



ļ

This is to certify that the

thesis entitled

THE DEGRADATION AND EVAPORATION OF DILUTE PESTICIDE RINSATES ON SOILS IN ABOVE GROUND STEEL VESSELS

presented by

Glenn Alan Dickmann

has been accepted towards fulfillment of the requirements for

<u>Masters</u> degree in <u>Entomology</u>

Major professor

Date <u>Sep 25, 1989</u>

O-7639

٠.

4.57

me . . .

MSU is an Affirmative Action/Equal Opportunity Institution



DATE DUE	DATE DUE	DATE DUE	
MSU Is An Affirmative Action/Equal Opportunity Institution			

····

PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due.

THE DEGRADATION AND EVAPORATION OF DILUTE PESTICIDE RINSATES ON SOILS IN ABOVE GROUND STEEL VESSELS

BY

GLENN ALAN DICKMANN

A THESIS

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

MASTER OF SCIENCE

Department of Entomology

ABSTRACT

THE DEGRADATION AND EVAPORATION OF DILUTE PESTICIDE RINSATES ON SOILS IN ABOVE GROUND STEEL VESSELS

BY

GLENN ALAN DICKMANN

A system was designed for the degradation and volatilization of the dilute pesticide rinsates generated by a large Michigan horticultural farm, to avoid potential groundwater contamination. The above ground, steel storage tanks permitted visual inspections for leaks and contained three soil types: sand; sandy-clay-loam; and sandy-loam. Five parent compounds were monitored: aldrin (organochlorine); simazine (s-triazine); azinphosmethyl and phosmet (organophosphates); and captan (phthalimide). Monthly air samples were taken at 2 m above the vessels and 20 meters downwind. Results from 1987 and 1988 indicated no significant build up of monitored pesticides. Air sampling detected no parent compounds downwind and occasional concentrations of the selected compounds were found in the air samples above the soils. Statistically, no best soil type was determined but, results indicated sandy-clay-loam soil to be the best soil for overall degradation in mid Michigan.

. ,

 $\frac{1}{2} \left(\frac{1}{2} + \frac{1$

.

en transformer stationer

ACKNOWLEDGMENTS

I am greatly indebted to many people for their help and guidance in preparing this thesis. I wish to thank the people at the Pesticide Research Center, especially Dr. Sue Erhardt-Zabik, Dr. Salah El-Din Abdel-Atty Selim, Dr. Leavitt and all the IR-4 group, Dr.Hai-dong Kim, Gamal El-din Khedr, and Mary Ann Heindorf. I must also thank Gerald Skeltis and the personnel at the Clarksville Horticultural Station for aiding me in procuring the equipment I needed at the research facility. I am most indebted to Dr. Matthew Zabik for his method of encouraging students to develop new ideas and permitting graduate students to vandalize the equipment. I have great respect for you. To my mother and father, Milton and Leila Dickmannn, I thank you for your ever present love and guidance. Finally, I thank my wife, Robin, for enduring, tolerating, and supporting me throughout the whole ordeal.

TABLE OF CONTENTS

Page
LIST OF TABLES
LIST OF FIGURES
INTRODUCTION AND LITERATURE REVIEW
MATERIALS
METHODS
RESULTS AND DISCUSSION
SUMMARY AND CONCLUSIONS
APPENDIX A PESTICIDE RESIDUE DATA IN 1987, 7-15 CM DEPTH 87
APPENDIX B PESTICIDE RESIDUE DATA IN 1987, 48-56 CM DEPTH89
APPENDIX C PESTICIDE RESIDUE DATA IN 1988, 7-15 CM DEPTH 91
APPENDIX D PESTICIDE RESIDUE DATA IN 1988, 48-56 CM DEPTH93
LIST OF REFERENCES

LIST OF TABLES

TABLE	1.	Soil texture composition as mechanically determined, % organic matter (OM), and cation exchange capacity (CEC)
TABLE	2.	Soil sample means (ppm), SE, soil sampling interaction and CV% of aldrin on soils
TABLE	3.	Estimated aldrin concentrations in soils based on the last sampling dates in 1987 and 1988
TABLE	4.	Soil sample means (ppm), SE, soil sampling interaction and CV% of Guthion on soils46
TABLE	5.	Estimated Guthion concentrations in soils based on the last sampling dates in 1987 and 1988
tabl e	6.	Soil sample means (ppm), SE, soil sampling interaction and CV% of phosmet on soils56
TABLE	7.	Estimated phosmet concentrations in soils based on the last sampling dates in 1987 and 1988
TABLE	8.	Soil sample means (ppm) SE, soil sampling interaction and CV% of simazine on soils58
TABLE	9.	Estimated simazine concentrations in soils based on the last sampling dates in 1987 and 1988
TABLE	10.	Soil sample means (ppm), SE, soil sampling interaction and CV% of captan on soils67
TABLE	11.	Estimated captan concentrations in soils based on the last sampling dates in 1987 and 1988

.

LIST OF FIGURES

		PACE
Figure	1.	Pesticide research vessels diagram
Figure	2.	Pesticide research building diagram 27
Figure	3.	Concentration of Guthion and aldrin in rinsate volumes applied to pesticide collection vessels for 1987
Figure	4.	Concentration of Guthion and aldrin in rinsate volumes applied to pesticide collection vessels for 1988
Figure	5.	Aldrin pesticide concentration in sandy- clay-loam soils at two depths, first season . 32
Figure	6.	Aldrin pesticide concentration in sandy- clay-loam soils at two depths, second season .33
Figure	7.	Aldrin pesticide concentration in sandy- loam soil at two depths, first season 34
Figure	8.	Aldrin pesticide concentration in sandy- loam soil at two depths, second season35
Figure	9.	Aldrin pesticide concentration in sandy soils at two depths, first season
Figure	10.	Aldrin pesticide concentration in sandy soils at two depths, second season
Figure	11.	Guthion pesticide concentration in sandy- clay-loam soil at two depths, first season . 40
Figure	12.	Guthion pesticide concentration in sandy- clay-loam soil at two depths, second season . 41
Figure	13.	Guthion pesticide concentration in sandy- loam soil at two depths, first season 42
Figure	14.	Guthion pesticide concentration in sandy- loam soil at two depths, second season 43
Figure	15.	Guthion pesticide concentration in sandy soil at two depths, first season

Figure	16.	Guthion pesticide concentration in sandy soil at two depths, second season	45
Figure	17.	Phosmet rinsates 1987	48
Figure	18.	Phosmet rinsates 1988	49
Figure	19.	Phosmet pesticide concentration in sandy- clay-loam soil at two depths, first season .	50
Figure	20.	Phosmet pesticide concentration in sandy- clay-loam soil at two depths, second season.	51
Figure	21.	Phosmet pesticide concentration in sandy- loam soil at two depths, first season	52
Figure	22.	Phosmet pesticide concentration in sandy- loam soil at two depths, second season	53
Figure	23.	Phosmet pesticide concentration in sandy soil at two depths, first season	54
Figure	24.	Phosmet pesticide concentreation in sandy soil at two depths, second season	55
Figure	25.	Simazine rinsates 1987	59
Figure	26.	Simazine rinsates 1988	60
Figure	27.	Simazine pesticide concentration in sandy- clay-loam soil at two depths, first season .	61
Figure	28.	Simazine pesticide concentration in sandy- clay-loam soil at two depths, second season .	62
Figure	29.	Simazine pesticide concentration in sandy- loam soil at two depths, first season	63
Figure	30.	Simazine pesticide concentration in sandy- loam soil at two depths, second season	64
Figure	31.	Simazine pesticide concentration in sandy soil at two depths, first season	65
Figure	32.	Simazine pesticide concentration in sandy soil at two depths, second season	66
Figure	33.	Captan rinsates 1987	68
Figure	34.	Captan rinsates 1988	69
Figure	35.	Captan pesticide concetration in sandy- clay-loam soil at two depths, first season .	70

Figure	36.	Captan pesticide concentration in sandy- clay-loam soil at two depths, second season .	71
Figure	37.	Captan pesticide concentration in sandy- loam soil at two depths, first season	72
Figure	38.	Captan pesticide concentration in sandy loam soil at two depths, second season	73
Figure	39.	Captan pesticide concentration in sandy soil at two depths, first season	74
Figure	40.	Captan pesticide concentration in sandy soil at two depths, second season	75
Figure	41.	Sandy-clay-loam soil pH for 1987-88	78
Figure	42.	Sandy-loam soil pH for 1987-88	79
Figure	43.	Sandy soil pH for 1987-88	80
Figure	44.	Recorded volume of rinsates entering the collection vessels for 1987	83
Figure	45.	Recorded volume of rinsates entering the collection vessels for 1988	84
Figure	46.	Total rinsate volume applied to each soil from collection vessels in 1987	85
Figure	47.	Total rinsate volume applied to each soil from collection vessels in 1988	86

INTRODUCTION

AND

LITERATURE REVIEW

The importance of potable groundwater is apparent by the fact that 96% of available freshwater in the United States is groundwater and it is the primary water source for half of the U.S. population. The rural population is the most dependent on groundwater, as 95% of their water is supplied by this source.

The U.S. Geological Survey of 1980 (Solley, 1980) estimated that 89 billion gallons of water are pumped from wells each day. Of this tremendous volume, 64.5 billion gallons are directed toward agricultural use. A further breakdown of use showed that 60 billion gallons are used for irrigation and 4.5 billion gallons are for other rural uses (domestic drinking and livestock).

Originally, groundwater contamination concerns were ignored as it was assumed that the soil was an efficient filter, retaining and degrading pollutants, thus protecting the groundwater. However, the extent of groundwater contamination problems are just now being realized and increased testing is locating many areas of contamination. As

· · · · ·

· · · · ·

of 1985, 38 states reported that agricultural sources were responsible or suspected causes of groundwater contamination and of these 38 states: 38 detected nitrates from fertilizers; 24 states reported fecal bacteria contamination from livestock and 21 reported herbicides/ insecticides were present (Water Pollution Control Administrators ,1985).

Agricultural pesticide contamination is generally due to some type of translocation, primarily being: volatilization; runoff; plant uptake; or leaching. The main focus of this research is directed toward one aspect of the agricultural problem; the safe disposal of dilute pesticide rinsates. These rinsates are the waste volumes remaining from containers, spray tanks or equipment wash water after pesticide application. The best method to minimize these rinsates is to mix only that amount of pesticide which is necessary to achieve the desired effect. However, occasionally an excessive volume may have been prepared or a pesticide which is to be applied is incompatible with the previously applied pesticide and to prevent any carryover, which may damage a crop, one must rinse out the sprayer.

