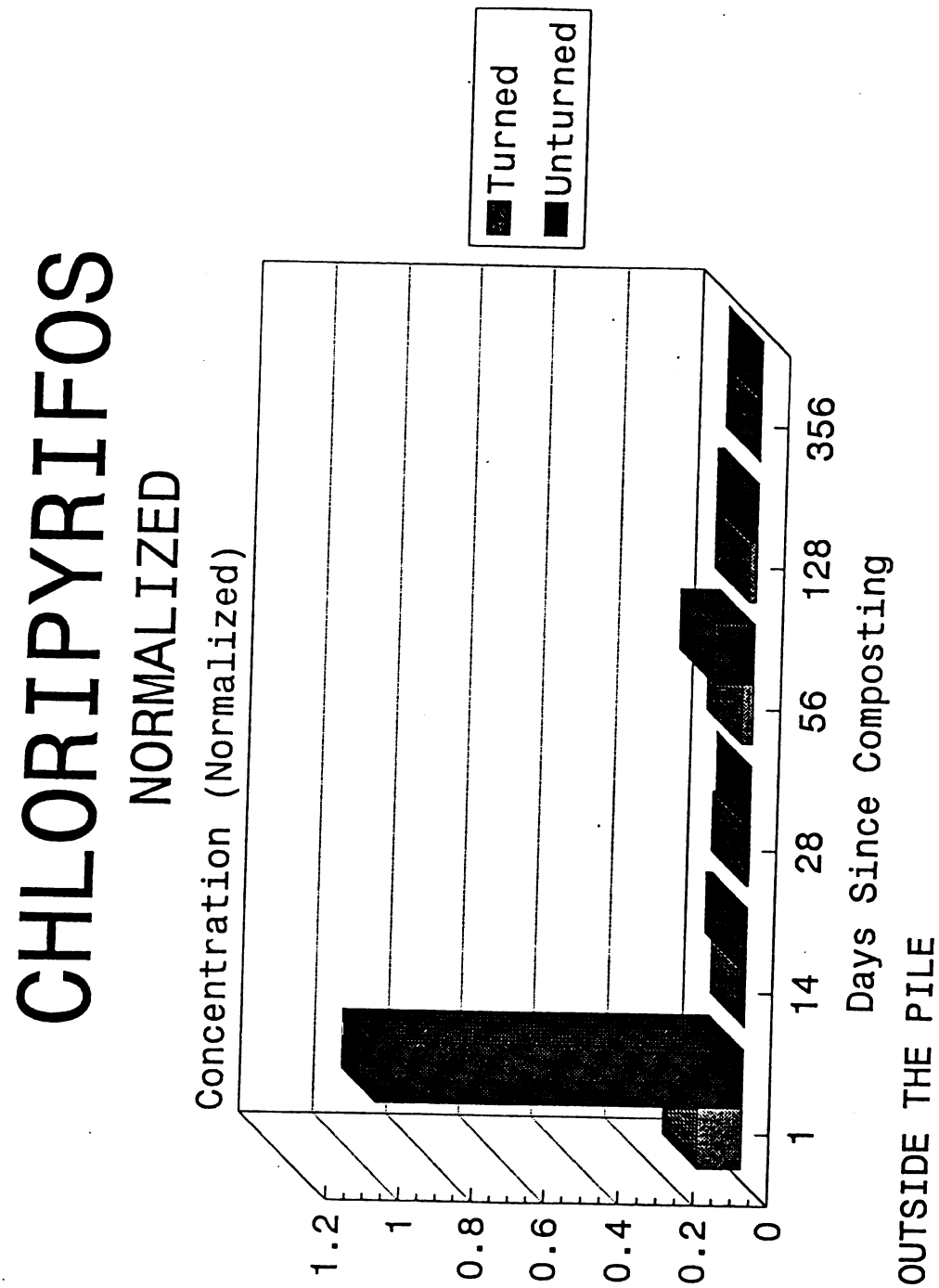


Figure 8 Triclopyr Inside the Pile

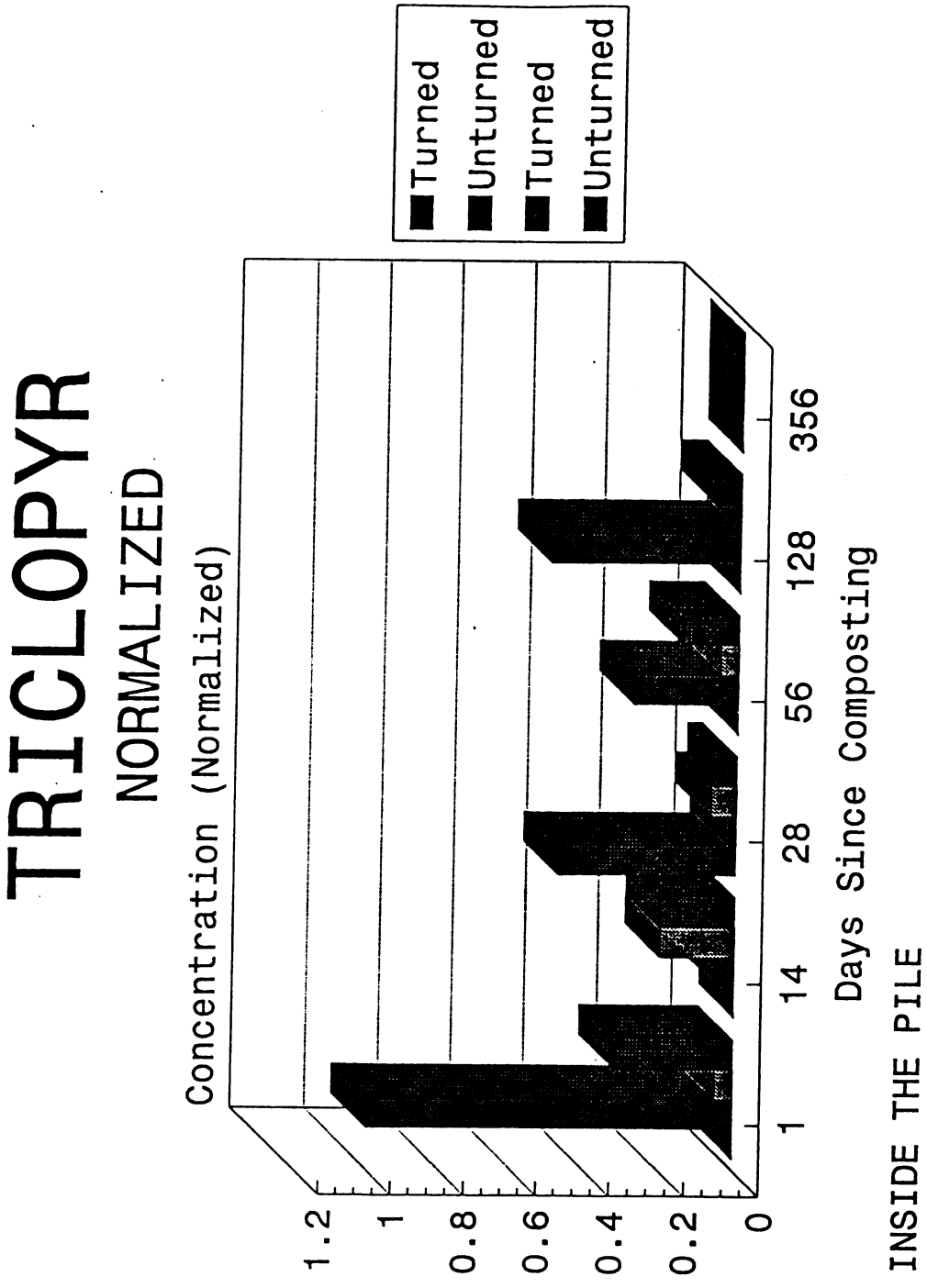


Figure 9 Triclopyr Outside the Pile

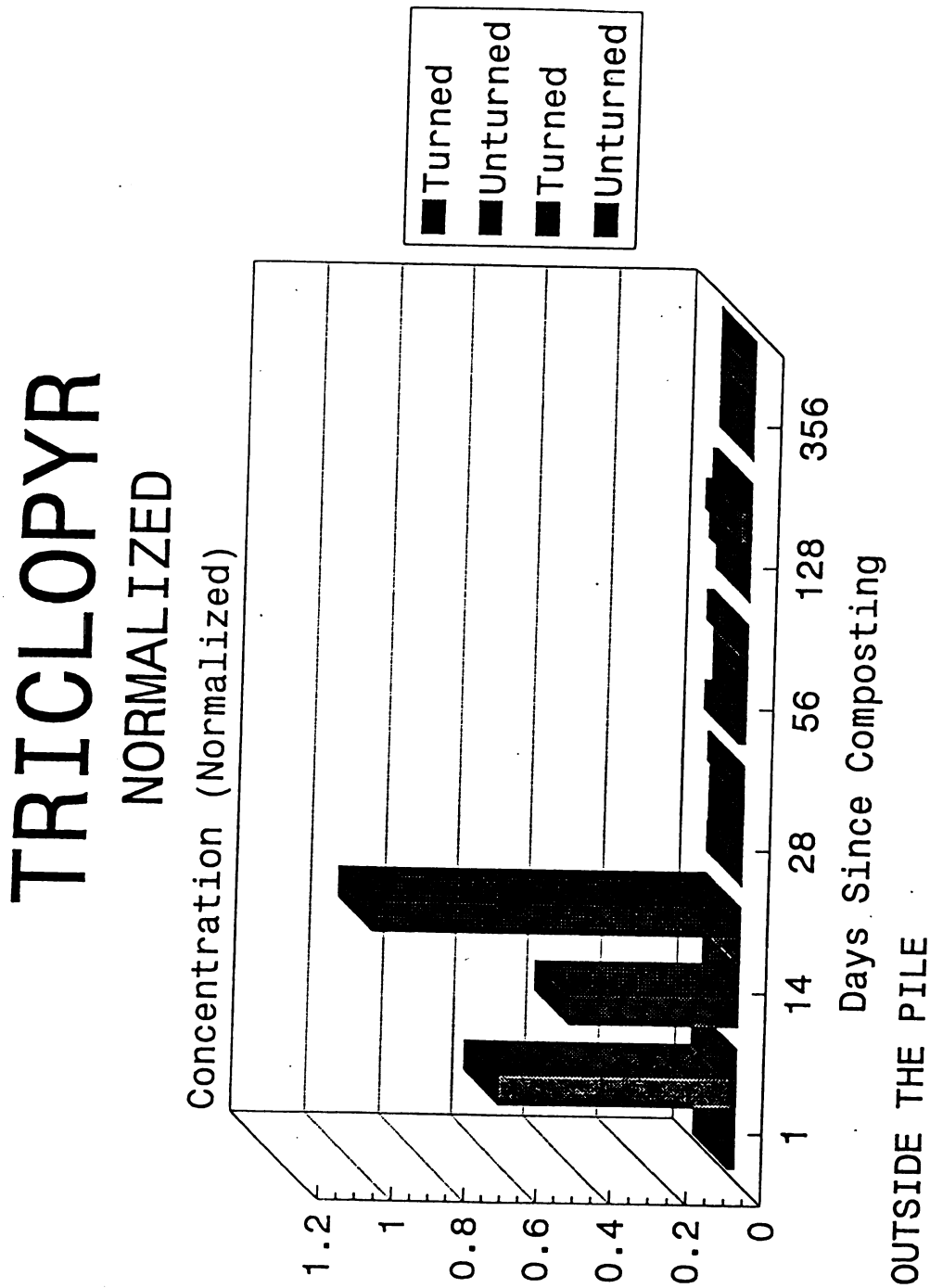


Figure 10 Isoxaben Inside the Pile

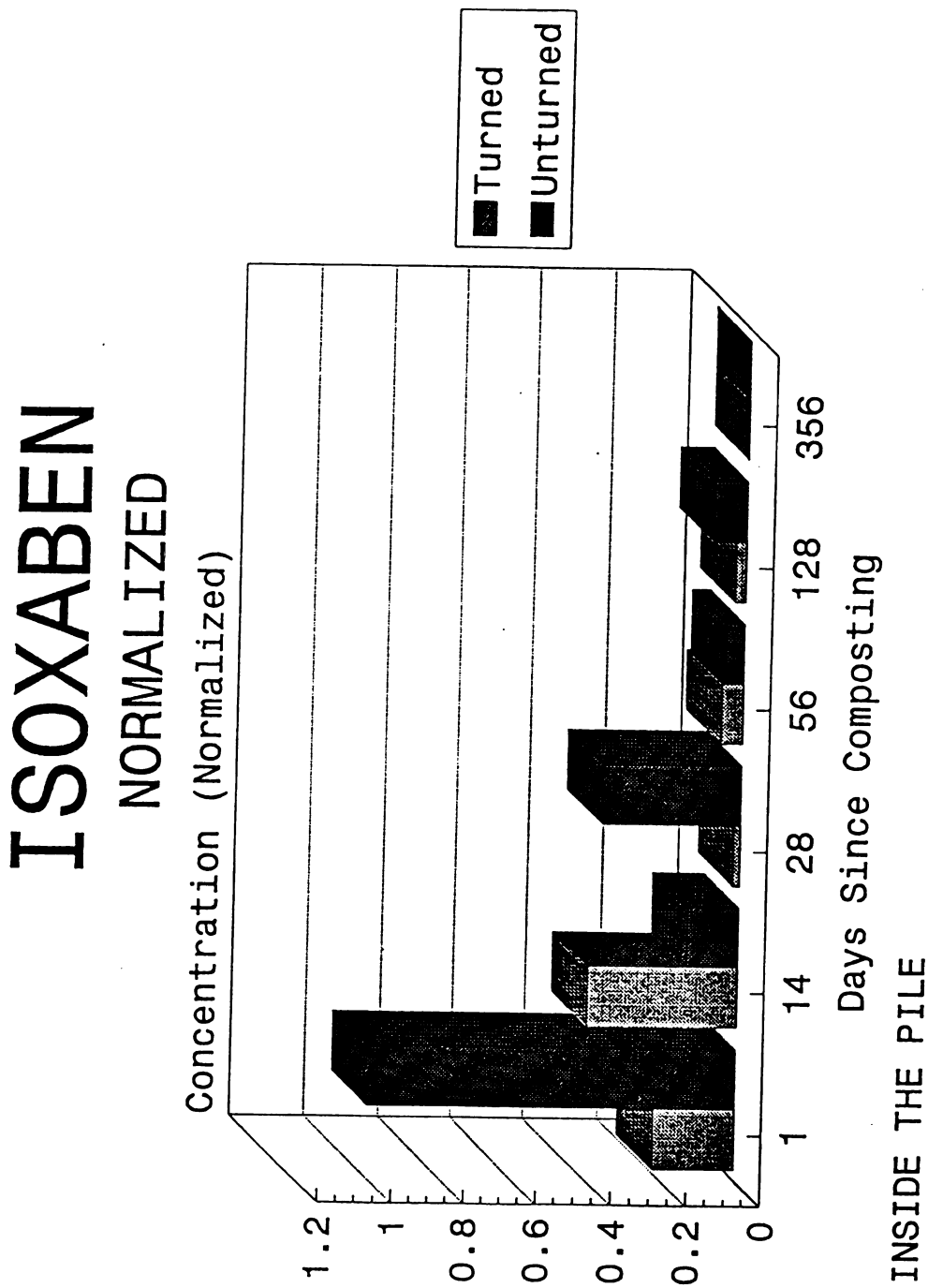


Figure 11 Isoxaben Outside the Pile

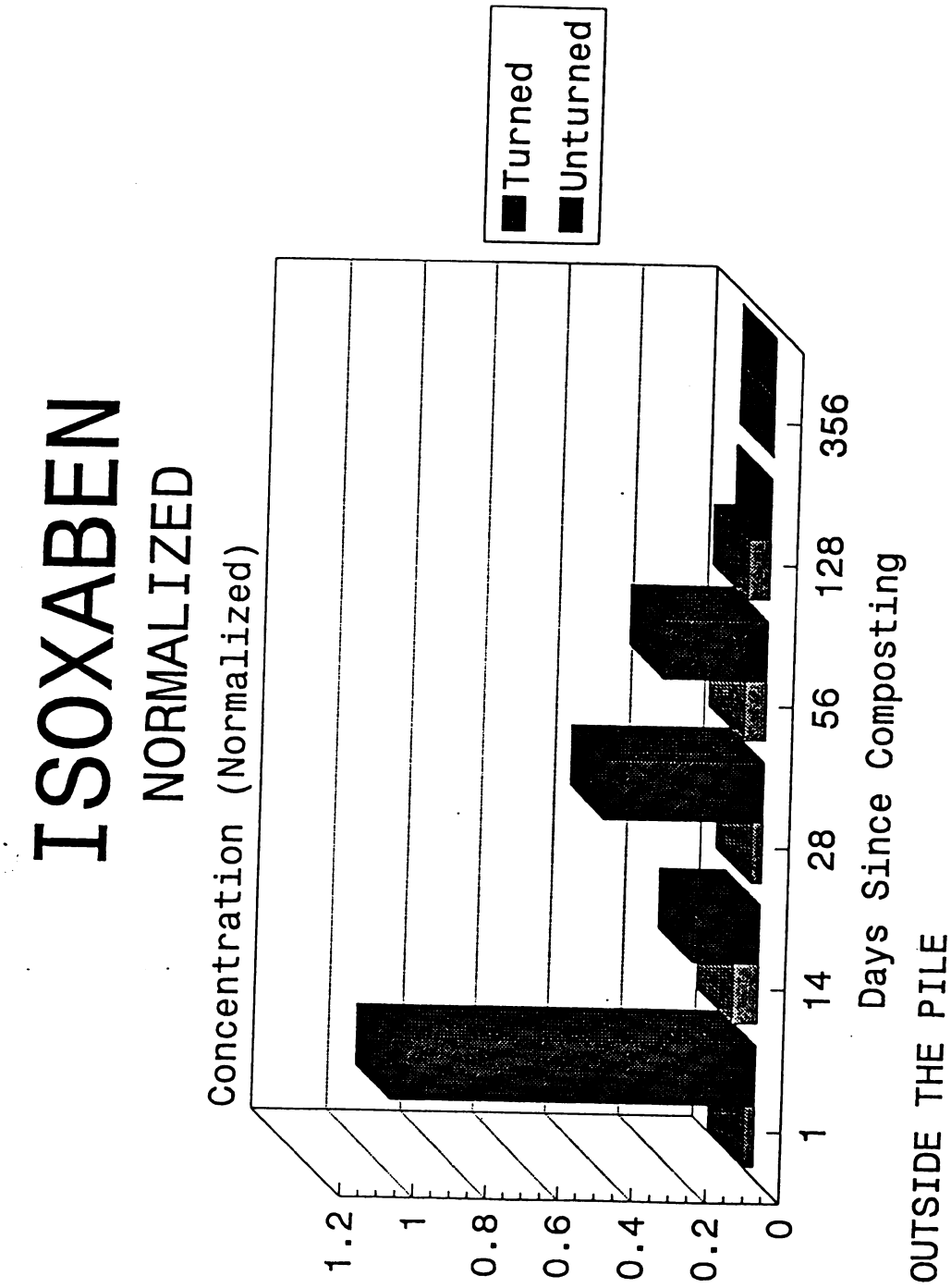


Figure 12 Flurprimidol Inside the Pile

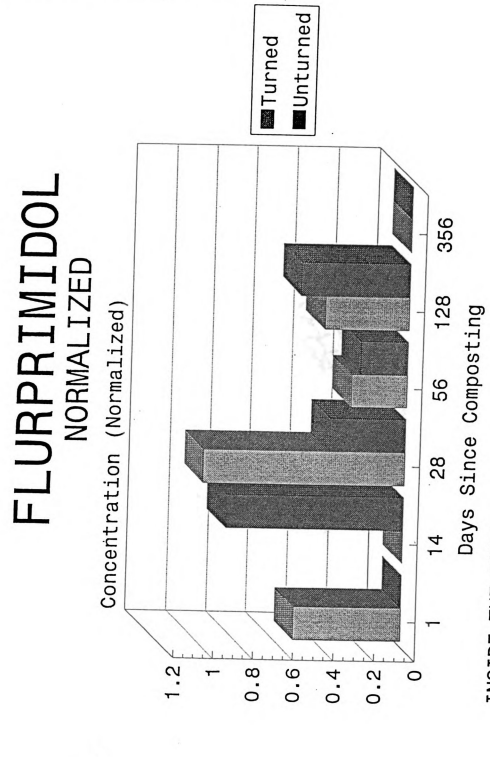


Figure 13 Flurprimidol Outside the Pile

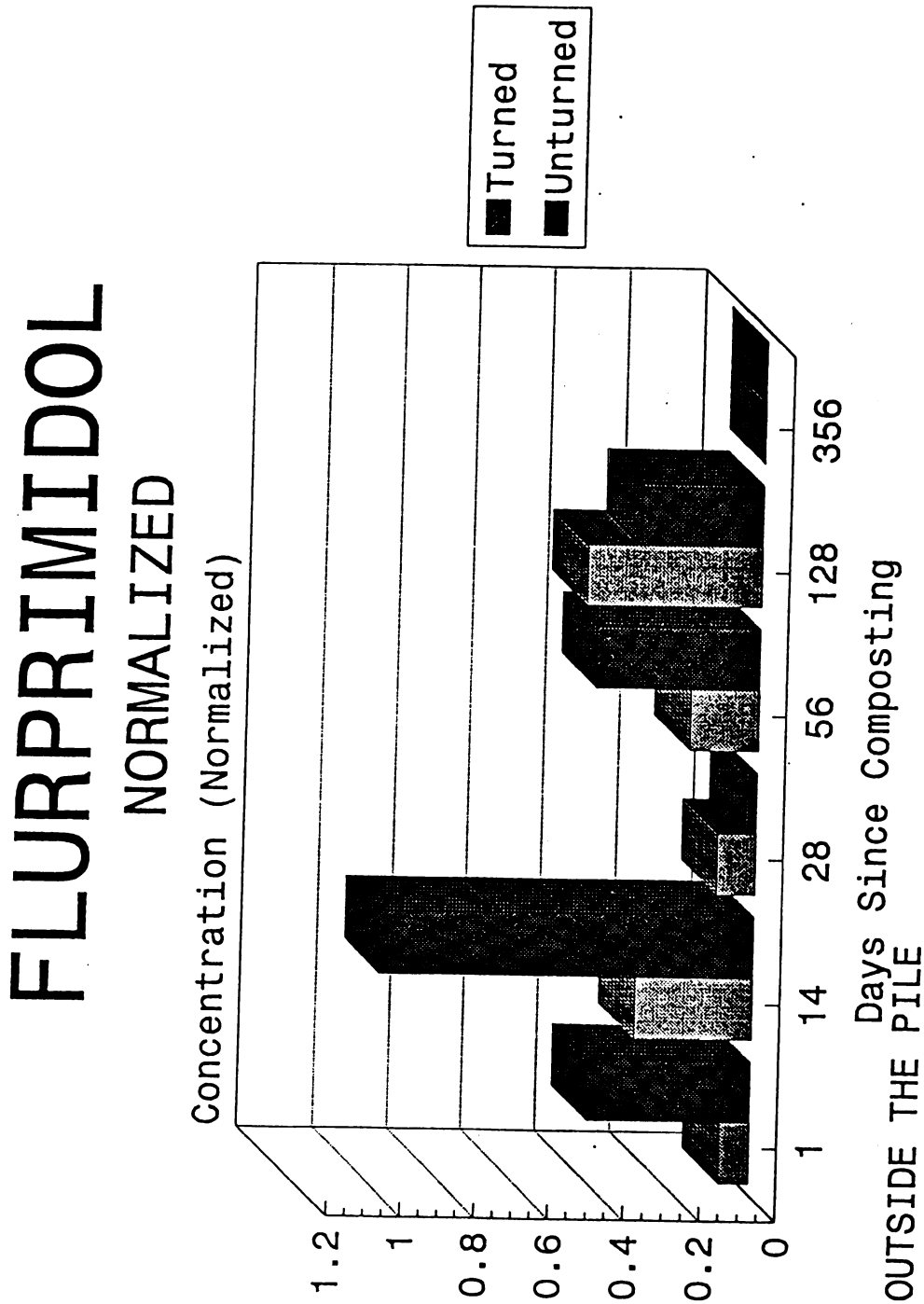


Figure 14 2,4-D Inside the Pile

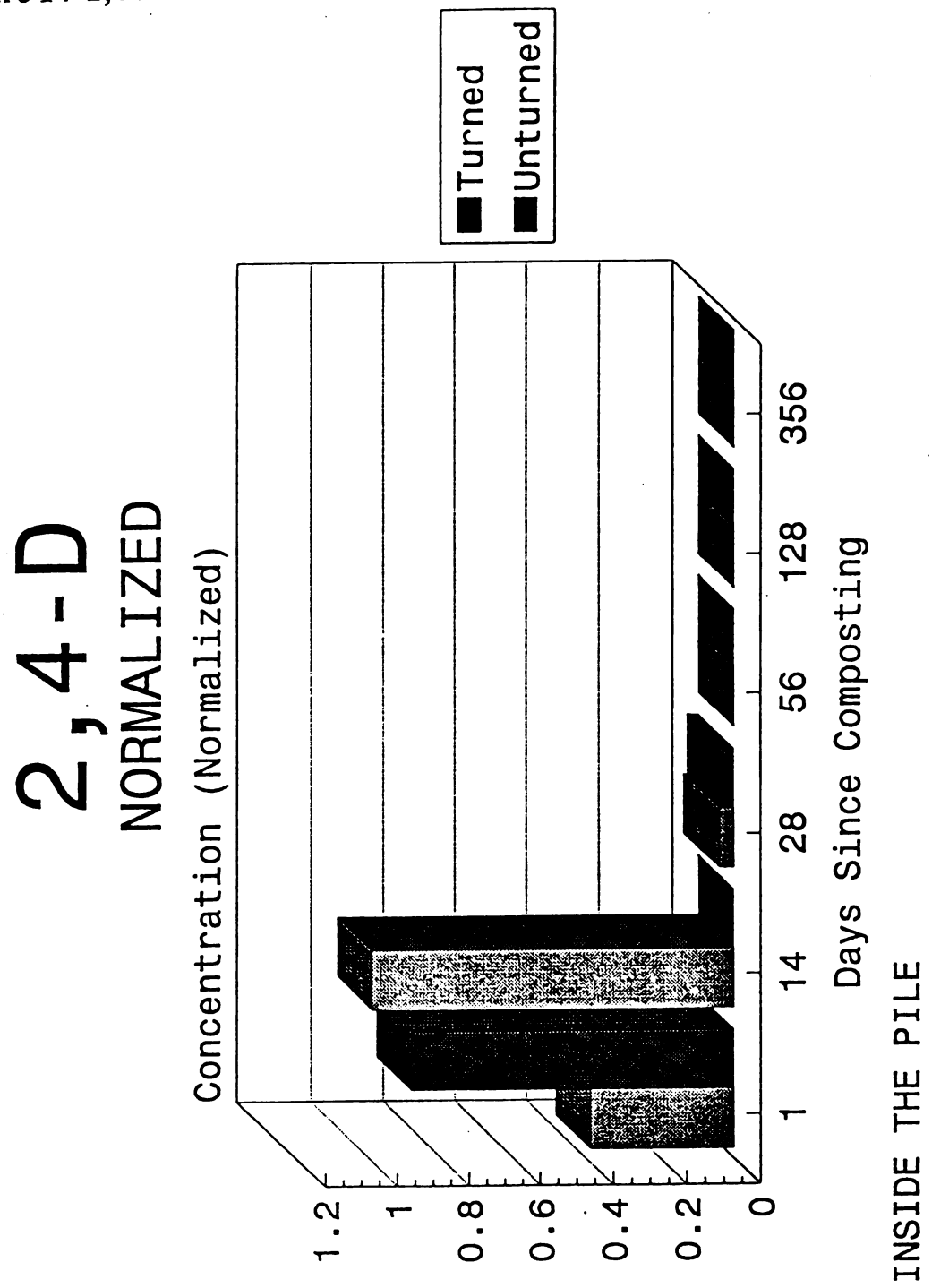


Figure 15 2,4-D Outside the Pile

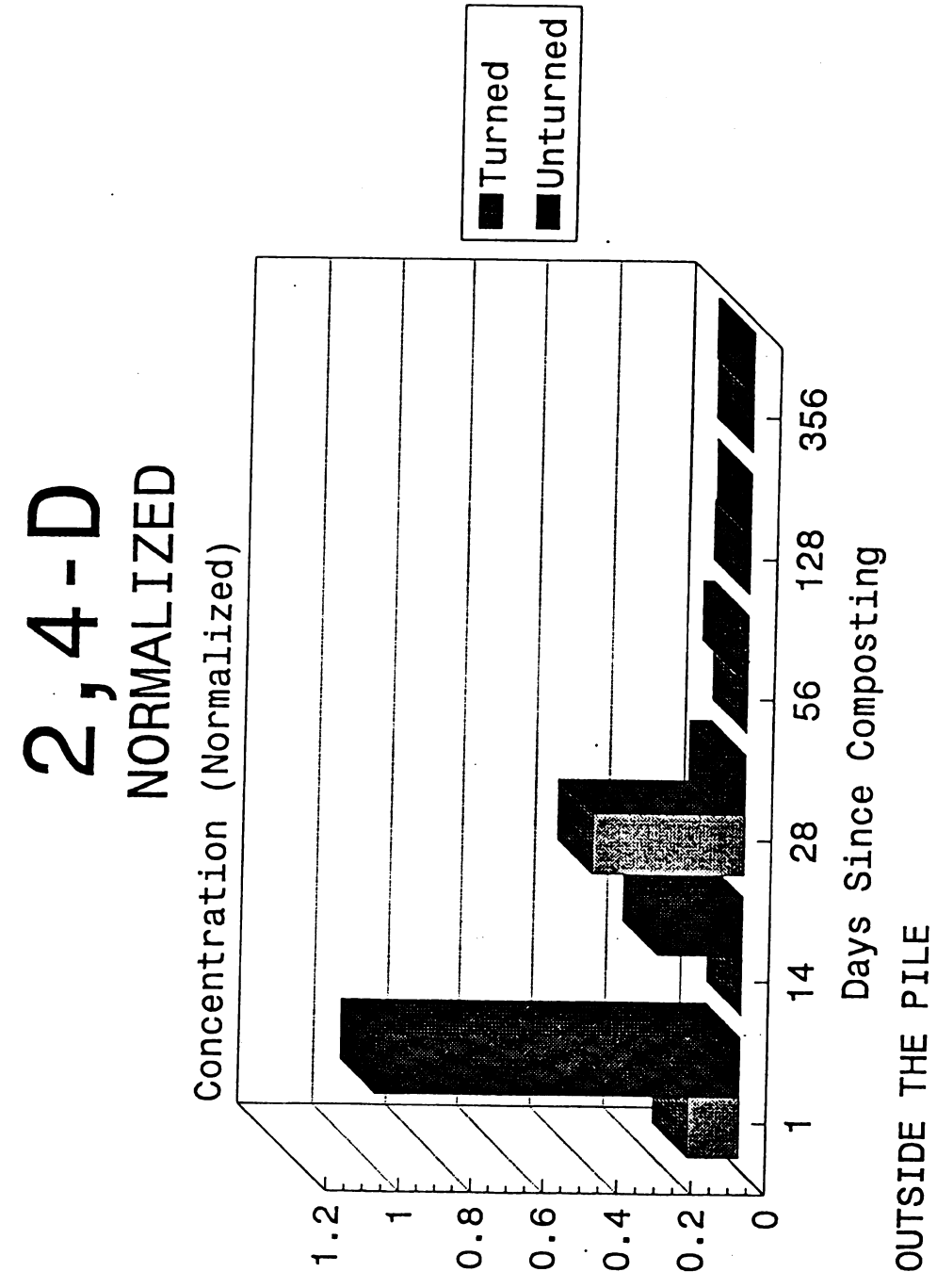


Figure 16 Clopyralid Inside the Pile

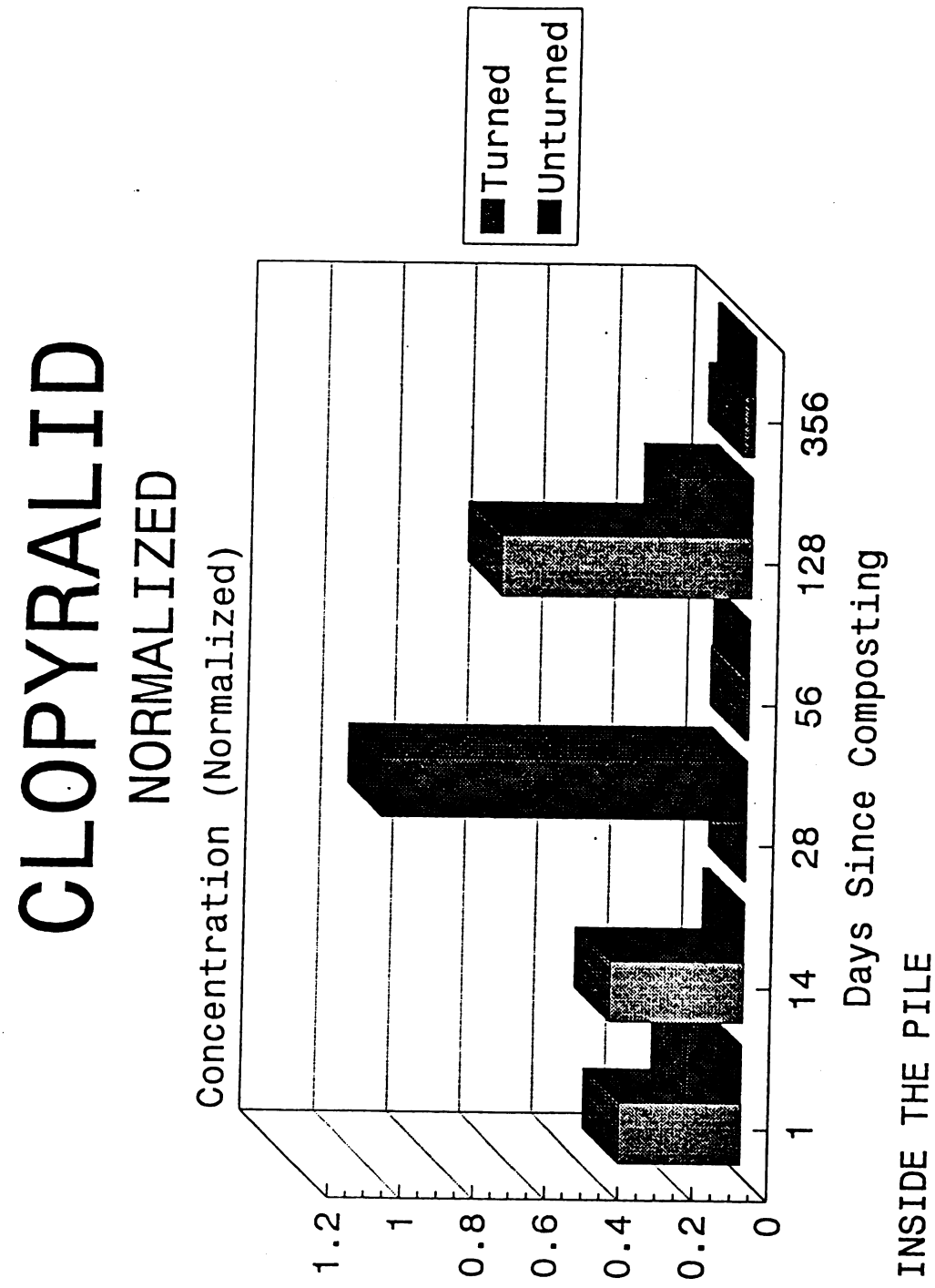


Figure 17 Clopyralid Outside the Pile

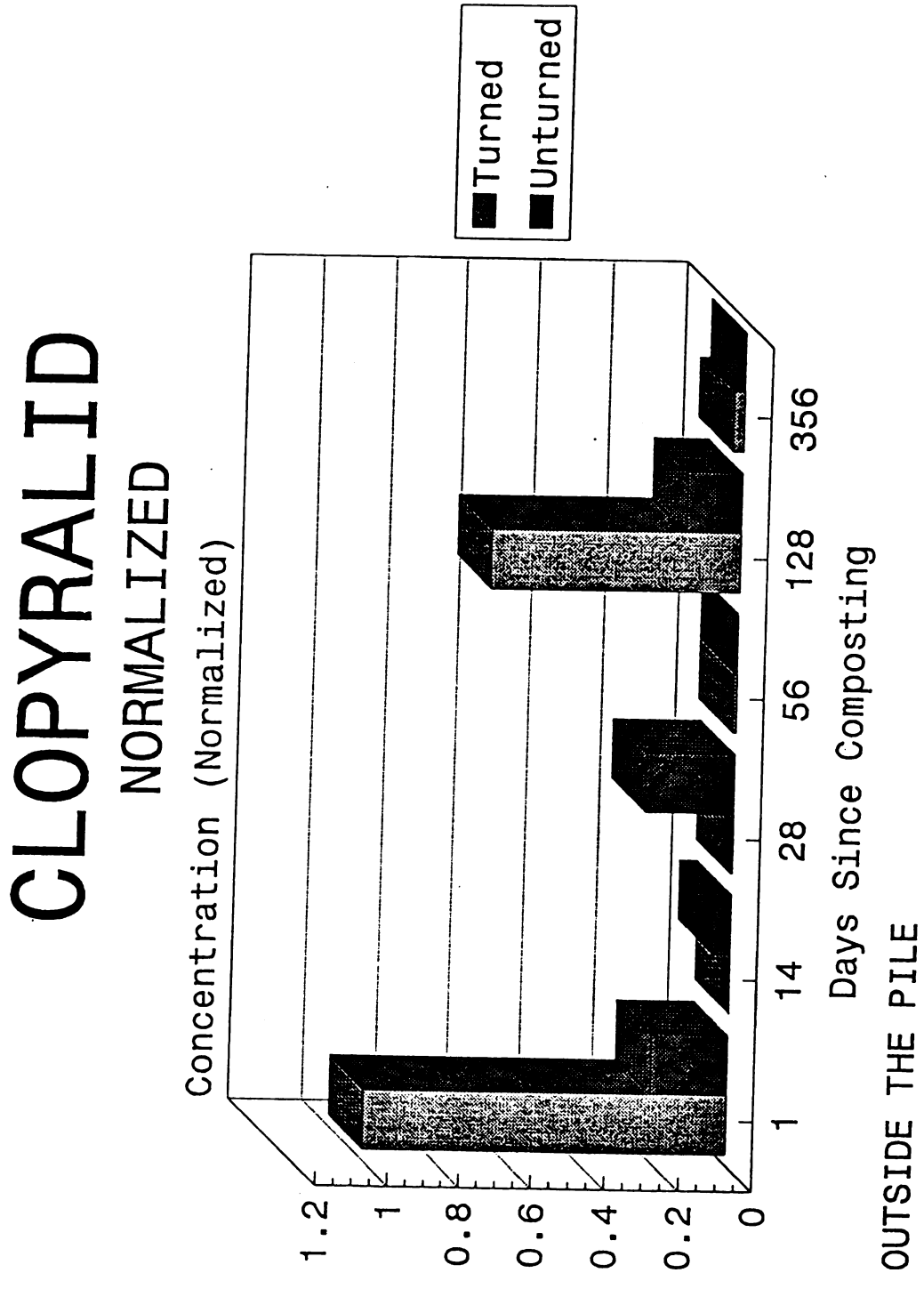


Table 9 First-order decay constants of the disappearance of applied Pesticides

Pesticide	Sample	k value (day $^{-1}$)	Average	Std Dev	CV
Chlorpyrifos	3-A-IN*	0.050			
	3-B-IN	0.224			
	3-A-OUT**	0.100			
	3-B-OUT	0.263	0.159	0.10	0.63
Triclopyr	3-A-IN	#			
	3-B-IN	0.226			
	3-A-OUT	-0.234			
	3-B-OUT	0.024			
	4-A-IN	-0.095			
	4-B-IN	0.033			
	4-A-OUT	0.024			
	4-B-OUT	-0.248	-0.039	0.17	4.36
2,4-D	3-A-IN	-0.067			
	3-B-IN	0.209			
	3-A-OUT	-0.038			
	3-B-OUT	0.106	0.053	0.13	2.45
Clopyralid	4-A-IN	-0.055			
	4-B-IN	0.141			
	4-A-OUT	0.181			
	4-B-OUT	0.099	0.104	0.10	0.96
Isoxaben	5-A-IN	-0.043			
	5-B-IN	0.143			
	5-A-OUT	-0.069			
	5-B-OUT	0.698	0.183	0.36	1.97
Flurprimidol	3-A-IN	-0.022			
	3-B-IN	0.063			
	3-A-OUT	-0.098			
	3-B-OUT	-0.060	-0.030	0.070	2.33
Average of All			0.072	0.094	1.31