The disposal of these rinsates poses a potential source of groundwater contamination. Michigan, as currently known, has no major pesticide contamination problem. Most of the known groundwater contamination sites in Michigan are attributed to landfills, underground storage tanks and septic systems (D'Itri et al., 1987). It is not clear whether high farm nitrate levels indicate a pesticide problem. The

probability is that the repeated dumping of dilute pesticide rinsates in one area would cause a pollution hazard and therefore should be avoided.

Presently, there is no practical guidance provided to the pesticide applicator who desires safe disposal of rinsates. Some previous advice is known to be in error, for example in the Pesticide Book(Ware,1978), it was stated if unwanted pesticides can not be given to a responsible person, one could bury dry pesticides at a depth of 18 inches in a safe disposal site. What constitutes a "safe site" was not discussed. As for liquids, it was recommended they should be poured into a sandy soil pit. The updated version of this book, Fundamentals of Pesticides: A self instruction guide (Ware,1982), no longer recommended burial but promoted contacting a state agency or expensive disposal in a hazardous landfill- but, the emphasis was placed on not simply burying toxic waste.

The state of Michigan has developed rules on the proper handling of hazardous waste, yet the potential for groundwater contamination remains. The Michigan Department of Natural Resources Hazardous Waste Division developed the Hazardous Waste Management Rules, revised September 6, 1986. Under rule 204, noted for exclusions, waste pesticides generated by a farmer can be disposed of on his own farm provided they are consistent with the disposal instructions on the pesticide container label and he empties each pesticide container according to the label instructions.

Thus, essentially it recommended no new methods for the disposal of pesticide rinsates.

The European nations convened in Strasbourg, Germany, in 1984, and the council recommended that pesticide containers, unless they are small, should be crushed and delivered to the local waste disposal plant. It recommended that all unwanted pesticides be disposed of by combustion, unless they contain mercury or arsenic.

In the case of in situ disposal of unwanted pesticides, some countries have permitted the disposal of wastes after dilution to a specified concentration into disposal pits. Some pits are collection pools constructed so as to prevent leakage or overflow. Other pits, constructed on farms, should be concrete lined and filled with alternating layers of gravel and soil to encourage microbial decomposition. All disposal sites must have restricted access.

In the United States, the general practice of farmers, who generate any pesticide rinsates, is to spray any excess volume on the road or land adjoining the mixing/spraying site. This was the method of disposal used by more than 12% of the farmers responding to a survey on their disposal methods for rinsates and thought to be under reported (Ryan,1974). The most common disposal methods used by the respondents were burial or deposition in a landfill, the use of a landfill would be cost prohibitive with large volumes, as well as inconvenient and increasing the potential for groundwater contamination.

• • • • •

By providing farmers with an effective, low cost on site disposal system compliance with the safe disposal of farm pesticide residues would be greatly enhanced. Besides the strong motivating force of protecting ones own water supply, there is the additional benefit of minimizing the contamination of neighboring wells and thus reducing ones liability.

Previous attempts for pesticide rinsate disposal involved the use of in ground containment vessels such as the water-soil system used by Junk et al. (1984) at Iowa State University. Their system consisted of maintaining 60 L of water over 15 kg of soil in 110 L plastic garbage containers to which controlled volumes of pesticides were added. Using six different classes of pesticides they concluded degradation rates vary widely and the half-lifes they observed for their system did not comply to those published. But they did not state whether the environmental conditions of the published half-lives were under the same conditions as their experiment. The resultant volatilization studies indicated insignificant losses of pesticide occurred, as not even the volatile trifluralin was detected. The vessels were initially spiked with 300 grams of active ingredient of each of the chosen pesticides.

Another system used at Iowa State University by Baker and Johnson (1984) employed a plastic lined pit with a metallic cloth to stop burrowing rodents. The pit was filled with original soil to a depth of 1.2 m, the top layer consisted of

•••

crushed limestone 0.5 m in depth, and 700 L of water was added to the system. This study was designed to examine water and pesticide volatilization in a northern midwestern state. It was concluded 20,000 to 30,000 L of water could be evaporated from their system (surface area of 113 m²) and of the pesticides used none had >8.4 % of their concentration in the air ,vapor pressures of all pesticides were <10⁻³ mm Hg. The weight of active ingredient varied from 84 to 6 kg depending on the selected compound.

In Davis, California, Winterlin et al. (1984), monitored pesticide evaporation beds for two years. Their system used butyl rubber lined evaporation beds filled with sandy loam soils. The pesticide solutions entered the system by underground leach lines so that water moves up through the soil by capillary action. The soil beds were covered and lime was added in varying concentrations and with variable mixing action. The conclusions showed that degradation/disappearance prevented high level pesticide build up and no excessive air exposure was observed. Furthermore, amending the soils with lime was thought to be an important factor in degradation of the organophosphate and carbamate pesticides.

The transport of chemicals into the groundwater has a multitude of complex, simultaneous interactions that can be classified under four major categories: the nature or properties of soil components; the properties of the pesticide; climatic conditions; and agricultural practices.

As for agricultural practices, their effect on this research will be related to the application frequency and pesticide concentration of the volumes added to the soils. None of the experimental soils are to be tilled. However, it is important to note the initial placement of soils into the tanks provided a disturbed system. Furthermore, the soil core samples for pesticide analysis (although the core holes were filled with soil) will provide an opportunity for channeling and thus bypassing the normal percolation.

The sorption of pesticides to a soil surface is a function of what type of charge is on the active site, the chemical nature of the pesticide and what competing molecule(s)/ion(s) is (are) present. Characterizing the active sites of the soil can be performed by examing the soil texture (% composition-clay, sand, silt) and the percentage of organic matter(O.M.). The make-up of soil texture and percent O.M. will determine the maximum pesticide capacity of the soil. excluding the presence of modifying factors such as pH. It is generally accepted that the higher the O.M. content of the soil, the less the opportunity for the compound to leach. This is because of the wide variety of functional groups present in organic matter that can bind a wide range of chemical compounds. Organic matter contains humic acids, fulvic acids and humin which possess the following functional groups: carboxyl; hydroxyl; carbonyl; methoxy; and amino (Saltzman, 1986).

Other physical properties that define pesticide behavior

in soils are bulk density, pore size, field moisture, and hydraulic conductivity. Bulk density is the weight per unit volume of a soil in $grams/cm^3$, which includes pore space. Pore space is the volume of the soil that contains only water or air, thus solids are excluded. Field moisture is the percentage, by weight, of water present to weight of the soil. Hydraulic conductivity is the process of water movement through the soil column, which is guite variable as it depends on uniformity of the soil texture. Even within the same soil texture the coefficients of variation will frequently be in excess of 100% All of these physical properties determine how water will percolate through the soil and thus the length of time for water/pesticide contact. A greater significance of pesticide/water contact would be observed as the water solubility of the pesticide increases (Helling and Gish, 1985).

The relationship between water solubility and adsorption had been controversial, but it is generally accepted that water solubility is related to adsorption within specific groups of compounds. The report of Bailey et al. (1980), indicated that within an analog series of compounds with a basic character, the magnitude of adsorption by clay is related to water solubility.

Besides the physical properties of the soil, one should also consider the chemical properties of the soil: pH; cation exchange capacity (CEC); and redox potential.

Studies of the affects of soil pH on the microbial and

and the second s

chemical degradation of pesticides have provided conflicting data. For example, studies have shown that the degradation of atrazine(s-triazine) and vernolate(dithiocarbamate) are not affected by changes in soil pH (Hance,1979 and Smith et al. 1970, respectiviely). Yet, a positive correlation was observed by Zimdahl et al. (1970) for atrazine and Sethunathan et al. (1969) for vernolate. A possible explaination for these opposing results may be attributed to differences in soil properties of the experiments (Saltzman, 1986). So the more thorough the soil characterization, the more likely the reproducibility of the study.

The biodegradation of some organic compounds by microorganisms depends upon the concentration of the chemicals present. Some compounds are mineralized, cometabolized, or resistant to microbial conversion at one concentration and yet, at a lower initial concentration they are not. Thus, a threshold may exist where an organism cannot maintain its metabolic needs by the low concentration of substrate (Alexander, 1985). The compounds analyzed for in the proposed experiment should be in the higher concentration ranges , > 1 ug/ml, which will make the threshold level less of a concern.

CEC (cation exchange capacity) involves the ability of the clay minerals in soils to adsorb positively charged molecules or ions. Many organic molecules are positively charged by protonation (amine, alcohol, and carbonyl groups) and available for sorption. CEC reactions produce no net

changes in energy and are usually temperature-independent, as illustrated by simazine or atrazine being adsorbed equally by organic soils at 50°C as at 0°C. CEC is a varying quantity that depends on both the pE and pH of the soil (Helling, 1986).

Oxidation-reduction reactions are important considerations in the environmental chemistry of soil/water systems. Many of the important redox reactions are catalyzed by microorganisms, for example, bacteria cause molecular oxygen to react with organic matter; Fe^{+5} reduction to Fe^{+2} ; or the ammonia to nitrate oxidation. An important effect seen in water saturated soils is the soil becomes much more reducing and the soil pE may fall from +13.6 to 1 or less(at pH=7). This reducing soil environment can cause the reduction of MnO₂ and Fe_2O_3 to their soluble +2 valences (Manahan, 1975).

The chemical properties of the pesticide, of course, greatly influences the ability of the compound to be transported into the groundwater. The major properties to be addressed are soil adsorption (K_d) ; water adsorption; ionization constant(pK_a , pK_b); chemical and biological stability (persistence); and volatility.

Adsorption of the pesticides to the soil can be examined by examing cationic, basic, acidic and non-ionic categories. From the discussion of CEC it would be reasoned that both mineral ions and organic cations would compete for the same adsorption sites. It has been shown (Best et al., 1972) that
the primary mechanism for adsorption of organic cations by soil organic matter is ion exchange. Likewise, ion exchange was observed by clays for cationic pesticides (Weber, Perry and Upchurch, 1965). Adsorption of cationic pesticides by clays is influenced by their molecular weight, functional groups and molecular configuration Other important adsorption mechanisms in soils are hydrogen bonding, ion-dipole, and physical forces.

Basic pesticides , such as the s-triazines, are strongly bound by soils depending on the surface acidity of specifically the clays. If surface acidity was more than ca. two pH units > the dissociation constant of the compound, then van der Waals forces were responsible for adsorption. When the surface acidity was one to two pH units below the pK_{n} , protonation occurred and chemical adsorption could occur. Protonation could be due to the presence of acid exchange sites on the clay or the dissociation of water associated with the exchangeable cations (Saltzman, 1986).

In the cases of weak bases, it was found that adsorption occurred greater at pH's above the dissociaton constant. The authors explained this as relating to more of the pH of the bulk solution rather than the clay surface. Performing calculations by the Boltzmann distribution law of the concentration of the adsorbed ions in the proximity of an adsorbing surface, the authors determined van der Waals forces as the primary cause of adsorption (Saltzman, 1986).

Most studies stated adsorption of weakly basic pesticides

by soils are related to soil organic matter. Again, it was shown that maximum adsorption of seven s-triazines in high organic matter soils occurred at pH levels near the pK_n of each compound (Weber et al. 1969). The best adsorbed compound depended on molecular structure versus pH (Morill, 1982).

Acidic pesticides are also adsorbed by soil organic matter. The molecular form is present at pH levels below the pK, and increasing the pH will cause dissociation. In their anionic form these pesticides are repelled by the negatively charged soil surfaces, some slight adsorption occurs due to van der Waals forces and H-bonding (Saltzman, 1986).

The vast majority of pesticides in use today are the non-ionic types ie. chlorinated hydrocarbons, organophosphates, carbamates, anilides, uracils, ureas, anilines and amides. Thus adsorption ability would vary greatly over these pesticides.

Neutral organic pesticides are not attracted to clay surfaces and must compete for sites with hydration water. Under drier conditions adsorption can be from cation-dipole and coordination bonds, hydrogen bonds, and van der Waals forces.

A study by Saltzman and Yariv (1976) indicated adsorption of parathion by montmorillonite was due to a water bridge. In aluminum saturated montmorillonite both the NO_2 and the P=S group could be bound to the cation via a water bridge. Usually more than one adsorption mechanism is involved in

binding and the binding is determined by the hydration status of the clay. But adsorption of neutral organic pesticides is better adsorbed by soil organic matter. Many studies, such as by Felsot and Dahm, (1979), have determined that the hydrophobic bonding sites of soil organic matter allowed the greatest mechanism for adsorption.

At 20°C and 20% relative humidity water forms a monolayer on the surfaces of soils(Quirk, 1955). Therefore initially, one can assume adsorption sites in a soil system are occupied by water. Walker (1961) observed that vermiculite clay particles are hydrated in two ways; primary hydration-where water is directly coordinated to the cation and secondary hydration- when water is indirectly linked to the cation. It has been observed that the primary waters of hydration are difficult to displace, but some organic molecules will displace weak polarizing cations like Na⁺ or Ba⁺. But it is unlikely that the multivalent cations such as Mg or Al would be displaced. At low moisture levels, some less polar organic compounds (BPTC and Tri-allate) are better competitors for adsorption sites. When water content is low the surface acidity of clay increases. Normally water is not acidic enough to protonate organic molecules, but when water is associated with a metal cation H⁺ is often produced by hydrolysis. So amines and amides can be protonated under low moisture conditions (Saltzman, 1986).

The tendency of pesticides to volatilize is influenced by several factors. The chemical structure is important as it

1 1 **1**

determines vapor pressure and solubility in soil/water. Cool, dry conditions in soils with high organic matter or clay content normally greatly reduce volatility losses. Whereas warm, moist conditions increase volatility. Spencer and Cliath (1974) discovered loss rates of trifluralin in field studies as high as 40% under warm, moist conditions. As mentioned before, soil properties can reduce or increase volatility by adsorption activity. Sandy soils will increase volatility and more organic matter type soils will decrease it.

Some primary factors that affect pesticide degradation in soils are moisture, soil/air temperature, aeration and depth of application. The chemical effect of water is to cause hydrolysis or displace the organic compounds from adsorption sites. Some compounds are unaffected by high moisture conditions such as the chloroanilines. The degradation rates of some pesticides increased with increasing moisture, up to the level just below saturation. These are the following: atrazine; azinphos-methyl; simazine; and trifluralin. Parathion, DDT, BHC and many chlorinated hydrocarbons are noted to degrade faster under flooded conditions.

Temperature affects pesticide decomposition by increasing abiotic reaction or microbial activity. Many references exist that confirm this general trend and some relevant examples are aldrin, simazine, azinphos-methyl, and trifluralin.

The aeration factor depends on microbial susceptibility to aerobic or anaerobic conditions. Some pesticides degrade

. .

, •• • • . • • • •

faster under anaerobic conditions, whereas others degrade faster in aerobic soils. Similarily, depth of application determines the amount of oxygen available, what types of microbes are present, and certainly decrease volatility and photodecomposition.

The rinsate disposal system for this research was built at the Clarksville Horticultural Station near Clarksville, Michigan. It is a 440-acre station, located about 45 miles west of Lansing. It is a facility for both fruit and vegetable research; ca. 120 acres for fruit research and another 100 acres are assigned for vegetables. Michigan's fruit and vegetable industries are valued at 200 and 140 million dollars a year, respectively. Thus the safe operation of the agricultural system is vitally important to the state's economy. The disposal system consisted of a concrete drainage pad that emptied by gravity into an above ground steel containment vessel. The above ground tank provided for easy inspection to assure containment of rinsates (Clarksville Horticultural Experimental Station, 1988).

MATERIALS AND METHODS

A. MATERIALS

Research containment vessels:

Two 3000 gallon steel storage tanks were cut in half, longitudinally, and epoxy-coated. The resultant 1500 gallon tank was further split into two equal research units of 750 gallons each and filled with locally obtained Michigan soils. Each storage tank was 18 feet long and 64 inches in diameter (see Figure 1).

All vessels were supported by steel frames, setting on a concrete floor which permitted visual inspections for leaks. The roof was covered by Lascolite^R panels, that transmitted visible light, but transmission cut off was at ca. 320 nm. The concrete floor was sloped slightly into a collection channel. This channel (trough) had a ball joint operated tee valve that could be opened as needed to remove collected mud and rain. The entire structure was enclosed by chain link fence with a door that could be locked. Electrical outlets were available for pumping of rinsates and weather data devices (see Figure 2).

· · · · ·

Reagents:

SOLVENTS-All solvents were pesticide grade, used as received, and were as follows: methanol; acetone; petroleum ether; ethyl ether (anhydrous); hexane; and methylene chloride.

CHEMICALS-These are listed as follows: anhydrous sodium sulfate (granular); florosil, pesticide grade 60-100 mesh that was activated @ 135° C for > 48 hours; and 0.2 M NH₄Cl.

Equipment:

-Perkin-Elmer Gas Chromatograph model 8500 with ⁶³Ni electron capture detector with a DB-5 capillary column 30 m by 0.25 mm ID .25 um film thickness (J&W Scientific).

-Beckman Gas Chromatograph model 65 flame photometric detector in the phosphorous mode with a DB-5 megabore column 30 m by 0.53 mm ID 1.5 um film thickness (J&W Scientific).

-Tracor 460 Gas Chromatograph with a nitrogenphosphorous detector (alkali flame) and a six foot glass, 1/4" ID, 3% OV-17 on 100/120 supelcoport packed column.

-hand held pH meter, by Omega model PHHH-80.

-muffle furnace

-vacuum oven

-Buchi rotovaporator

-Nermag R10-10C quadrupole mass spectrometer interfaced

.

an an an Arrange ann an Arrange ann

to a Delsi Gas Chromatograph model Di700 with a DB-1 capillary column 60 m by 0.25 mm ID .25 um film thickness (J&W Scientific).

Soils:

Two soils were obtained from the Clarksville Horticultural Experimental Station (CHES), the sand and sandy-loam soils. The third soil was transported from the Michigan State University campus, a sandy-clay-loam. All tanks were filled with soils to within approximately 10 inches of the top of the tank (approximately 1990 kg). All soils were analyzed for the selected pesticides and were below detectable limits.

Miscellaneous:

-boiling chips
-silanized glasswool
-Whatman cellulose extraction thimbles 25mmx80mm
-Reference standards from BPA Research Triangle Park,N.C.
-Polyurethane foam plugs
-air compressor
-10 ml disposable pipettes
-submersible pump(Little Giant), a non-submersible pump,
40 feet of rubber hose, water meter(0.1 gallon increments).

B. METHODS

All laboratory equipment was cleaned by soaking and

• · . .

. -: . · · · · · · · · · · · ·

and scrubbing in hot, soapy water >50°C, followed by a triple rinse of hot water and distilled water. A final rinse of acetone was performed prior to placement in a drier oven (methlyene chloride and acid washes were also used as needed).

The three soils were mechanically characterized at the Crop and Soil Sciences building at Michigan State University by Dr. Mokma. Soil volume was estimated at ca. 150 cubic feet for each of the research units. The soils were further characterized by organic matter content and soil pH (Methods of Soil Analysis 1982). The cation-exchange-capacity of the three soils were performed by the Soils Testing Laboratory at Michigan State University (a centrifugation method by D.D. Warncke).

Four pesticides were chosen for analysis based on prior high frequency of application at the facility, and these are as follows: azinphos-methyl(Guthion) and phosmet(Imidan), both organophosphates; captan, a phthalimide; and simazine(Princep), a s-triazine. Aldrin, a chlorinated hydrocarbon, was the fifth pesticide and it was added directly to the soil by the researcher. An unforeseen problem occurred over the past two spraying seasons, as no Guthion was sprayed at the CHES (Clarksville Horticultural Experimental Station). Thus, it too was added directly to the soils.

Rinsates were gravity fed in PVC pipe into one of the unused research units, henceforth called a holding tank. The

holding tank, capable of containing 750 gallons, was covered by a wooden lid and had a faucet at the bottom where a pump could be connected to spray the rinsates on the soils. An additional tank (polyethylene type) was procured June 25, 1987, for temporary storage, as initially too much volume entered the system. The primary reason for this additional tank was that rain had entered from the drainage pad.

A submersible pump was operated in the holding tank for 60 to 90 minutes prior to rinsate application to throughly mix the volume (rated circulation 500 gallons @ one foot). Generally, the tank contained 400 to 600 gallons maximum, any rinsate volume above 600 gallons was transferred to the temporary tank until such time as a low volume occurred in the holding tank.