* IN is inside the compost pile, A is the pile is turned

** OUT is outside the compost pile, B the pile is not turned

The research on 2,4-D (Table A5, pp 72) has shown a decline from a high of about 183 ppm to less than 2 ppm in 365 days. 2,4-D was applied to bluegrass turf at 0.73 kg ai/acre in a laboratory experiment (Extoxnet, 1993) and a half-life of ten days was determined. Other studies have shown half-lives of 1.5 to 16 days in non-sterile soils. EPA has included 2,4-D in a list of chemicals likely to leach from soil and this agrees with the water solubility of 890 mg/l but the persistence as indicated in the half-lives implies that it will breakdown before becoming a ground water problem. 2,4-D has been found in five states groundwater and surface waters (Extoxnet, 1993).

Studies have shown chlorpyrifos (Table A1, pp 70) to be relatively persistent as compared to 2,4-D in that the half-life can range from 2 weeks to over a year, this research confirms the long half-life in that at 56 days chlorpyrifos was still detectable at 0.7 ppm and 0.1 ppm at 128 days. Some of the persistence can be related to it strongly absorbing to soil particles and grass.

All of the chemicals except 2,4-D and clopyralid (Table A6, pp72) were below detection at 365 days, although 2,4-D had a high concentration of 183 ppm at initiation it was down to 1.4 ppm after 365 days. Clopyralid declined from 32 ppm to less than 1.4 ppm after 365 days.

In summary for all the chemicals applied, the composting environment has shown itself to be a good degrader of pesticides. The initial concentrations could cause damage to plants if applied immediately after composting but within several