After mixing, a non-submersible pump was attached to the faucet. Next, a forty foot garden hose was connected to the pump, which was then connected to a water meter device. This device was accurate to 0.1 gallons and a strainer type filter was installed to remove particulates to prevent frequent clogging of the pump. The strainer required cleaning normally after 30 gallons was applied.

The volume applied to the soils was dependent on total volume in the rinsate collection system. Since there was no control over input into the system, application of volume would vary. Both in 1987 and 1988, the maximum applications were 63 gallons/ application and the minimum 13 gallons, with an average of nearly 30 gallons. Rinsate volume was

applied almost every week.

Equal volumes were applied to all soils by a hand held hose as uniformly as possible. Once per tank application, the volume delivery was checked by a polyethylene measuring pail. A one gallon sample was collected from each tank and then composited for a one gallon sample to be analyzed for the selected pesticides. The sequence of rinsate application to all tanks were randomly selected.

Only three pesticides were analyzed for in the rinsates because Guthion and aldrin were applied directly. Phosmet, captan and simazine were determined by the multi-residue method of the EPA. The general summary is as follows: 1 L of solvent was extracted with methylene chloride by shaking in a separatory funnel. The methylene chloride was isolated, dried and concentrated to a volume of 3 ml after solvent replacement with 15% diethyl ether/hexane, substituted for MTBE (methylated tri-butyl ether).

A modification was made to this procedure as a florisil column clean up was necessary. Micro florisil columns were made by adding a small amount of silanized glass wool to a disposable pipet. PR grade Florisil (5 grams,60/80 mesh) was added and capped with 1 cm of anhydrous sodium sulfate. Prior to sample placement on the column, the column was rinsed with 20 ml of petroleum ether(pe). Six 15 ml fractions were collected: I- 15% EE/PE; II,III- 50% EE/PE; IV,V,VI- 100% EE. Fractions II to VI were composited. Captan was quantitated on the Perkin- Elmer electron capture

detector GC, phosmet with the Beckman flame photometric detector (P-mode) GC and simazine with the Tracor nitrogenphosphorous detector GC.

The following GC conditions existed for each of the pesticide determinations (rinsate and soil analyses):

Compounds- captan, aldrin were determined by electron capture detector MDL: 0.5 ppm captan, 0.005 ppm aldrin

> INJECTOR : 230°C OVEN : 200-230°C 2°/min, 230-260°C 10°/min, 2 minute hold @ 260°C DETECTOR : 300 °C

CARRIER GAS: Helium 20 ml/min

MAKE-UP GAS: N2 ml/min

INTEGRATOR : GP-100

COLUMN : DB-5, 30m

Compounds- phosmet, Guthion were determined by a flame photometric detector MDL: 0.5 ppm for both

INJECTOR	:	250° C
OVEN	:	240° C
DETECTOR	:	300° C
CARRIER GAS	:	He 20 ml/min
FLAME GAS	:	Air150 cc/min
		H2 150 cc/min
INTEGRATOR	:	Spectra Physics SP4270
COLUMN	:	DB-5, 15m

- A second s

))	i.
₽	:	,
• . • • •		· · · · ·
,		

Compound- simazine was determined by a alkali-flame

detector MDL: 0.01 ppm INJECTOR : 230°C OVEN : 195°C DETECTOR : 240°C CARRIER GAS: N₂ 25 ml/min FLAME GAS: H₂ 3.5 ml/min Air 110 ml/min INTEGRATOR : Hewlett-Packard 3390A COLUMN : 3% OV-17, 6 ft glass

Soil sampling was performed by a stainless steel soil corer with an open side for sampling. In order to minimize channeling and soil depletion two fractions were taken at each sample site. These were 7-15 cm and 48-56 cm(the bottom of the tank). Three soil samples from each tank were placed in air tight glass containers and transported on ice. Upon arrival at the analysis point, the samples were placed in a freezer @ -15°C until analyzed.

To determine the percent recovery for each of the pesticides from the variouw soils, 25 gms of each soil type were spiked with 1 ml of an 8 ppm mix consisting of all of the standards. The soils remained in the dark for 12 hr prior to extraction. The initial recovery determination were performed in triplicate and thereafter only one recovery was performed per batch of a soil type. All analyses were performed by the procedure in the following paragraph.

· --, ·

Soils were allowed to thaw at room temperature before pesticide extraction was performed. The extraction procedures for simazine, aldrin and captan were based on those of the Pesticide Analytical Manual (1980) and adapted for Guthion and phosmet determinations. First, a 20 to 30 gram soil sample was weighed into a thimble for soxhlet extraction. The 250 ml round- bottom flask contained 150 ml of a 1:4 mix of hexane/acetone and two boiling chips. Extraction occurred over a six hour period at 8 to 10 cycles per hour. The extraction volume was reduced to 3-5 ml and 15% BE/PE was substituted under further concentration. The extract was next dried over anhydrous Na₂ SO₄. Micro columns with Florisil, as described under the rinsates analysis section were used. Six fractions were collected as follows: I- 15 ml of 15% BE/PE contained aldrin; II and III were 15 ml of 50% EE/PE and IV through VI were 100% EE which when combined they contained captan, simazine, phosmet and Guthion. Volume was reduced to ca. 10 ml by rotovap and further concentrated over a gentle stream of N_2 . One blank and one recovery soxhlet extraction was performed with each batch of samples.

The next step was to inject a 1-2 ul sample volume on the appropriate GC. Two injections were performed for each sample and they had to be within 15% or else repeat injections were made. Standard curves were performed by using four concentrations. Each batch of soil extractions were run with a blank and a recovery to evaluate the

the procedure.

Air Sampling:

Air sampling was performed once a month from June through September in the summer of 1987 with porous polyurethane foam plugs (PUF). The PUFs were five cm long and 4.5 cm in diameter. The PUFs were previously prepared by rinsing with distilled deionized water in a pipet washer for six hours, a soxhlet extraction with 500 ml acetone for six hours and finally a six hour soxhlet extraction with hexane. This is a method used by Turner and Glotfelty(1977).

The air was sampled over each research unit by an electric vacuum pump. Two PUFs were placed in tapered glass cylinders, 2 m above the surface of the tanks with flowrates of 33 L/Min passing through each one. The pump was operated for 90 minutes to sample 10,000 L of air. One air sample was performed downwind of the facility. After sampling each PUF was placed in a sealed glass container and stored at -15°C until analyzed.

Airborne residues were analyzed by soxhlet extraction, 150 ml of methanol at 8-10 cycles per hour. The volume was concentrated by rotovap to ca. 5 ml and further blown down to 2 ml by a gentle stream of N_2 . The next step was to inject 1-2 ul of sample onto the appropriate GC. Again, two injections were performed and more if the values were not within 15% of each other.

.





Results and Discussion

The results of the mechanical determination of the soil textures indicated the presence of the following soils: sand; sandy-loam; and sandy-clay-loam. The analysis may be viewed in Table 1 below.

Table 1. Soil texture composition as mechanically determined, % organic matter(OM), and cation exchange capacity(CEC).

	San dy- Loam	Sandy-Clay-Loam	Sand
Sand &	53	51	95
silt %	34	29	1
Clay %	13	20	4
ON %	1.9	2.0	0.3
CEC	6.49	8.38	0.88

Over the 2 year study period, the average precipitation recorded for 1987 was 31.8 and 33.9 inches for 1988. This compares to a 30 year average of 30.4 inches for the area. The average maximum temperature for the area is 57.2° F, but the averages during this period were slightly higher, 57.4° F in 1987 and 57.3° F in 1988. The 30 year average minimun temperature for the area is 37.7° F and the observed average low temperatures were 39.1 and 39.4° F for 1987 and 1988, respectively.

Since the summer temperatures were above average and the relative humidity was below average, the evaporation and microbial activity was thought to be above normal over the experimental period. Another factor to consider is the thermal conductivity of the soils, which is as follows: sand > loam > clay. The greatest modifying factor of thermal

.

conductivity is water content. With an increase in water content, one will see an increase in thermal conductivity.

Each of the pesticides will be addressed separately, beginning with the properties of the pesticide and followed by the results. The data was analyzed by a computer program, MSTAT (Michigan State University, 1989). Mechanically, the data was analyzed as a 2-way analysis of variance (ANOVA), but no proper test for the main effects of soil was possible as only one block (no replicate soil) was used. However, the soil-time interaction was appropriately analyzed and was important because the investigation was to examine the pesticide over time to note if accumulation or degradation was occuring in the storage vessels. The two factors for the ANOVA were the three soil types and the sampling dates.

Aldrin, a cyclodiene, has several degradation pathways of which the first step is epoxidation of the non-chlorinated ring. Further degradation reactions are molecular rearrangements that are primarily thought to be caused by microbes. The metabolites produced are ketones, aldehydes, and alcohols; the precise mode of degradation is unclear (Morill, 1982). It has been shown to be stable over a pH range of 4 to 8, with acids attacking the unchlorinated ring (Pesticide Manual, 1983). The half life of aldrin, dependent upon many aforementioned variables, is measured in years, ranging from 3 to 4 years.

The recovery for aldrin on spiked sandy-clay-loam soils was 78 % <u>+</u> 8 sd; sandy-loam was 85 % <u>+</u> 7 sd; and sand was 88%
















+ 11 sd (n=10). Although, this was a broad range, the average was near 80%. Upon review of aldrin in Table 2, as expected the highest concentrations remained in the sandy soil. The sandy-loam soil performed slightly better than the sandy-clay-loam in reducing the aldrin concentration.

Table 2 Soil sample means in ppm, standard error, soilsampling interaction (A*B), and coefficient of variation (CV%) of aldrin on sandy-loam (S-L), sandy-clay-loam (S-C-L) and sand (S) soils at 7-15 and 48-56 cm for 1987 and 1988.

		S-L	S-C-L	8	S y	<u>A*B</u>	CV%
<u>1987</u>						• •	
7-15	CI	0.71	1.56	1.77	0.27	**	34.9
48-56	CM	0.57	0.57	0.83	0.28	NS	73.0
1988							
7-15	CR	1.43	0.98	2.00	0.56	**	66.0
48- 56	CM	0.72	1.26	1.73	0.28	**	39.2
		**= p<.01	NS=	not sig	mificant		

The total input of aldrin into each experimental tank in 1987 was 11,357 mg (active ingredient, A.I.) and 11,166 mg A.I., in 1988. To provide a general idea of the concentration of compounds in the soils, the upper and lower data were averaged and multiplied by the weight of the soil in the tanks (approximately 1993 kg). It is understood that the following results are based on three core samples from the selected depths of 7-15 and 48-56 cm and may not necessarily represent the total concentration present. The following table shows year end concentrations of A.I. of aldrin on the three soils.

Table 3. Estimated aldrin concentrations (mg A.I.) in soils based on the last sampling date in 1987 and 1988.

₹ ₹ €

Table 3 (cont'd)

	Sandy-Loam	Sandy-Clay-Loam	Sand
1987	681	737	2385
1988	4351	864	5713

As can be seen all concentrations are less than total input values. The sandy-clay-loam soil had a much lower concentration than the other soils, and this difference is not due to adsorp- tion as both sandy-loam and sandyclay-loam had similar recover- ies. As seen in table 2, the soil-sampling interaction confirmed that the decrease in concentrations were significant at the 1% level.

The graphs of aldrin in soils over time appeared to agree with application because two spikes are seen which represented two applications. The high value for the last sampling date in 1988 for the sandy-clay-loam and the sand indicated that possibly the second application of aldrin was too high. The previous year only 12 ppm aldrin was added whereas in 1988 44 ppm was applied. Another question that arose is that aldrin would be expected to remain in the upper soil strata but in some cases it was higher in the lower strata. Two plausible explainations are that an even distribution of pesticides over a large area is difficult to achieve, as seen by the generally large coefficients of variation and larger discrepancies are seen in the second year indicating channeling from sample core removal.

Azinphos-methyl (Guthion), is an organophosphate insecticide that degrades readily in cold alkali or acid.

• -a ser internation of the second s













Its vapor pressure (v.p.) is a relatively low 1 u pascal at 20°C, aldrin's v.p.= 10 u Pascal. Most decomposition of organophosphates and organochlorines are believed to be mediated by microbes (Organic Chemicals in the Soil Environment, 1972). The half-life of Guthion as provided by EPA leaching criteria is 40 days.

The recovery of Guthion on sandy-clay-loam was $92\% \pm 5$ sd; sandy-loam was $86\% \pm 7$ sd; and sand was $87\% \pm 4$ sd (n=10). From Table 4 one notes that no soil appeared to decrease the Guthion concentration better than the others. Again the soil-sampling interaction is significant at the 1% level. Although the grand means for some of 1988 soils are higher than the 1987 grand means one must recall that nearly 33% more Guthion was added to the soil in 1988.

Table 4 Soil sample means in ppm, standard error, soilsampling interaction (A*B), and coefficient of variation (CV%)of Guthion on sandy-loam (S-L), sandy-clay-loam(S-C-L), and sand (S) at 7-15 and 48-56 cm for 1987 and 1988.

1007	<u>S-L</u>	S-C-L	<u> </u>	<u>s</u> ,	<u>A*B</u>	<u>CV%</u>
<u>7-15</u> cm	0.69	0.64	1.03	0.26	**	59.3
48-56 cm	1.13	0.40	0.65	0.30	**	70.9
1988						
7-15 cm	0.46	0.89	0.84	0.14	**	33.8
48-56 cm	0.85	0.51	0.97	0.31	**	68.0
	**= p<	.01				

As was aldrin, Guthion concentrations were prepared in the lab and applied directly to the soils. Guthion and aldrin were added only by the authors. The total active ingredient of Guthion added to the soils in 1987 was 11,357

- · · · · · · · · · · ·

and the second second

la service de la construcción de la

ender in der Bernen von der Bernen von der Bernen auf der Bernen von der Ber Bernen von der Bernen v

mg A.I. and 14,991 mg A.I. in 1988. Based on averaging the final sample dates in 1987 and 1988, the year end concentrations are seen in Table 5.

Table 5 Estimated Guthion concentrations (mg of A.I.) in soils from the last sampling date in 1987 and 1988.

	Sandy-Loam	Sandy-Clay-Loam	Sand	
1987	2700	1229	3241	
1988	1269	1415	1541	

From Table 5, only the sandy-loam soil showed a slight increase (15%) over the previous year's end. Again, one must recall that a higher application of A.I. was made in 1988 and the sampling date in 1988, was 2 months earlier. A third consideration is that some of the sample areas may have been areas of unusually high concentrations. Both aldrin and Guthion were applied to the soils at higher concentrations in the two 1988 applications, whereas, the other rinsates were applied at lower concentrations over frequent intervals. The graphs for Guthion in 1987 and 1988 basically illustrate two peak concentrations which would correspond to the two applications.

Phosmet is another organophosphate and according to EPA leaching criteria has a half-life of 20 days. With such a short half-life and a v.p. of 133 m Pascals \bullet 50°C, one would not anticipate any accumulation under normal usage. At 20°C and pH= 7, fifty percent of phosmet is hydrolyzed in about 12 hr. and only 4 hr. if pH> 8.3 (The Pesticide Manual, 1983).

















The recovery of phosmet on sandy-clay-loam soils was 86% \pm 11 sd; sandy-loam 83% \pm 6 sd; and for sandy soils it was 78% \pm 6 sd, n=10 for all soils. Table 6 indicated the sandy-clay-loam to have lower mean concentration of phosmet, and the sand and sandy-loam were about the same. The soil-sampling interaction was as before found to be significant. An important factor to consider with this compound is that the greatest amount of variation is present as C.V.'s of 469.7 and 116.6% occurred.

Table 6 Soil sample means in ppm, standard error, soilsampling interaction (A*B), and coefficient of variation (CV%) of phosmet on sandy-loam (S-L), sandy-clay-loam (SCL), sand (S) at 7-15 and 48-56 cm for 1987 and 1988.

		<u>8-L</u>	S-C-L	<u> </u>	<u>8</u> ,	A*B	<u>CV%</u>
<u>1987</u> 7-15	C	1.07	0.51	0.85	0.20	**	41.9
48-56	CM	0.55	0.46	0.55	0.15	**	50.0
$\frac{1988}{7-15}$	CB	0 12	0 05	0 70	0 08	**	116 9
48-56	CM	0.66	0.12	0.08	0.78	*	469.7
		**= p<	.01 *=	p<.05			

The total input of phosmet (as determined by analysis of the rinsates) into each experimental unit for 1987 was 9601 mg A.I. and 2426 mg A.I.in 1988. The reason for lower input in 1988 was less insect damage due to such a dry season. The averaged phosmet concentrations for the end of both seasons were the best for all compounds that were analyzed. In the sandy-clay-loam the results were 13 mg and below detection; in sandy-loam soil it was 797 and 399 mg; and in sandy soil phosmet was 1000 and 13 mg; respectively, for 1987 and 1988 final sampling dates. This is also presented in tabular form

 Here is the second sec cond second s

as follows:

Table 7 Estimated phosmet concentrations (mg A.I.) in soils based on the last sampling date in 1987 and 1988.

	Sandy-Loam	Sandy-Clay-Loam	Sanđ
1987	797	13	1000
1988	399	BD	13
	BD= below detec	tion	

All concentrations for 1988 are well below input values which is what would be expected for this compound. As seen in the succeeding figures the major phosmet peaks coincided with the highest rinsate inputs.

Simazine, an s-triazine herbicide, posesses a low v.p., 0.81 u Pascals, and undergoes slow hydrolysis in a neutral environment, but will persist in either a more acidic or alkaline media (The Pesticide Manual, 1983). The EPA leaching criteria stated the half-life of simazine to be 75 days.

The recoveries for the soils were: sandy-clay-loam was 844 ± 12.8 sd; sandy-loam was 884 ± 8 sd; and the sandy soil had 913 ± 7 sd (n= 10 for all recoveries). The total input of A.I. for simazine on each soil was 3108 mg for 1987 and 1126 mg for 1988. Table 8 illustrates that for both the sandy-clay-loam and sandy-loam, the concentrations are halved in the second year. But this is not the case for the sand, as in both upper and bottom soil samples the concentrations increased slightly. A possible explaination for this large discrepancy may be that a larger microbial population is required or some catalytic agent is present. However, it is more likely an abberation and would not be present if

replicate soils were present. The soil-sampling interaction is again significant.

Table 8 Soil sample means in ppm, standard error, soilsampling interaction (A*B), and coefficient of variation, simazine on sandy-loam (S-L), sandy-clay-loam (S-C-L) and sand (S) soils at 7-15 cm and 48-56 cm for 1987 and 1988.

1987	<u>S-L</u>	S-C-L	<u> </u>	S	<u>A*B</u>	<u>CV</u> %
7-15 cm	1.17	1.38	1.73	0.28	**	34.5
48-56 CM	1.63	0.75	1.03	0.23	**	35.7
1988						
7-15 cm	0.84	0.72	1.77	0.35	**	54.9
48-56 cm	0.58	0.38	0.65	0.25	**	82.2
	**= D4	.01				

The concentrations of simazine in the soils based on the last sampling date (Table 9) indicate the sandy-clay-loam soil to be significantly lower than the other two soil types. However, this is questionable as the 1988 grand means (compare Table 8) show less of a difference between the two loamy types. Table 9 indicates that the sandy soil has a lower concentration than the sandy-loam and again the grand mean indicates the reverse.

Table 9 Estimated simazine concentrations (mg A.I.) in soils from the last sampling date in 1987 and 1988.

	Sandy-Loam	Sandy-Clay-Loam	Sand
1987	4185	1395	3338
1988	3069	678	2145

The following graphs correlate with the rinsate applications for both 1987 and 1988. In both years the highest applications were made late in the season and the graphs indicate the highest concentrations at these times. Simazine In the second sec

A second s
















has low water solubility and is unlikely to leach, thus it would be expected to remain in the upper soil column and this generally appears to be the case.

The last compound to be examined is captan, a fungicide and phthalimide, which is unstable in alkaline conditions. It has a high v.p. of < 1.3 m Pascal second to phosmet of the five compounds examined and would not normally cause accumulation (The Pesticide Manual, 1983). The EPA leaching criteria state its half-life to be <14 days. Soil microbes are believed to be of little importance in degradation. Captan may pesist in conditions of high moisture, high application rates and high organic matter.

The captan recoveries were as follows: sandy-loam 83 ± 8 sd; sandy-clay-loam 76 ± 7 sd; and sand 78 ± 8 sd (n= 10 for all soils). From table 10, the sandy-clay-loam soil average is the best. Problems that surface from this table are the large coefficient's of variation and standard error. Yet, the soil-sampling date interaction was significant in 3 of 4 sampling depths (see Table 10).