months the compost piles should be benign enough to apply to gardens.

Future studies should control the variability by taking more samples from the piles and then compositing them as one sample, also increasing the number of replicate piles. Future work could focus on the metabolites also. Further studying of the depth of penetration of the pesticide within the turf and thatch layer would bring some understanding as to were the pesticide goes after application.

CONCLUSIONS

The two studies complement each other in the aspect of showing that degradation and control of pesticides after application is a multi-faceted task. The lysimeter study showed that significant movement of pesticides to groundwater is unlikely in typical applications to vegetative areas. Laboratory studies indicate considerable pesticide mobility, leaching in field situations are effected by soil adsorption , degradation, and upward movement of water in response to evaporation. Movement of pesticides at high flow velocities show increased penetration in the soil column (Leonard, 1976) and this was evident in the detection of triademefon in two lysimeters by the large amount of rain recieved before and after the application to the turf.

Pesticides applied to turfgrass may be found in the clippings for several months after application. Two, four-Dichlorophenoxyacetic acid and clopyralid were found in composted turf up to one year after application. The composting of turf showed greatly reduced to non-detectable residues in the turf after one year.

Knowledge of the behavior of pesticides in the terrestrial environment is paramount before release, to avoid past mistakes and future problems as seen in organochlorine pesticides.