Table 10 Soil sample means in ppm, standard error, soilsampling interaction (A*B), and coefficient of variation (CV%) of captan on sandy-loam (S-L), sandy-clay-loam (S-C-L), and sand (S) soils at 7-15 and 48-56 cm for 1987 and 1988.

1007		<u>S-L</u>	<u>8-C-L</u>		<u>s</u> y	<u>A*B</u>	<u>CV%</u>
7-15	CM	0.60	0.22	1.08	1.15	ns	215.3
48-56	CM	0.76	0.37	0.48	0.20	**	63.0
1988							
7-15	CM	0.50	0.13	0.42	0.31	**	152.7
48-56	CM	0.32	0.10	0.18	0.10	**	86.2
		**= p<.01		= not si	.gnifican	t	

instation of the state of the

















The total input of captan on each of the soils for 1987 was 4448 mg A.I. and 1549 mg A.I. in 1988. As stated previously, the summer of 1988 was quite dry and little fungal activity was observed. In determining the amount of A.I. based on the last sample date (Table 11), general agreement is seen between the grand means and the estimated concentration of the last sample date. The sandy-clay-loam soil was by far the best, followed by sand and then the sandy-loam. Expectations were that the sand and sandy-loam soils would be as low as the sandy-clay-loam. Replication of soils would clarify this.

Table 11 Estimated captan concentrations (mg A.I.) in soils from the last sampling date in 1987 and 1988.

	Sandy-Loam	Sandy-Clay-Loam	Sand
1987	727	897	1518
1988	611	13	352

The graph for the captan rinsates in 1987 show a high concentration on 7-1-87, this corresponds to a large volume of rinsate remaining in the sprayer that could not be used and was emptied into the rinsate holding tank. All soils show a spike shortly after this application. Another small spike is seen in August but the reason is not clear. A late rise in soil concentration is seen in 1987 and this is due to the last two applications of rinsates.

The rinsate graph for 1988 shows much lower concentrations of captan and this is reflected in the soil sample graphs that flatten out below 0.5 ppm.

· · · · ·

Air sampling was performed in 1987 by polyurethane foam (PUF) plugs. Air samples were taken once a month in mid June through September both above the experimental tanks and downwind. The samples were taken 1 m above the surfaces and prior to spraying of the soils with rinsates.

The June 7 sample showed 1.25 ug/m^3 of simazine above an anaerobic tank, which was also located adjacent to the rinsate holding tank. The July 15 sampling found Guthion in three samples of 2.6, 3.3 and 3.2 ug/m^3 . Aldrin was found at 1.0, 0.3, and 0.2 ug/m^3 above three soils. Only one sample was found to contain captan at 1.2 ug/m^3 . The only other month to contain any pesticides was August 11 which had three samples of 0.8, 0.3 and 1.0 ug/m^3 of captan and aldrin in two samples at 0.3 and 0.2 ug/m^3 .

The pH of the soils, as seen from graphs 41-43, revealed much greater variation in the sandy-loam and sandy-clay-loam soils versus the sandy soil. The initial pHs of the soils were as follows: sandy soil, 7.3; sandy-loam,6.2; and sandy-clay-loam, 6.7. The pH of the well water as tested from the faucet adjacent to the disposal site was 6.9. The clay/loam soils had higher organic matter content and more CEC sites and were able to neutralize the more alkaline rinsates causing greater pH fluctuations. Since the sandy soil had a higher average pH, it would be more capable of degrading compounds that rely upon alkaline hydrolysis, e.g. captan, simazine and the organophosphates.

A major problem that arose was the large volumes of









rinsates being generated. Initially, only a 750 gallon holding tank was used for storage but soon an additional 1100 gallon tank was required. Most of the excess volume was due to rain that would enter the drains if there were winds from a south or easterly direction. Some volume was caused by human error such as allowing tanks to overflow or excessive washing of equipment.

The log book for rinsates entering the system indicated 1600 gallons, yet 4900 gallons were applied to the various soils. The volume added to each soil was nearly 700 gallons. This is 300% recording error that was greatly reduced the following year, 1988, to only 200%. The log in 1988 indicated a 1548 gallon input versus the actual applied total of 530 gallons. (See figures 44-47).

In evaluating the applied rinsates it is important to note that two different storage tanks were used and thus the inputs were blended. This would account for observing pesticides such as captan late in the season when they would not normally be used.

In summary, no significant build up occurred with any of the selected compounds. This can be confirmed by comparing both of the grand year means for 1987 and 1988, and also the last sampling date (bear in mind that the last sample date was 12 September 1988). One must likewise take heed of the wide coefficient of variation and standard error, which were expected because sampling would cause channeling in the soils and the even distribution of rinsates would be difficult to

rinsates being generated. Initially, only a 750 gallon holding tank was used for spocage nut soon an additional (1) gallon tank Was required. Most of the excess volume was due to rain that would extend the mains if there were winco proa s ath or easterly cir-dtron. Some volume was can exhuman error such as all wind rapid to control of easterly washed of equipment.

The Log Drew Contract entropy of the cynetic of the system of the contract is a space well of the contract of the space of the off the contract of the Tee contract of the space of the space of the contract of the test for space of the contract when the entry of the second of the test of the contract of the contract of the contract of the test of the contract of the contract of the contract of the test of the contract of the contract of the contract of the test of the contract of the contract of the contract of the test of the contract of the contract of the contract of the test of the test of the contract of the contract of the test of the test of the contract of the contract of the test of the test of the test of the test of the contract of the test of te

The style algorithm is step for a constructed in the security of the construction of the security of the se

achieve. A clearer picture would have been provided if replication of soils occurred.

As for future work, a better accounting of the compounds is required- a mass balance. This would examine the parent and metabolites in both the soil and air. An additional aid to pesticide decomposition would be to investigate the feasibility of exposing the rinsates to uv light and/or ozonation.









APPENDIX A

APPENDIX A

Pesticide residue data at the 7-15 cm depth for the monitored pesticides on three soil types in 1987.

List of variables: 1 replications 2 soil type 1=sandy-loam 2=sandy-clay-loam 3=sand 3 sampling dates 1 to 9 for 1987 4 aldrin in soils (ppm) 5 Guthion in soils (ppm) 6 phosmet in soils (ppm) 7 simazine in soils (ppm) 8 captan in soils (ppm)

CASE

NO.	1	2	<u>3</u>	4	5	6	7	8
1	1	1	1	0.00	0.00	0.16	0.28	0.86
2	2	1	1	0.00	0.00	0.33	0.25	0.82
3	3	1	1	0.00	0.00	0.20	0.41	0.86
4	1	1	2	0.00	0.00	0.30	0.87	0.07
5	2	1	2	0.00	0.00	1.00	1.54	0.03
6	3	1	2	0.00	0.00	0.80	1.79	0.03
7	1	1	3	0.56	0.48	2.80	0.48	0.52
8	2	1	3	0.35	0.95	4.01	0.42	1.94
9	3	1	3	0.70	0.70	3.12	0.90	1.69
10	1	1	4	0.60	1.42	1.90	1.24	0.12
11	2	1	4	0.45	1.17	3.30	2.23	0.51
12	3	1	4	0.83	1.78	2.94	1.75	0.31
13	1	1	5	0.52	0.52	0.10	0.66	0.45
14	2	1	5	0.14	0.68	0.48	0.43	2.40
15	3	1	5	1.13	0.67	0.63	0.45	1.95
16	1	1	6	0.61	0.37	1.40	2.67	0.13
17	2	1	6	1.10	0.40	0.58	1.22	0.10
18	3	1	6	0.30	0.64	1.32	1.73	0.50
19	1	1	7	0.60	0.82	0.11	1.39	0.06
20	2	1	7	0.50	1.88	0.30	2.52	0.00
21	3	1	7	0.74	1.80	0.82	1.19	0.12
22	1	1	8	3.25	1.40	0.20	1.92	0.10
23	2	1	8	4.15	0.48	0.45	1.62	0.15
24	3	1	8	2.10	2.53	0.44	0.54	0.08
25	1	1	9	0.20	0.05	0.32	1.58	0.87
26	2	1	9	0.18	0.00	0.28	1.30	0.43
27	3	1	9	0.25	0.35	0.60	0.42	1.12
28	1	2	1	0.00	0.00	0.25	0.12	0.24
29	2	2	1	0.00	0.00	0.43	0.76	0.16
30	3	2	1	0.00	0.00	0.49	0.46	0.18
31	1	2	2	0.00	0.00	0.40	0.98	0.06
32	2	2	2	0.00	0.00	0.98	1.12	0.08
33	3	2	2	0.00	0.00	0.72	1.53	0.03
34	1	2	3	0.03	0.01	0.10	0.55	0.00

. • : . .
CASE								
NO.	1	2	3	4	5	6	7	8
35	2	2	3	0.10	2.00	0.61	0.14	0.21
36	3	2	3	0.60	1.10	0.51	0.21	0.03
37	1	2	4	0.00	0.20	0.22	0.42	0.00
38	2	2	4	0.20	0.15	0.42	0.30	0.00
39	3	2	4	0.40	0.25	0.34	0.78	0.00
40	1	2	5	1.00	0.70	0.16	0.50	0.29
41	2	2	5	0.90	0.95	0.34	0.18	0.61
42	3	2	5	0.83	0.60	0.00	0.53	0.60
43	1	2	6	0.90	1.70	2.89	2.51	0.54
44	2	2	6	1.40	1.43	2.08	4.23	0.33
45	3	2	6	1.04	1.99	0.81	5.29	0.72
46	1	2	7	8.10	0.43	0.00	1.27	0.16
47	2	2	7	9.20	0.00	0.00	0.89	0.13
48	3	2	7	7.00	0.71	0.00	1.32	0.13
49	1	2	8	1.20	0.69	0.74	3.12	0.00
50	2	2	8	4.50	1.20	0.58	3.38	0.00
51	3	2	8	3.42	0.91	0.52	4.20	0.00
52	1	2	9	0.36	0.80	0.02	0.35	0.31
53	2	2	9	0.12	0.62	0.02	0.35	0.31
54	3	2	9	0.57	0.94	0.00	1.38	0.58
55	1	3	1	0.00	0.00	0.14	1.02	0.72
56	2	3	1	0.00	0.00	0.18	1.48	0.19
57	3	3	1	0.00	0.00	0.04	1.55	0.98
58	1	3	2	0.00	0.00	0.70	1.30	0.05
59	2	3	2	0.00	0.00	0.70	1.30	0.05
60	3	3	2	0.00	0.00	0.70	1.30	0.05
61	1	3	3	1.31	0.87	1.86	0.45	0.73
62	2	3	3	1.31	0.87	1.86	0.45	0.73
63	3	3	3	1.31	0.8/	1.80	0.45	0.73
04	Ţ	3	4	1.24	0.83	1.52	1.10	0.10
00	2	3	-	1.24	0.83	1.52	1.10	0.10
67	3	3	4 5	1.24	0.83	1.52	1.10	0.10
	1	3	2 5	1.00	0.93	0.10	0.88	0.30
60	2	3	5 5	2.10	2.07	0.09	2.47	0.40
70	3	3	5	2.67	1.22	0.42	2.04	0.33
70	2	3	6	2.07	1.03	1 51	2.94	0.39
72	2	3	6	2.07	1.03	1.51	2.74	0.39
72	3 1	3	7	2.07	1.03	0.21	2.74	0.39
73 74	2	2	י ר	4.50 4 KA	0.71	0.21	1.4J	0.10
75	2	2	, ,	1. 50 1 En	0.74	0.12	1 43	0.10
75	J 1	2	¢	1.30 2 12	1 20	0.12	1.7J 2 Ac	0.10
70	2	2	0 0	3.13	1 20	0.49	2.40	0.00
79	2	2	2	3.13	1 20	0.49	2.40	0 06
79	1	2	9		2.20	0 27	2.40	1 01
80	2	2	2	1.76	£.95	0.02	2.70	0 10
<u>81</u>	2	2	2	1 22	$\frac{1}{1}$	0.40	2.47	1 42
91	J	J	7	1.20	1.16	V. TV	J.7/	*•76