APPENDICES

APPENDIX A--TURFGRASS COMPOST DATA

APPENDIX A

TURFGRASS COMPOST DATA

TABLE A1 **CHLORPYRIFOS CONCENTRATION (ppm)**

DAYS SINCE PESTICIDE APPLIED

SAMPLE #	1	14	28	56	128	356
3-A-IN	0.04	nd	0.01	nd	0.04	nd
3-B-IN	0.23	0.01	nd	nd	nd	nd
2-A-OUT	0.82	nd	0.05	0.21	0.11	nd
2-B-OUT	6.8	0.17	nd	0.73	0.11	nd

TABLE A2 **TRICLOPYR CONCENTRATION (ppm)**

DAYS SINCE PESTICIDE APPLIED

SAMPLE #	1	14	28	56	128	356
3-A-IN	nd	nd	0.45	nd	nd	nd
3-B-IN	0.94	0.04	0.03	0.26	0.48	nd
3-A-OUT	0.12	3.18	0.02	0.17	nd	nd
3-B-OUT	0.07	0.05	0.01	nd	0.17	nd
4-A-IN	0.05	0.19	0.07	0.05	nd	nd
4-B-IN	0.30	0.19	0.04	0.14	0.07	nd
4-A-OUT	4.54	nd	nd	nd	0.21	nd
4-B-OUT	0.22	7.13	0.05	0.15	0.11	nd

TABLE A3 **ISOXABEN CONCENTRATION (ppm)**

DAYS SINCE PESTICIDE APPLIED

SAMPLE #	1	14	28	56	128	356
5-A-IN	8.12	14.72	0.59	2.22	0.98	nd
5-B-IN	36.83	4.99	13.68	1.90	3.20	nd
5-A-OUT	4.98	12.99	5.09	10.58	10.17	nd
5-B-OUT	175.51	32.35	76.27	49.99	0.81	nd

TABLE A4 **FLURPRIMIDOL CONCENTRATION (ppm)**

DAYS SINCE PESTICIDE APPLIED

SAMPLE #	1	14	28	56	128	356
6-A-IN	2.24	nd	4.19	1.14	1.73	nd
6-B-IN	nd	3.67	1.53	0.97	2.21	nd
6-A-OUT	0.43	1.69	0.55	1.00	2.52	nd
6-B-OUT	2.36	5.50	0.17	2.35	1.75	nd

TABLE A5 **2,4-D CONCENTRATION (ppm)**

DAYS SINCE PESTICIDE APPLIED

SAMPLE #	1	14	28	56	128	356
3-A-IN	38.12	97.02	3.71	nd	nd	nd
3-B-IN	86.61	nd	0.25	nd	nd	nd
3-A-OUT	26.32	nd	75.79	nd	0.62	0.51
3-B-OUT	183.15	41.54	11.42	6.06	nd	1.37

TABLE A6 **CLOPYRALID CONCENTRATION (ppm)**

DAYS SINCE PESTICIDE APPLIED

SAMPLE #	1	14	28	56	128	356
4-A-IN	15.6	16.8	0.3	0.5	31.9	1.3
4-B-IN	7.2	1.0	46.9	0.3	9.6	0.6
4-A-OUT	32.0	nd	0.2	0.2	10.6	0.9
4-B-OUT	6.8	1.7	7.7	0.4	4.7	0.1

APPENDIX B--WATER LYSIMETER DATA

APPENDIX B

Table B0 Sample Dates for Water Collection

Sample #	Date	Sample #	Date	Sample #	Date	Sample #	Date
1001	5/1/91	1024	2/27/92	1047	9/4/92	1070	4/5/93
1002	5/17/91	1025	3/7/92	1048	9/8/92	1071	4/13/93
1003	6/12/91	1026	3/18/92	1049	9/10/92	1072	4/21/93
1004	7/22/91	1027	3/25/92	1050	9/15/92	1073	4/22/93
1005	8/17/91	1028	3/27/92	1051	9/29/92	1074	5/11/93
1006	8/23/91	1029	4/4/92	1052	10/15/92	1075	6/8/93
1007	8/29/91	1030	4/10/92	1053	Missing	1076	6/9/93
1008	8/30/91	1031	4/16/92	1054	10/26/92	1077	6/24/93
1009	9/3/91	1032	4/21/92	1055	11/3/92	1078	7/9/93
1010	9/16/91	1033	4/24/92	1056	11/12/92	1079	7/27/93
1011	10/22/91	1034	4/25/92	1057	11/13/92	1080	7/30/93
1012	10/26/91	1035	4/27/92	1058	11/20/92	1081	8/5/93
1013	10/27/91	1036	5/6/92	1059	11/23/92	1082	8/17/93
1014	10/30/91	1037	6/8/92	1060	11/29/92	1083	8/24/93
1015	11/8/91	1038	6/17/92	1061	12/14/92	1084	9/14/93
1016	11/20/91	1039	7/792	1062	12/28/92	1085	9/21/93
1017	11/23/91	1040	7/14/92	1063	12/31/92	1086	9/28/93
1018	12/3/91	1041	7/16/92	1064	1/4/93	1087	10/7/93
1019	12/12/91	1042	7/20/92	1065	1/4/93	1088	10/19/93
1020	12/18/91	1043	7/29/92	1066	1/8/93	1089	10/22/93
1021	1/3/92	1044	7/31/92	1067	1/29/93	1090	11/16/93
1022	1/22/91	1045	8/4/92	1068	3/9/93	1091	12/9/93
1023	2/21/92	1046	Missing	1069	Missing	1092	12/23/93

Table B1 Bayleton Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	#	1047	*	1070	*
1002	#	1025	#	1048	*	1071	*
1003	#	1026	#	1049	*	1072	*
1004	#	1027	#	1050	*	1073	*
1005	#	1028	#	1051	*	1074	*
1006	#	1029	#	1052	0.03	1075	*
1007	#	1030	#	1053	Missing	1076	*
1008	#	1031	#	1054	*	1077	*
1009	#	1032	#	1055	*	1078	*
1010	#	1033	#	1056	*	1079	*
1011	#	1034	#	1057	*	1080	*
1012	#	1035	#	1058	*	1081	*
1013	#	1036	#	1059	*	1082	*
1104	#	1037	#	1060	0.01	1083	*
1015	#	1038	#	1061	*	1084	*
1016	#	1039	#	1062	*	1085	*
1017	#	1040	#	1063	*	1086	*
1018	#	1041	*	1064	*	1087	*
1019	#	1042	*	1065	*	1088	*
1020	#	1043	*	1066	*	1089	*
1021	#	1044	*	1067	*	1090	*
1022	#	1045	*	1068	*	1091	*
1023	#	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B1 Bayleton Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	#	2047	*	2070	*
2002	#	2025	#	2048	*	2071	*
2003	#	2026	#	2049	*	2072	*
2004	#	2027	#	2050	0.01	2073	*
2005	#	2028	#	2051	*	2074	*
2006	#	2029	#	2052	*	2075	*
2007	#	2030	#	2053	Missing	2076	*
2008	#	2031	#	2054	*	2077	*
2009	#	2032	#	2055	*	2078	*
2010	#	2033	#	2056	*	2079	*
2011	#	2034	#	2057	*	2080	*
2012	#	2035	#	2058	*	2081	*
2013	#	2036	#	2059	*	2082	*
2104	#	2037	#	2060	0.01	2083	*
2015	#	2038	#	2061	0.01	2084	*
2016	#	2039	#	2062	*	2085	*
2017	#	2040	#	2063	*	2086	*
2018	#	2041	*	2064	*	2087	*
2019	#	2042	*	2065	*	2088	*
2020	#	2043	*	2066	*	2089	*
2021	#	2044	*	2067	*	2090	*
2022	#	2045	*	2068	*	2091	*
2023	#	2046	Missing	2069	Missing	2092	*

Table B2 Isazofos Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	*	1047	*	1070	*
1002	#	1025	*	1048	*	1071	*
1003	*	1026	*	1049	*	1072	*
1004	*	1027	*	1050	*	1073	*
1005	*	1028	*	1051	*	1074	*
1006	*	1029	*	1052	*	1075	*
1007	*	1030	*	1053	Missing	1076	*
1008	*	1031	*	1054	*	1077	*
1009	*	1032	*	1055	*	1078	*
1010	*	1033	*	1056	*	1079	*
1011	*	1034	*	1057	*	1080	*
1012	*	1035	*	1058	*	1081	*
1013	*	1036	*	1059	*	1082	*
1104	*	1037	*	1060	*	1083	*
1015	*	1038	*	1061	*	1084	*
1016	*	1039	*	1062	*	1085	*
1017	*	1040	*	1063	*	1086	*
1018	*	1041	*	1064	*	1087	*
1019	*	1042	*	1065	*	1088	*
1020	*	1043	*	1066	*	1089	*
1021	*	1044	*	1067	*	1090	*
1022	*	1045	*	1068	*	1091	*
1023	*	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B2 Isazofos Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	*	2047	*	2070	*
2002	#	2025	*	2048	*	2071	*
2003	*	2026	*	2049	*	2072	*
2004	*	2027	*	2050	*	2073	*
2005	*	2028	*	2051	*	2074	*
2006	*	2029	*	2052	*	2075	*
2007	*	2030	*	2053	Missing	2076	*
2008	*	2031	*	2054	*	2077	*
2009	*	2032	*	2055	*	2078	*
2010	*	2033	*	2056	*	2079	*
2011	*	2034	*	2057	*	2080	*
2012	*	2035	*	2058	*	2081	*
2013	*	2036	*	2059	*	2082	*
2104	*	2037	*	2060	*	2083	*
2015	*	2038	*	2061	*	2084	*
2016	*	2039	*	2062	*	2085	*
2017	*	2040	*	2063	*	2086	*
2018	*	2041	*	2064	*	2087	*
2019	*	2042	*	2065	*	2088	*
2020	*	2043	*	2066	*	2089	*
2021	*	2044	*	2067	*	2090	*
2022	*	2045	*	2068	*	2091	*
2023	*	2046	Missing	2069	Missing	2092	*

Table B3 Fenarimol Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	#	1047	*	1070	*
1002	#	1025	#	1048	*	1071	*
1003	#	1026	#	1049	*	1072	*
1004	#	1027	#	1050	*	1073	*
1005	#	1028	#	1051	*	1074	*
1006	#	1029	#	1052	*	1075	*
1007	#	1030	#	1053	Missing	1076	*
1008	#	1031	#	1054	*	1077	*
1009	#	1032	#	1055	*	1078	*
1010	#	1033	#	1056	*	1079	*
1011	#	1034	*	1057	*	1080	*
1012	#	1035	*	1058	*	1081	*
1013	#	1036	*	1059	*	1082	*
1104	#	1037	*	1060	*	1083	*
1015	#	1038	*	1061	*	1084	*
1016	#	1039	*	1062	*	1085	*
1017	#	1040	*	1063	*	1086	*
1018	#	1041	*	1064	*	1087	*
1019	#	1042	*	1065	*	1088	*
1020	#	1043	*	1066	*	1089	*
1021	#	1044	*	1067	*	1090	*
1022	#	1045	*	1068	*	1091	*
1023	#	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B3 Fenarimol Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	#	2047	*	2070	*
2002	#	2025	#	2048	*	2071	*
2003	#	2026	#	2049	*	2072	*
2004	#	2027	#	2050	*	2073	*
2005	#	2028	#	2051	*	2074	*
2006	#	2029	#	2052	*	2075	*
2007	#	2030	#	2053	Missing	2076	*
2008	#	2031	#	2054	*	2077	*
2009	#	2032	#	2055	*	2078	*
2010	#	2033	#	2056	*	2079	*
2011	#	2034	*	2057	*	2080	*
2012	#	2035	*	2058	*	2081	*
2013	#	2036	*	2059	*	2082	*
2104	#	2037	*	2060	*	2083	*
2015	#	2038	*	2061.	*	2084	*
2016	#	2039	*	2062	*	2085	*
2017	#	2040	*	2063	*	2086	*
2018	#	2041	*	2064	*	2087	*
2019	#	2042	*	2065	*	2088	*
2020	#	2043	*	2066	*	2089	*
2021	#	2044	*	2067	*	2090	*
2022	#	2045	*	2068	*	2091	*
2023	#	2046	Missing	2069	Missing	2092	*

Table B4 Propiconazole Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	#	1047	*	1070	*
1002	#	1025	#	1048	*	1071	*
1003	#	1026	#	1049	*	1072	*
1004	#	1027	#	1050	*	1073	*
1005	#	1028	#	1051	*	1074	*
1006	#	1029	#	1052	*	1075	*
1007	#	1030	#	1053	Missing	1076	*
1008	#	1031	#	1054	*	1077	*
1009	#	1032	#	1055	*	1078	*
1010	#	1033	#	1056	*	1079	*
1011	#	1034	#	1057	*	1080	*
1012	#	1035	#	1058	*	1081	*
1013	#	1036	#	1059	*	1082	*
1104	#	1037	*	1060	*	1083	*
1015	#	1038	*	1061	*	1084	*
1016	#	1039	*	1062	*	1085	*
1017	#	1040	*	1063	*	1086	*
1018	#	1041	*	1064	*	1087	*
1019	#	1042	*	1065	*	1088	*
1020	#	1043	*	1066	*	1089	*
1021	#	1044	*	1067	*	1090	*
1022	#	1045	*	1068	*	1091	*
1023	#	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B4 Propiconazole Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	#	2047	*	2070	*
2002	#	2025	#	2048	*	2071	*
2003	#	2026	#	2049	*	2072	*
2004	#	2027	#	2050	*	2073	*
2005	#	2028	#	2051	*	2074	*
2006	#	2029	#	2052	*	2075	*
2007	#	2030	#	2053	Missing	2076	*
2008	#	2031	#	2054	*	2077	*
2009	#	2032	#	2055	*	2078	*
2010	#	2033	#	2056	*	2079	*
2011	#	2034	#	2057	*	2080	*
2012	#	2035	#	2058	*	2081	*
2013	#	2036	#	2059	*	2082	*
2104	#	2037	*	2060	*	2083	*
2015	#	2038	*	2061	*	2084	*
2016	#	2039	*	2062	*	2085	*
2017	#	2040	*	2063	*	2086	*
2018	#	2041	*	2064	*	2087	*
2019	#	2042	*	2065	*	2088	*
2020	#	2043	*	2066	*	2089	*
2021	#	2044	*	2067	*	2090	*
2022	#	2045	*	2068	*	2091	*
2023	#	2046	Missing	2069	Missing	2092	*

Table B5 Chlorothalonil Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	*	1047	*	1070	*
1002	#	1025	*	1048	*	1071	*
1003	#	1026	*	1049	*	1072	*
1004	*	1027	*	1050	*	1073	*
1005	*	1028	*	1051	*	1074	*
1006	*	1029	*	1052	*	1075	*
1007	*	1030	*	1053	Missing	1076	*
1008	*	1031	*	1054	*	1077	*
1009	*	1032	*	1055	*	1078	*
1010	*	1033	*	1056	*	1079	*
1011	*	1034	*	1057	*	1080	*
1012	*	1035	*	1058	*	1081	*
1013	*	1036	*	1059	*	1082	*
1104	*	1037	*	1060	*	1083	*
1015	*	1038	*	1061	*	1084	*
1016	*	1039	*	1062	*	1085	*
1017	*	1040	*	1063	*	1086	*
1018	*	1041	*	1064	*	1087	*
1019	*	1042	*	1065	*	1088	*
1020	*	1043	*	1066	*	1089	*
1021	*	1044	*	1067	*	1090	*
1022	*	1045	*	1068	*	1091	*
1023	*	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B5 Chlorothalonil Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	*	2047	*	2070	*
2002	#	2025	*	2048	*	2071	*
2003	#	2026	*	2049	*	2072	*
2004	*	2027	*	2050	*	2073	*
2005	*	2028	*	2051	*	2074	*
2006	*	2029	*	2052	*	2075	*
2007	*	2030	*	2053	Missing	2076	*
2008	*	2031	*	2054	*	2077	*
2009	*	2032	*	2055	*	2078	*
2010	*	2033	*	2056	*	2079	*
2011	*	2034	*	2057	*	2080	*
2012	*	2035	*	2058	*	2081	*
2013	*	2036	*	2059	*	2082	*
2104	*	2037	*	2060	*	2083	*
2015	*	2038	*	2061	*	2084	*
2016	*	2039	*	2062	*	2085	*
2017	*	2040	*	2063	*	2086	*
2018	*	2041	*	2064	*	2087	*
2019	*	2042	*	2065	*	2088	*
2020	*	2043	*	2066	*	2089	*
2021	*	2044	*	2067	*	2090	*
2022	*	2045	*	2068	*	2091	*
2023	*	2046	Missing	2069	Missing	2092	*