. **د**..

. .

•

APPENDIX B

- r.

APPENDIX B

Pesticide residue data at the 48-56 cm depth for the monitored pesticides on three soil types in 1987.

List of variables: 1 replications 2 soil type 1=sandy-loam 2=sandy-clay-loam 3=sand 3 sampling dates 1 to 9 for 1987 4 aldrin in soils (ppm) 5 Guthion in soils (ppm) 6 phosmet in soils (ppm) 7 simazine in soils (ppm) 8 captan in soils (ppm)

CASE

NO.	1	2	<u>3</u>	4	5	6	7	8
1	1	1	1	0.00	0.00	0.6	0.26	4.55
2	2	1	1	0.00	0.00	0.07	0.89	2.90
3	3	1	1	0.00	0.00	0.08	0.66	2.30
4	1	1	2	0.00	0.00	1.90	0.17	0.13
5	2	1	2	0.00	0.00	1.28	0.54	0.50
6	3	1	2	0.00	0.00	2.00	0.20	0.10
7	1	1	3	0.40	2.71	1.30	1.15	1.56
8	2	1	3	0.20	3.34	0.30	2.74	1.12
9	3	1	3	0.49	5.10	1.40	2.05	1.83
10	1	1	4	1.30	0.75	0.70	0.50	0.08
11	2	1	4	1.10	0.51	2.50	1.81	0.12
12	3	1	4	1.40	1.14	1.91	1.20	0.16
13	1	1	5	0.73	0.43	0.00	1.38	0.00
14	2	1	5	0.54	0.49	0.00	1.10	0.00
15	3	1	5	0.94	0.32	0.00	1.42	0.00
16	1	1	6	0.44	0.00	0.00	0.69	0.06
17	2	1	6	0.52	1.00	0.00	0.99	0.07
18	3	1	6	0.70	0.00	0.00	0.90	0.40
19	1	1	7	0.20	0.68	0.00	1.16	0.14
20	2	1	7	0.00	2.22	0.00	1.34	0.20
21	3	1	7	0.45	2.98	0.00	0.71	0.11
22	1	1	8	1.55	0.25	0.00	3.66	0.00
23	2	1	8	2.25	0.53	0.00	4.50	0.00
24	3	1	8	0.71	0.39	0.00	4.70	0.00
25	1	1	9	0.50	2.50	0.45	4.22	1.20
26	2	1	9	0.35	0.91	0.31	1.51	1.40
27	3	1	9	0.59	4.32	0.45	3.57	1.59
28	1	2	1	0.00	0.00	0.05	0.21	0.35
29	2	2	1	0.00	0.00	0.18	0.18	0.15
30	3	2	1	0.00	0.00	0.04	0.00	0.10
31	1	2	2	0.00	0.00	2.81	1.24	0.64
32	2	2	2	0.00	0.00	1.95	0.91	1.40
33	3	2	2	0.00	0.00	2.49	0.85	1.2 <u>0</u>

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccc} & 7 & 8 \\ 0 & 0.33 & 1.57 \\ 2 & 0.22 & 0.51 \\ 8 & 0.05 & 1.22 \\ 2 & 0.32 & 0.00 \\ \end{array}$
34 1 2 3 0.50 1.30 0.4 35 2 2 3 0.53 0.89 0.8 36 3 3 3 0.45 1 00 0.5	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
35 2 2 3 0.53 0.89 0.8	2 0.22 0.51 8 0.05 1.22 2 0.32 0.00
	8 0.05 1.22 2 0.32 0.00
36 32 3 0.45 1.00 0.5	2 0.32 0.00
37 1 2 4 0.31 0.30 0.1	
38 2 2 4 0.33 0.15 0.3	1 0.15 0.00
39 3 2 4 0.15 0.43 0.1	8 0.13 0.00
40 1 2 5 0.40 0.48 0.0	0 1.38 0.18
41 2 2 5 0.20 0.72 0.0	0 1.17 0.24
42 3 2 5 0.65 0.60 0.0	0 0.45 0.15
43 1 2 6 0.40 0.68 0.2	3 1.25 0.31
44 2 2 6 0.8 0 0.03 0.9	3 1.18 0.09
45 3 2 6 1.10 1.42 1.0	3 0.95 0.14
46 1 2 7 0.00 0.00 0.0	0 0.79 0.05
47 2 2 7 0.90 0.00 0.0	9 0.63 0.25
48 3 2 7 1.30 0.00 0.0	0 0.40 0.28
49 1 2 8 1.98 0.22 0.1	6 2.41 0.00
50 2 2 8 3.70 0.71 0.1	0 1.85 0.00
51 3 2 8 1.71 0.51 0.0	4 1.40 0.00
52 1 2 9 0.30 0.50 0.0	0 0.92 0.44
53 2 2 9 0.12 0.00 0.0	0 0.59 0.35
54 3 2 9 0.57 0.84 0.0	2 0.39 0.41
55 1 3 1 0.00 0.00 0.1	0 0.21 0.49
56 2 3 1 0.00 0.00 0.0	8 0.50 0.55
57 3 3 1 0.00 0.00 0.1	2 0.46 0.24
58 1 3 2 0.00 0.00 2.0	7 0.65 0.67
59 2 3 2 3.00 0.00 2.0	7 0.65 0.67
60 3 3 2 3.00 0.00 2.0	7 0.65 0.67
61 1 3 3 0.44 2.39 0.8	0 1.00 1.30
62 2 3 3 0.43 2.39 0.8	0 1.10 1.30
63 3 3 3 0.43 2.39 0.8	0 1.10 1.30
64 1 3 4 0.76 0.55 0.9	5 0.68 0.06
65 2 3 4 0.76 0.55 0.9	5 0.68 0.06
66 3 3 4 0.76 0.55 0.9	5 0.68 0.06
67 1 3 5 1.20 0.59 0.2	5 1.14 2.30
68 2 3 5 0.65 0.13 0.4	7 1.44 1.20
69 3 3 5 1.90 0.36 0.3	3 1.06 0.36
70 1 3 6 0.49 0.52 0.3	7 0.99 0.18
71 2 3 6 0.49 0.52 0.3	7 0.99 0.18
72 3 3 6 0.49 0.52 0.2	7 0.99 0.18
73 1 3 7 0.47 0.98 0.0	2 0.84 0.10
74 2 3 7 0.47 0.98 0.0	2 0.84 0.10
75 3 3 7 0.47 0.98 0.0	2 0.84 0.10
76 1 3 8 1.90 0.43 0.0	5 3.08 0.00
77 2 3 8 1.90 0.43 0.0	5 3.08 0.00
78 3 3 8 1.90 0.43 0.0	5 3.08 0.00
79 1 3 9 1.09 0.81 2.4	1 0.60 0.29
80 2 3 9 1.77 0.62 0.3	0 0.47 0.39
81 3 3 9 0.81 0.43 0.2	8 0.28 0.24

			•	-		
		-				
					.•	•
						-
			+			
						,
				-		;
				•		
		•				
				•		
			•	•		
		• "	•	•-		
	-			+		
		-				
			•			
	· .			r		-
				2		
			•	r.		•
				•		
	-		•	-		
			•	•		
			÷* .			•
			44 • •			· ·
		1 a				•
		·			•	
		. •		-		i.
				•		
		.1	•	•	,	
	•					

•

• ,. .

APPENDIX C

APPENDIX C

Pesticide residue data at the 7-15 cm depth for the monitored pesticides on three soil types in 1988.

List of variables: 1 replications 2 soil type 1=sandy-loam 2= sandy-clay-loam 3=sand 3 sampling dates 1 to 5 for 1988 4 aldrin in soils (ppm) 5 Guthion in soils (ppm) 6 phosmet in soils (ppm) 7 simazine in soils (ppm) 8 captan in soils (ppm)

CASE

NO.	1	2	3	4	5	6	7	8
1	1	1	1	0.30	0.22	0.00	0.53	0.68
2	2	1	1	0.13	0.33	0.00	0.23	1.73
3	3	1	1	0.54	0.15	0.00	0.15	0.58
4	1	1	2	1.40	0.17	0.19	0.28	0.03
5	2	1	2	1.27	0.49	0.15	0.97	0.09
6	3	1	2	1.70	0.28	0.23	0.66	0.20
7	1	1	3	0.31	0.27	0.00	0.84	0.00
8	2	1	3	0.26	1.06	0.00	0.75	3.00
9	3	1	3	0.39	0.37	0.00	0.49	0.00
10	1	1	4	1.68	0.56	0.05	0.70	0.00
11	2	1	4	0.21	0.42	0.79	1.14	0.00
12	3	1	4	4.40	0.58	0.12	0.87	0.00
13	1	1	5	3.37	0.67	0.20	1.45	0.78
14	2	1	5	5.27	0.83	0.00	1.69	0.24
15	3	1	5	0.20	0.53	0.11	1.81	0.18
16	1	2	1	0.40	0.20	0.13	0.45	0.35
17	2	2	1	0.44	0.00	0.21	1.30	0.14
18	3	2	1	0.35	0.50	0.00	0.65	0.11
19	1	2	2	0.90	0.53	0.10	0.54	0.16
20	2	2	2	1.10	0.81	0.16	0.32	0.00
21	3	2	2	0.73	0.67	0.13	0.64	0.18
22	1	2	3	0.31	0.51	0.00	0.47	0.14
23	2	2	3	0.35	0.96	0.00	0.52	0.06
24	3	2	3	0.27	1.08	0.00	0.52	0.06
25	1	2	4	2.97	1.76	0.00	1.23	0.20
26	2	2	4	3.47	2.05	0.00	1.43	0.28
27	3	2	4	2.53	1.39	0.00	0.55	0.22
28	1	2	5	0.28	0.90	0.00	0.41	0.00
29	2	2	5	0.55	1.13	0.00	0.58	0.00
30	3	2	5	0.05	0.82	0.00	0.63	0.00
31	1	3	1	1.37	0.89	0.79	1.80	0.79
32	2	3	1	1.05	0.69	1.06	4.36	0.27
33	3	3	1	1.68	0.64	0.52	3.83	1.39
34	1	3	1	2.60	0.97	9.20	1.69	0.29

.

CASE								
NO.	1	2	3	4	5	6	7	8
35	2	3	1	2.10	0.61	0.01	5.01	0.11
36	3	3	2	2.72	0.82	0.03	3.82	0.43
37	1	3	2	3.19	0.75	0.00	0.10	0.58
38	2	3	2	2.50	0.51	0.00	0.06	0.20
39	3	3	2	0.39	0.63	0.00	0.16	1.20
40	1	3	2	1.50	1.21	0.00	0.12	0.00
41	2	3	3	1.00	1.03	0.00	0.28	0.07
42	3	3	3	1.00	1.99	0.00	0.24	0.11
43	1	3	3	2.60	0.41	0.00	1.68	0.22
44	2	3	3	2.80	0.65	0.02	1.46	0.03
45	3	3	3	2.50	0.74	0.01	0.02	0.54

APPENDIX D

APPENDIX D

Pesticide residue data at the 48-56 cm depth for the monitored pesticides on three soil types in 1988.

List of variables: 1 replications 2 soil type 1=sandy-loam 2=sandy-clay-loam 3=sand 3 sampling dates 1 to 5 for 1988 4 aldrin in soils (ppm) 5 Guthion in soils (ppm) 6 phosmet in soils (ppm) 7 simazine in soils (ppm) 8 captan in soils (ppm)

CASE

NO.	1	2	3	4	5	6	7	8
1	1	1	ī	0.10	2.52	0.10	0.31	1.30
2	2	1	1	0.12	0.91	0.20	0.69	1.32
3	3	1	1	0.06	4.33	0.34	0.59	0.98
4	1	1	2	0.16	0.31	0.06	0.28	0.07
5	2	1	2	0.25	0.24	0.04	0.18	0.04
6	3	1	2	0.18	0.35	0.08	0.56	0.11
7	1	1	3	0.86	0.12	0.00	0.37	0.03
8	2	1	3	0.57	0.19	0.00	0.40	0.01
9	3	1	3	1.21	0.03	0.00	0.28	0.06
10	1	1	4	0.61	0.68	0.00	0.17	0.07
11	2	1	4	0.18	0.79	9.00	0.25	0.06
12	3	1	4	2.11	0.48	0.00	0.32	0.05
13	1	1	5	1.13	0.54	0.00	0.77	0.29
14	2	1	5	2.40	0.69	0.00	2.13	0.64
15	3	1	5	0.80	0.56	0.00	1.39	0.00
16	1	2	1	0.40	0.21	0.12	0.29	0.14
17	2	2	1	0.44	0.14	0.09	0.00	0.06
18	3	2	1	0.38	0.30	0.11	0.61	0.11
19	1	2	2	1.70	0.36	0.20	0.32	0.02
20	2	2	2	1.90	0.00	0.19	0.52	0.00
21	3	2	2	1.20	0.85	0.08	0.57	0.04
22	1	2	3	3.50	1.23	0.45	0.24	0.14
23	2	2	3	4.10	0.72	0.25	0.74	0.29
24	3	2	3	2.90	1.74	0.29	0.22	0.23
25	1	2	4	0.21	0.22	0.00	1.00	0.06
26	2	2	4	0.38	0.44	0.00	0.66	0.08
27	3	2	4	0.12	0.00	0.00	0.14	0.05
28	1	2	5	0.52	0.47	0.00	0.180	0.00
29	2	2	5	0.48	0.15	0.00	0.16	0.19
30	3	2	5	0.72	0.79	0.00	0.08	0.03
31	1	3	1	0.57	0.71	0.28	0.00	0.38
32	2	3	1	1.10	0.43	0.30	0.06	0.05
33	3	3	1	0.30	0.72	0.25	0.10	0.66
34	1	3	2	0.41	0.43	0.08	0.15	0.09

CASE NO. 35 36 37 38 39 40 41 42 43	1 2 3 1 2 3 1 2 3 1 2 3	2333333333	322 23 33 44 45	4 0.53 0.34 1.47 1.10 1.80 3.60 2.41 3.00 3.10	5 0.03 0.38 0.12 0.29 0.49 2.54 3.40 2.05 0.84	6 0.20 0.07 0.04 0.00 0.01 0.00 0.00 0.00 0.00	7 0.26 0.24 2.66 0.82 3.56 0.16 0.18 0.20 0.56	8 0.08 0.11 0.00 0.08 0.90 0.04 0.00 0.10 0.07
43	1	3	5	3.10	0.84	0.00	0.56	0.07
44	2	3	5	3.80	1.27	0.02	0.28	0.04
45	3	3	5	2.40	0.89	0.01	0.48	0.16

LIST OF REFERENCES

LIST OF REFERENCES

- Association of State and Inter state Water Pollution Control Administrators. America Clean Water: The State nonpoint Source Assessment. Wash. DC 1985 24 p.
- Bailey, G.. J. White and T. Rothberg. (1968) Adsorption of organic Herbicides by Montmorillonite: Role of pH and chemical characteristics of adsorbates. Pesticides in the Soil ed. Saltzman and Yaron. p75-87.
- Baker, J.L. and I. Johnson. (1984) Water and pesticide volatization from a waste disposal pit. Am. Soc. of Engr. volume 27, No. 3 p. 809-816.
- Best, J.A., J.Weber and S. Weed. (1972) Competitive Adsorption of Diquat, Paraquat and Ca⁺² on organic matter and exchange resins. Soil Sci. 144:444-450.
- Council of Europe. (1984) Pesticides. 6th ed. Pub. by the Council of Europe Strasbourg, Germ. p. 90-92.
- D'Itri, F.M. and L.Wolfson ed. (1984) Rural Groundwater Contamination. John Wiley and Sons. NY p 69-84.
- Felsot, A. and P. Dahm. (1979) Sorption of organophosphate and carbamate insecticides by soil. Jour. Agric. Food Chem 27: 557-563.
- Hance, R. J. (1979) Effect of pH on the degradation of atrazine, dichloroprop, linuron and propyzamide in soil. Pest. Sci. 10:83-86.
- Helling, C. and T. Gish. (1985) Soil characteristics affecting pesticide movement into groundwater. Evaluation of Pesticides in Groundwater p. 14-35.
- Junk,G.A., J.J. Richard and P. Dahm. Degradation of pesticides in controlled water-soil systems. Treatment and Disposal of Pesticide Wastes. Kruger and Seiber ed. 1984 p. 37-65.
- Manahan, S. Environmental Chemistry. 2nd ed. 1975. U. of Missouri. Willard Grant Press. Boston, Ma.

Martin, A. (1985) Biodegradation of organic chemicals.

• •

. . . •

· · ·

-.

. .

Environ. Sci. Technol. Vol. 18 No.2 p 106-111.

- McLean, E. Soil pH and lime requirements. 1984. Methods of Soil Analysis. p 199-210.
- Michigan Department of Natural Resources. Hazardous Waste Division. Hazardous Waste Management Rules. rev. Sep.6,1985. p 14-18.
- Michigan State University Agricultural Experiment Station. (1988) Clarksville Horticultural Experiment Station Brochure.
- Morill,L.G., B. Mahilum, and S. Mohiuddin. Organic Compounds in Soils: Sorption, degradation and persistance. 1982. Ann Arbor Sci. Pub.
- Quirk, J.P. (1955) Significance of surface areas calculated from water vapor sorption isotherms by use of the BET equation. Soil Sci. 80: 423-430.
- Ryan, S.O. (1974) A study of pesticide use, storage and disposal in Iowa. PhD. Dissertation, Iowa State U.,Ames, Ia.
- Saltzman, S. and B. Yaron. ed. (1986) Pesticides in Soil. Van Nostrand Rheinhold Co.
- Smith,A.E. and A. Fitzpatrich. (1970) The loss of five thiocarbamate herbicides in nonsterile soils and their stability in acidic and bascic solutions. Jour. Agric. Food Chem. 18: 720-722.
- U.S. Geological Survey. Estimated Use of Water in the United States in 1980. W.B. Solley . Geological Survey Circular 1001. Alexandria Va. 1983. p 32-43.
- Ware, G. 1982. Fundamentals of Pesticides: A self instructional guide. Thomson Pub. Fresno, Ca. p 204-206.
- Ware, G. 1978. Pesticide Book. W. H. Freeman and Co. San Francisco, Ca. p 134-135.
- Warnecke, D.D. Centrifugation Procedure for CEC determination Dept. of Crops and Soil Sciences, Michigan State University, E. Lansing, Mi.
- Weber, J.B., S. Weed and T. Ward. (1969) Adsorption of s-triazines by soil organic matter. Weed Sci. 17: 417-421.
- Winterlin, W.L., S. Schoen and C. Mourer. Disposal of pesticide wastes in lined evaporation beds. Treatment and Disposal of Pesticide Wastes. Kruger and Seiber

-

.

•

ed. 1984 p. 97-116.

- Yariv, S. and S. Saltzman. (1976) Infrared and x-ray study of parathion-montmorillonite sorption complexes. Soil Sci. Soc. Am. Jour. 40: 34-38.
- Zimdahl, R.L., V. Freed and W. Furtick. (1970) Degradation of triazine and uracil herbicides in soil. Weed Res. 10:18-26.