Table B5 Chlorothalonil Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
3001	#	3024	*	3047	*	3070	*
3002	#	3025	*	3048	*	3071	*
3003	#	3026	*	3049	*	3072	*
3004	*	3027	*	3050	*	3073	*
3005	*	3028	*	3051	*	3074	*
3006	*	3029	*	3052	*	3075	*
3007	*	3030	*	3053	Missing	3076	*
3008	*	3031	*	3054	*	3077	*
3009	*	3032	*	3055	*	3078	*
3010	*	3033	*	3056	*	3079	*
3011	*	3034	*	3057	*	3080	*
3012	*	3035	*	3058	*	3081	*
3013	*	3036	*	3059	*	3082	*
3104	*	3037	*	3060	*	3083	*
3015	*	3038	*	3061	*	3084	*
3016	*	3039	*	3062	*	3085	*
3017	*	3040	*	3063	*	3086	*
3018	*	3041	*	3064	*	3087	*
3019	*	3042	*	3065	*	3088	*
3020	*	3043	*	3066	*	3089	*
3021	*	3044	*	3067	*	3090	*
3022	*	3045	*	3068	*	3091	*
3023	*	3046	*	3069	Missing	3092	*

Table B5 Chlorothalonil Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
4001	#	4024	*	4047	*	4070	*
4002	#	4025	*	4048	*	4071	*
4003	#	4026	*	4049	*	4072	*
4004	*	4027	*	4050	*	4073	*
4005	*	4028	*	4051	*	4074	*
4006	*	4029	*	4052	*	4075	*
4007	*	4030	*	4053	Missing	4076	*
4008	*	4031	*	4054	*	4077	*
4009	*	4032	*	4055	*	4078	*
4010	*	4033	*	4056	*	4079	*
4011	*	4034	*	4057	*	4080	*
4012	*	4035	*	4058	*	4081	*
4013	*	4036	*	4059	*	4082	*
4104	*	4037	*	4060	*	4083	*
4015	*	4038	*	4061	*	4084	*
4016	*	4039	*	4062	*	4085	*
4017	*	4040	*	4063	*	4086	*
4018	*	4041	*	4064	*	4087	*
4019	*	4042	*	4065	*	4088	*
4020	*	4043	*	4066	*	4089	*
4021	*	4044	*	4067	*	4090	*
4022	*	4045	*	4068	*	4091	*
4023	*	4046	Missing	4069	Missing	4092	*

Table B6 2,4-D Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	*	1047	*	1070	*
1002	#	1025	*	1048	*	1071	*
1003	#	1026	*	1049	*	1072	*
1004	#	1027	*	1050	*	1073	*
1005	#	1028	*	1051	*	1074	*
1006	#	1029	*	1052	*	1075	*
1007	#	1030	*	1053	Missing	1076	*
1008	#	1031	*	1054	*	1077	*
1009	*	1032	*	1055	*	1078	*
1010	*	1033	*	1056	*	1079	*
1011	*	1034	*	1057	*	1080	*
1012	*	1035	*	1058	*	1081	*
1013	*	1036	*	1059	*	1082	*
1104	*	1037	*	1060	*	1083	*
1015	*	1038	*	1061	*	1084	*
1016	*	1039	*	1062	*	1085	*
1017	*	1040	*	1063	*	1086	*
1018	*	1041	*	1064	*	1087	*
1019	*	1042	*	1065	*	1088	*
1020	*	1043	*	1066	*	1089	*
1021	*	1044	*	1067	*	1090	*
1022	*	1045	*	1068	*	1091	*
1023	*	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B6 2,4-D Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	*	2047	*	2070	*
2002	#	2025	*	2048	*	2071	*
2003	#	2026	*	2049	*	2072	*
2004	#	2027	*	2050	*	2073	*
2005	#	2028	*	2051	*	2074	*
2006	#	2029	*	2052	*	2075	*
2007	#	2030	*	2053	Missing	2076	*
2008	#	2031	*	2054	*	2077	*
2009	*	2032	*	2055	*	2078	*
2010	*	2033	*	2056	*	2079	*
2011	*	2034	*	2057	*	2080	*
2012	*	2035	*	2058	*	2081	*
2013	*	2036	*	2059	*	2082	*
2104	*	2037	*	2060	*	2083	*
2015	*	2038	*	2061	*	2084	*
2016	*	2039	*	2062	*	2085	*
2017	*	2040	*	2063	*	2086	*
2018	*	2041	*	2064	*	2087	*
2019	*	2042	*	2065	*	2088	*
2020	*	2043	*	2066	*	2089	*
2021	*	2044	*	2067	*	2090	*
2022	*	2045	*	2068	*	2091	*
2023	*	2046	Missing	2069	Missing	2092	*

Table B7 Dicamba Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	*	1047	*	1070	*
1002	#	1025	*	1048	*	1071	*
1003	#	1026	*	1049	*	1072	*
1004	#	1027	*	1050	*	1073	*
1005	#	1028	*	1051	*	1074	*
1006	#	1029	*	1052	*	1075	*
1007	#	1030	*	1053	Missing	1076	*
1008	#	1031	*	1054	*	1077	*
1009	*	1032	*	1055	*	1078	*
1010	*	1033	*	1056	*	1079	*
1011	*	1034	*	1057	*	1080	*
1012	*	1035	*	1058	*	1081	*
1013	*	1036	*	1059	*	1082	*
1104	*	1037	*	1060	*	1083	*
1015	*	1038	*	1061	*	1084	*
1016	*	1039	*	1062	*	1085	*
1017	*	1040	*	1063	*	1086	*
1018	*	1041	*	1064	*	1087	*
1019	*	1042	*	1065	*	1088	*
1020	*	1043	*	1066	*	1089	*
1021	*	1044	*	1067	*	1090	*
1022	*	1045	*	1068	*	1091	*
1023	*	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B7 Dicamba Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	*	2047	*	2070	*
2002	#	2025	*	2048	*	2071	*
2003	#	2026	*	2049	*	2072	*
2004	#	2027	*	2050	*	2073	*
2005	#	2028	*	2051	*	2074	*
2006	#	2029	*	2052	*	2075	*
2007	#	2030	*	2053	Missing	2076	*
2008	#	2031	*	2054	*	2077	*
2009	*	2032	*	2055	*	2078	*
2010	*	2033	*	2056	*	2079	*
2011	*	2034	*	2057	*	2080	*
2012	*	2035	*	2058	*	2081	*
2013	*	2036	*	2059	*	2082	*
2104	*	2037	*	2060	*	2083	*
2015	*	2038	*	2061	*	2084	*
2016	*	2039	*	2062	*	2085	*
2017	*	2040	*	2063	*	2086	*
2018	*	2041	*	2064	*	2087	*
2019	*	2042	*	2065	*	2088	*
2020	*	2043	*	2066	*	2089	*
2021	*	2044	*	2067	*	2090	*
2022	*	2045	*	2068	*	2091	*
2023	*	2046	Missing	2069	Missing	2092	*

Table B8 Metalaxyl Residue Data

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
1001	#	1024	#	1047	*	1070	*
1002	#	1025	#	1048	*	1071	*
1003	#	1026	#	1049	*	1072	*
1004	#	1027	#	1050	*	1073	*
1005	#	1028	#	1051	*	1074	*
1006	#	1029	#	1052	*	1075	*
1007	#	1030	#	1053	Missing	1076	*
1008	#	1031	#	1054	*	1077	*
1009	#	1032	#	1055	*	1078	*
1010	#	1033	#	1056	*	1079	*
1011	#	1034	#	1057	*	1080	*
1012	#	1035	#	1058	*	1081	*
1013	#	1036	#	1059	*	1082	*
1104	#	1037	#	1060	*	1083	*
1015	#	1038	#	1061	*	1084	*
1016	#	1039	#	1062	*	1085	*
1017	#	1040	#	1063	*	1086	*
1018	#	1041	#	1064	*	1087	*
1019	#	1042	#	1065	*	1088	*
1020	#	1043	#	1066	*	1089	*
1021	#	1044	*	1067	*	1090	*
1022	#	1045	*	1068	*	1091	*
1023	#	1046	Missing	1069	Missing	1092	*

Pesticide has not been applied * Not Detected

Table B8 Metalaxyl Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
2001	#	2024	#	2047	*	2070	*
2002	#	2025	#	2048	*	2071	*
2003	#	2026	#	2049	*	2072	*
2004	#	2027	#	2050	*	2073	*
2005	#	2028	#	2051	*	2074	*
2006	#	2029	#	2052	*	2075	*
2007	#	2030	#	2053	Missing	2076	*
2008	#	2031	#	2054	*	2077	*
2009	#	2032	#	2055	*	2078	*
2010	#	2033	#	2056	*	2079	*
2011	#	2034	#	2057	*	2080	*
2012	#	2035	#	2058	*	2081	*
2013	#	2036	#	2059	*	2082	*
2104	#	2037	#	2060	*	2083	*
2015	#	2038	#	2061	*	2084	*
2016	#	2039	#	2062	*	2085	*
2017	#	2040	#	2063	*	2086	*
2018	#	2041	#	2064	*	2087	*
2019	#	2042	#	2065	*	2088	*
2020	#	2043	#	2066	*	2089	*
2021	#	2044	*	2067	*	2090	*
2022	#	2045	*	2068	*	2091	*
2023	#	2046	Missing	2069	Missing	2092	*

Table B8 Metalaxyl Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
3001	#	3024	#	3047	*	3070	*
3002	#	3025	#	3048	*	3071	*
3003	#	3026	#	3049	*	3072	*
3004	#	3027	#	3050	*	3073	*
3005	#	3028	#	3051	*	3074	*
3006	#	3029	#	3052	*	3075	*
3007	#	3030	#	3053	Missing	3076	*
3008	#	3031	#	3054	*	3077	*
3009	#	3032	#	3055	*	3078	*
3010	#	3033	#	3056	*	3079	*
3011	#	3034	#	3057	*	3080	*
3012	#	3035	#	3058	*	3081	*
3013	#	3036	#	3059	*	3082	*
3104	#	3037	#	3060	*	3083	*
3015	#	3038	#	3061	*	3084	*
3016	#	3039	#	3062	*	3085	*
3017	#	3040	*	3063	*	3086	*
3018	#	3041	*	3064	*	3087	*
3019	#	3042	*	3065	*	3088	*
3020	#	3043	*	3066	*	3089	*
3021	#	3044	*	3067	*	3090	*
3022	#	3045	*	3068	*	3091	*
3023	#	3046	*	3069	Missing	3092	*

Table B8 Metalaxyl Data cont.

Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)	Sample #	Conc (ppm)
4001	#	4024	#	4047	*	4070	*
4002	#	4025	#	4048	*	4071	*
4003	#	4026	#	4049	*	4072	*
4004	#	4027	#	4050	*	4073	*
4005	#	4028	#	4051	*	4074	*
4006	#	4029	#	4052	*	4075	*
4007	#	4030	#	4053	Missing	4076	*
4008	#	4031	#	4054	*	4077	*
4009	#	4032	#	4055	*	4078	*
4010	#	4033	#	4056	*	4079	*
4011	#	4034	#	4057	*	4080	*
4012	#	4035	#	4058	*	4081	*
4013	#	4036	#	4059	*	4082	*
4104	#	4037	#	4060	*	4083	*
4015	#	4038	#	4061	*	4084	*
4016	#	4039	#	4062	*	4085	*
4017	#	4040	*	4063	*	4086	*
4018	#	4041	*	4064	*	4087	*
4019	#	4042	*	4065	*	4088	*
4020	#	4043	*	4066	*	4089	*
4021	#	4044	*	4067	*	4090	*
4022	#	4045	*	4068	*	4091	*
4023	#	4046	Missing	4069	Missing	4092	*

Table B9-Rainfall and Irrigation Data

Collection Date/Sample #	Rainfall & Irrigation		Collection Date/Sample #	Rainfall & Irrigation
May 5, 1991/1	11.1		September 4/47	5.16
May 17/2	2.9		September 8/48	2.57
June 12/3	11.43		September 10/49	2.59
July 22/4	12.78		September 15/50	0.03
August 17/5	14.99		September 29/51	4.06
August 23/6	4.95		October 15/52	5.56
August 29/7	3.12		October 16/53	1.19
August 30/8	0.48		October 26/54	0.43
September 3/9	3.93		November 3/55	3.3
September 16/10	2.6		November 12/56	2.67
October 22/11	8.35		November 13/57	1.55
October 26/12	2.01		November 20/58	0.05
October 27/13	1.7		November 23/59	2.84
October 30/14	0.38		November 29/60	0.33
November 8/15	0.69		December 14/61	0.99
November 20/16	3.68		December 28/62	0.84
November 23/17	0.03		December 31/63	3.4
December 3/18	3.99		January 4, 1993/64	3.53
December 12/19	1.09		January 4/65	0
December 18/20	1.42		January 8/66	0.48
January 3, 1992/21	0.38		January 29/67	4.17
January 22/22	0		March 9/68	3.63
February 21/23	2.34		April 5/70	4.95
February 27/24	0.48		April 13/71	1.04
March 7/25	0.91		April 21/72	7.87
March 18/26	1.32		April 22/73	0.51
March 25/27	0		May 11/74	4.22
March 27/28	0.61		June 8/75	9.3
April 4/29	0.56		June 9/76	1.37
April 10/30	1.65		June 24/77	5.38
April 16/31	2.77		July 9/78	3.28
April 21/32	1.35		July 27/79	11.28
April 24/33	2.69		July 30/80	2.06
April 25/34	1.57		August 5/81	0.79
April 27/35	0.94		August 17/82	4.06
May 6/36	1.3		August 24/83	2.21
June 8/37	12.12		September 14/84	8.94
June 17/38	0		September 21/85	2.39
July 7/39	6.45		September 28/86.	3.33
July 14,40	7.37		October 7/87	
July 16/41	1.7		October 19/88	
July 20/42	1.63		October 22/89	
July 29/43	2.06		November 16/90	1.27
July 31/44	4.32		December 9/91	3.02
August 4/45	0		December 23/92	0.61
August 13/46	3.58		Sub Total	127.25
Sub Total	149.72		Total	276.97

Table B10-Volume of Water Collected

Collection Date/Sample #	Lysimeter 1 (ml)	Lysimeter 2 (ml	Lysimeter 3 (ml	Lysimeter 4 (ml)
May 5, 1991/1	8144	9083		
May 17/2	4961	6728		
June 12/3	9638	7448		
July 22/4	6931	311		
August 17/5	9247	3242		
August 23/6	3098	4956		
August 29/7	12021	10987		
August 30/8	5365	6420		
September 3/9	29438	33688		
September 16/10	4367	6600		
October 22/11	1520	8160		
October 26/12	2421	1509		
October 27/13	9633	8618		
October 30/14	6241	9236		
November 8/15	7879	9459	10352	10217
November 20/16	13887	10081	8394	9978
November 23/17	11497	15062	16132	15611
December 3/18	37006	37053	26769	24616
December 12/19	42017	46235	12473	17780
December 18/20	12687	13685	12776	13117
January 3, 1992/21	17008	16254	11387	13784
January 22/22	13363	14904	16284	14682
February 21/23	25963	31760	5284	16881
February 27/24	11665	11568	10980	8157
March 7/25	5137	5969	7319	4864
March 18/26	28553	22315	20412	21236
March 25/27	9717	10127	11429	13247
March 27/28	3508	13169	2630	8307
April 4/29	9280	12469	9378	11690
April 10/30	9316	12469	5661	6500
April 16/31	8520	8985	6644	5599
April 21/32	12490	12419	10251	9711
April 24/33	17734	16418	11543	13020
April 25/34	12844	12991	12977	12556
April 27/35	12682	15187	15606	15240
May 6/36	11189	12478	13467	15240
June 8/37	23023	17282	25968	16109
June 17/38	5454	8487	13641	7745
July 7/39	317	529	1049	629
July 14,40	27312	28283	7601	778
July 16/41	19338	25623	20949	16623
July 20/42	9836	10724	8482	8478
July 29/43	10025	10464	11475	8474
July 31/44	19286	14904	11037	10668
August 4/45	8765	13321	15621	13444
August 13/46	8802	7044	4242	3495
September 4/47	13959	17586	929	4641
September 8/48	32286	36588	32379	32502
September 10/49	15396	14287	11941	13042

Table 1

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Table 10-Volume of Water Collected cont.

Collection Date/Sample #	Lysimeter 1 (ml)	Lysimeter 2 (ml)	Lysimeter 3 (ml)	Lysimeter 4 (ml)
September 15/50	6610	10155	12149	10967
September 29/51	8994	10616	6128	9740
October 15/52	9112	8151	6276	6576
October 16/53	18988	19289	17672	18247
October 26/54	10742	15411	17281	15070
November 3/55	15878	13096	13701	13963
November 12/56	24328	22830	21310	20238
November 13/57	12925	16885	17761	17950
November 20/58	10286	13492	15020	13468
November 23/59	23255	19315	17838	17946
November 29/60	9703	11648	13281	11751
December 14/61	8401	9366	8281	7877
December 28/62	9074	10127	6316	5897
December 31/63	19254	17348	12931	17368
January 4, 1993/64	13096	12491	11557	10498
January 4/65	10263	10425	9992	10264
January 8/66	15412	18238	19163	17608
January 29/67	47655	51901	16657	14325
March 9/68	7145	19271	7700	19158
April 5/70	14308	19148	12614	13006
April 13/71	9700	11332	9966	8527
April 21/72	19247	19274	19681	18304
April 22/73	9367	14516	13695	11645
May 11/74	13763	16586	14719	14389
June 8/75	11896	6378	3980	16927
June 9/76	8713	9184	8521	8558
June 24/77	41264	46235	44619	47069
July 9/78	4246	6643	5847	6805
July 27/79	36262	36306	36757	36141
July 30/80	19543	19622	16886	14269
August 5/81	10020	16062	9385	19151
August 17/82	15040	19156	14194	20842
August 24/83	26583	30667	23139	27756
September 14/84	10949	14324	10981	11392
September 21/85	40518	37563	31365	40923
September 28/86	23618	26848	23724	25589
October 7/87	9954	13118	15787	14023
October 19/88	26224	23834	20245	23948
October 22/89	8976	9484	8744	8421
November 16/90	6017	10306	11577	11235
December 9/91	17498	15730	14486	14789
December 23/92	5650	7244	8125	8019
Total	1311243	1422780	1053513	1099307
Average	14409.26374	15634.94505	13681.98701	14276.71429

APPENDIX C--STANDARD OPERATING PROCEDURES

QUALITY ASSURANCE
STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: Chris Vandervoort Date: 07Feb92

0.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

0.0 QA/QC Golf Course Project

0.0 Method Validation

1. Spike a control with 2 -5 times the limit of quantification.
2. Run a solvent blank to look for interferences in the chromatogram with the analyte of interest.
3. Run 10 % of the samples in duplicate to assure repeatability.
4. Run a standard curve and do a least squares regression for a line for quantification of samples.
5. Place one liter of water in refrigerator. Spike with about 1 ppm of the pesticide of interest. Run recovery on GC.

Approved:_____ Date:_____

Matthew Zabik, Laboratory Director

QUALITY ASSURANCE
STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: C. Vandervoort Date: 30Apr92

1.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

1.0 Determination of Chlorothalonil in Water

1.0 Extraction of Chlorothalonil

1. Weigh 100 g of water and place in 250 ml separatory funnel, add 20 g of NaCl, solubilization.
2. Extract 3 times with 20 ml of hexane, each time shake for three minutes and combine extracts, then with small amount of hexane rinse separatory funnel and transfer to hexane extracts.
3. Reduce the volume of extracts to about 1 ml, in Turbo-Vap. Never let extracts go to dryness.
4. Bring the final volume to 5 ml with hexane.
5. Analyze with electron capture detector and 30 m DB-5 capillary column equipped GC.

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Matthew Zabik, Laboratory Director

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STANDARD OPERATING PROCEDURES FORM

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Version #: 1 By: C. Vandervoort Date: 30Apr92

2.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

2.0 Determination of Chlorpyrifos in Grass

2.0 Extraction of Chlorpyrifos

1. Weigh 10 g of and homogenize with 100 ml acetone for 5-10 minutes. Filter with a sintered glass funnel with vacuum. Repeat with fresh 100 ml of acetone and combine extracts.
2. Roto-vap to dryness and add 20 ml of hexane. Put through 2 g of silica-gel 70-230 mesh (oven dried at 110° C for 4 hours) with a glass wool pledget. Rinse flask with 15 ml of hexane twice and add to the column.
3. Turbo-Vap to dryness and add 4 ml of acetone.
4. Analyze with GC.

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Michigan State University

Version #: 1 By: C. Vandervoort Date: 30Apr92

3.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

3.0 Determination of Clopyralid in Grass

3.0 Extraction of Clopyralid

1. Weigh 10 g of and place in 250 ml Erlenmeyer flask and shake for 5 minutes, with 150 ml of KOH.
2. Transfer to separatory funnel. Add 100 ml of diethyl ether, 5 g NaCl and 20 ml of 4 M H_2SO_4. Shake and separate the ether from the aqueous layer and save ether layer , and repeat ether extraction with fresh ether and combine ether extracts. Put through a bed of Na_2SO_4.
3. Reduce the volume of extracts to about 1 ml, in Turbo-Vap.
4. Esterification with diazomethane. Add ca. 2 ml of diazomethane to sample til yellow color remains for 1 hour.
5. Analyze with electron capture detector and 30 m DB-5 capillary column equipped GC.

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Matthew Zabik, Laboratory Director

QUALITY ASSURANCE
STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: Chris Vandervoort Date: 13-Apr-92

4.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

4.0 Determination of Dicamba in Water

4.0 Extraction and clean-up of Dicamba

1. Weigh 10 g of water and place in a 125 mL separatory funnel: acidify to pH 1 by adding 5 mL of 10 % H_2SO_4. Extract 3 times with 25 mL of diethyl ether and combine ether extracts. Reduce the volume of extract to about 10 mL.

2. Prepare a Celite column. To 100 g of Celite add 40 mL of buffer solution. The buffer solution is prepared by mixing equal volumes of 2M sodium dihydrogen phosphate and 2M potassium monohydrogen phosphate. Store the ether for one week then discard. Equilibrate 1.5 l of diethyl ether with 100 mL of phosphate buffer shake and discard aqueous portion. Add 15 g of buffered Celite to a column with periodic draining and addition of equilibrated ether to keep packing covered. Add extract and elute with 265 mL of equilibrated ether. Reduce in volume to about 2 mL.

3. Esterification with diazomethane. Add ca. 2 mL of diazomethane to sample til yellow color remains for 1°. Then reduce volume to < 0.5 mL.

4. ECD-GC analysis

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STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

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Version #: 1 By: Chris Vandervoort Date: 07Feb92

5.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

5.0 Determination of Fenarimol in Water

5.0 Extraction of Fenarimol

1. Weigh a 100 g sample of water add 50 ml of 10% NaCl and extract twice with 40 mL of methylene chloride, combine extracts in a drying flask.
3. Turbo-Vap to dryness at 40-45 ° C.

5.1 Clean-up of samples

1. Prepare an alumina column with
   To a 12 mm i.d. column with a glass wool pledget rinse with 15 mL of methylene chloride and then add 13 +/- 0.5 g alumina, rinse with 10 mL of methylene chloride. Add 1.7 cm of anhydrous sodium sulfate, rinse with 10 mL of methylene chloride. Drain methylene chloride down to the top of the bed level of the column and add sample. Add 40 mL 9:1 methylene chloride:ethyl acetate, discard eluate.
   Add 120 mL 99:1 methylene chloride:methanol, collect and reduce to dryness in turbo-vap.
   Bring to volume with hexane for GC analysis.

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STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: Chris Vandervoort Date: 30Apr92

6.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

6.0 Determination of Isazofos in Water

6.0 Extraction of Isazofos

1. Weigh 100 g of water and place in 250 mL separatory funnel, add 20 g of NaCl, solubilization.
2. Extract 3 time with 20 mL of Chloroform, each time shake for three minutes and combine extracts, then with small amount of chloroform rinse separatory funnel and transfer to chloroform extracts.
3. Reduce the volume of extracts to about 1 mL, in Turbo-Vap. Never let extracts go to dryness.
4. Bring the final volume to 5 mL with chloroform.
5. Analyze with a GC equipped with nitrogen/phosphorus detector and DB-5 capillary column.

Approved:_____ Date:_____
Matthew Zabik, Laboratory Director

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STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: C.Vandervoort Date: 30Apr92

7.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

7.0 Determination of Isoxaben in Grass

7.0 Extraction of Isoxaben

Preparation of Plant Samples: Bulk quantities of plant tissue should be finely ground and thoroughly mixed to provide a homogeneous mixture.

1. Weigh 10 g of grass and place in gyratory shaker with 150 ml of methanol, reagent grade. Cover and shake for one hour.
2. Filter the extract through a Whatman No. 1 filter with a Buchner funnel with the aid of vacuum if necessary.
3. Return plant and filter to rotary shaker with 100 ml of methanol and shake for 0.5 hours.
4. Repeat step 2 with additional methanol to rinse the jar.
5. Transfer the extract to 1000 ml separatory funnel. Add 75 ml of 5 % NaCl solution and 200 ml of water.
6. Extract with two 125 ml of glass distilled hexane. Discard the hexane extracts.
7. Extract with three 75 ml of dichloromethane. Filter the extracts through sodium sulfate with 20 ml of dichloromethane.
8. Evaporate the extract to dryness using rotary vacuum evaporation at 40° C +/- 5° C.

Purification

1. Prepare a alumina/Florisil column for each sample as follows:
   a. Place a pledget of glass wool in the column and tamp it down to the bottom.
   b. Add 13 ml +/- 0.5 ml of standardized alumina and tap gently.
   c. Add 5 ml +/- 0.5 ml of standardized Florisil and tap gently.

d. Add 4 ml of anhydrous sodium sulfate, tap gently.
Note: The alumina and Florisil must be added to the columns in a reproducible manner to assure a consistent elution pattern for all samples within a set.

e. Wash column with 30 ml of dichloromethane and discard the washings. Drain the solvent only to the top to the column packing.

2. Transfer the sample residue to the column using two 5 ml portions of dichloromethane, allowing each addition to pass into the absorbent. Rinse the boiling flask with 25 ml dichloromethane. Allow the solvent to drain to the top of the adsorbent. Discard the eluate.
3. Wash the column with 50 ml of 8:2 dichloromethane/ethyl acetate. Discard the eluate.
4. Wash with 25 ml of 99:1 dichloromethane/methanol. Discard the eluate.
5. Add 50 ml of 99:1 dichloromethane/methanol and collect the eluate in a 125 ml boiling flask.
Note: The solvent volumes used in steps 3, 4, and 5 are dependent on the column profile.
6. Evaporate the eluate to dryness.
7. Add 2 ml of 2 % potassium permanganate solution, and swirl.
8. Add 2 ml of 2 M KOH, swirl.
9. Transfer the solution to a screw-cap vial or test tube. Wash with 4 ml of dichloromethane
10. Seal and shake vigorously for 30 seconds. Let stand for at least 5 minutes.
11. Remove dichloromethane layer by pipet. Filter through anhydrous sodium sulfate into an evaporating flask.
12. Repeat steps 9-11 twice, starting with the addition of dichloromethane.
13. Rinse the sodium sulfate with additional dichloromethane, evaporate with rotary evaporator.
14. Dissolve the residue in 1 ml of 1:1 methanol/water mobile phase and proceed with HPLC analysis.

Approved:_____Date:_____
Matthew Zabik, Laboratory Director

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STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: Chris Vandervoort Date: 30Apr92

8.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

8.0 Determination of Metalaxyl in Water

8.0 Extraction of Metalaxyl

1. Weigh 100 g of water and place in 250 mL separatory funnel, add 20 g of NaCl, solubilization.
2. Extract 3 time with 20 mL of methanol, each time shake for three minutes and combine extracts, then with small amount of methanol rinse separatory funnel and transfer to methanol extracts.
3. Reduce the volume of extracts to about almost dryness, in Turbo-Vap.
4. Bring the final volume to 5 mL with methanol.
5. Analyze with a GC equipped with nitrogen/phosphorus detector and DB-5 capillary column.

Approved:_____Date:_____
Matthew Zabik, Laboratory Director

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STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: Chris Vandervoort Date: 07Feb92

9.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

9.0 Determination of Propiconazole in Water

9.0 Extraction of Propiconazole

1. Weigh a 100 g sample of water and place in a 250 mL separatory funnel, add 20 g NaCl to the sample.
2. Extract 3 times with 20 mL of dichloromethane, each time shake for three minutes, and combine dichloromethane extracts. Rinse separatory funnel with small amount of dichloromethane. Add 1 mL of iso-octane to the Turbo-Vap tube and evaporate to < 1 mL.
3. Bring to volume with iso-octane of about 2 ml.

4. Use a N/P flame ionization detector GC.

Approved:_____ Date:_____

Matthew Zabik, Laboratory Director

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Analytical Laboratory-Pesticide Research Center

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Version #: 1 By: Chris Vandervoort Date: 07Feb92

10.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

10.0 Determination of Triadimefon in Water

10.0 Extraction of Triadimefon

1. Weigh a 100 g sample of water, add 100 ml of chloroform and shake for 30 seconds. Allow the layers to separate and drain the lower organic phase into drying flask. Repeat the extraction 2 times with portion 50 mL of chloroform and combine the extracts.
2. Turbo-Vap just to dryness.

Clean-up of samples

1. Prepare a Florisil column
   To a 20 mm i.d. column with a glass wool pledget fill with 6:4 hexane:ethyl acetate mixture. Add 10 g of 2.5 % water-deactivated Florisil. Top with 5 g of anhydrous sodium sulfate. Drain the solvent down to the top of the bed level of the column. Dissolve the residue from 9.4.1.2 in 10 mL of 6:4 hexane-ethyl acetate and transfer to the column. Adjust the flow rate to 2-3 drops per second. Rinse with 2 additional 10 mL of 6:4 hexane-ethyl acetate. Eluate with additional 120 mL of the 6:4 hexane-ethyl acetate mixture and save all 150 mL of eluant. Reduce volume in turbo-vap to dryness. Bring to volume with hexane for GC analysis.

Approved:_____ Date:_____
Matthew Zabik, Laboratory Director

QUALITY ASSURANCE
STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: C. Vandervoort Date: 30Apr92

11.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

11.0 Determination of Triclopyr in Grass

11.0 Extraction of Triclopyr

1. Weigh 10 g of grass and add 6 g NaCl and one ml of 9 M H_2SO_4, 50 ml of diethyl ether, and 50-100 ml of H_2O to a Erlenmeyer flask and shake for 10 minutes. Run through a filter with vacuum applied. Separate the aqueous from the ether phase. Take the filter paper and aqueous phase and again extract with 50 ml ether. Combine the ether extracts. Wash extract with 20 ml of 10 % NaCl w/v, dry over anhydrous Na_2SO_4.
2. Prepare a silica-gel column by adding 3 g of silica-gel to 1 cm i.d. column as a slurry pack with hexane. Then the column is washed with 100 ml 1:9 toluene and hexane . The residue from step 1 is added to the column with 35:65 toluene and hexane. The compound is eluted with 100 ml 35:65 toluene and hexane. Reduce to < 0.5 ml.
3. Esterification with BF_3 in methanol by adding 0.25 ml of BF_3. Keep vial covered and at 80°C for 1 hour. Let cool then transfer to a separatory funnel with 30 ml of hexane and wash extract with 20 ml of 10 % NaCl w/v, dry over anhydrous Na_2SO_4. Reduce to about 0.5 ml.
5. Analyze with electron capture detector and 30 m DB-5 capillary column equipped GC.

Approved:_____ Date:_____

Matthew Zabik, Laboratory Director

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Version #: 1 By: C. Vandervoort Date: 30Apr92

12.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

12.0 Determination of Flurprimidol in Grass

12.0 Extraction of Flurprimidol

1. Weigh 10 g of grass and place in 250 ml boiling flask connected to a water-cooled reflux condensing tube. Add 100 ml of 4:1 methanol:water and heat to boiling and reflux for 1 hour.
2. Cool to room temperature and pour through a # 7 Whatman filter into a 250 ml separatory funnel with 30 ml of 5 % NaCl. Extract the flurprimidol with 3 x 50 ml of hexane. Collect the hexane extract and pass through Na_2SO_4. Rinse the Na_2SO_4 with 20 ml of hexane. Evaporate the hexane to dryness and dissolve residue in 3 ml of dichloromethane.
3. Attach the Alumina B Sep-Pak cartridge (same as the Acidic alumina) to a Sep-Pak cartridge rack. Rinse the Sep-Pak with 5 ml of dichloromethane:methanol (3:1), followed by 10 ml of dichloromethane. Discard the eluate. Place the sample extract on the Sep-Pak. Rinse with 2 x 3ml of dichloromethane and discard the eluate. Add 8 ml of dichloromethane:methanol (3:1) and collect this fraction. Reduce to dryness and bring to volume for the GC analysis.
4. Analyze with electron capture detector and 30 m DB-5 capillary column equipped GC.

Approved:_____ Date:_____

Matthew Zabik, Laboratory Director

QUALITY ASSURANCE
STANDARD OPERATING PROCEDURES FORM

Analytical Laboratory-Pesticide Research Center

Michigan State University

Version #: 1 By: C. Vandervoort Date: 30Apr92

13.0 GENERAL LABORATORY STANDARD OPERATING PROCEDURES

13.0 Determination of 2,4-D in Grass

13.0 Extraction of 2,4-D

1. Weigh 10 g of grass and place in 250 ml Erlenmeyer flask, add 5 ml of water, 8 ml of H_2SO_4, and 50 ml methanol and shake for 20 minutes. Filter through Whatman # 1 filter. Repeat process of the filter. The combined filtrates are reduced to the water phase.
2. Extract the aqueous phase with 2 x 50 ml of dichloromethane and reduce to about 1 ml.
3. Add 3 g of Florisil to a 1 cm i.d. column and top with about 2-4 mm of Na_2SO_4. Rinse with 30 ml of petroleum ether and discard. Add sample to the column and follow with 15 ml of petroleum ether and discard the eluate. Add 25 ml of 1:1 petroleum ether:ethyl ether. Reduce volume < 0.5 ml.
4. Add diazomethane til yellow color remains for one hour. Reduce volume < 0.5 ml and bring up in volume with hexane.
5. Analyze with electron capture detector and 30 m DB-5 capillary column equipped GC.

Approved:_____ Date:_____

Matthew Zabik, Laboratory Director

LIST OF REFERENCES

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