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Glenn Alan Dickmann

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THE FATE OF SELECTED PESTICIDES IN ABOVE GROUND DISPOSAL VESSELS

By

GLENN ALAN DICKMANN

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ABSTRACT

THE FATE OF SELECTED PESTICIDES IN ABOVE GROUND DISPOSAL VESSELS

By

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Pesticide use occurs on most farms and may lead to groundwater contamination if improperly handled. The residual pesticide in sprayers, pesticide rinse water and rinse water from sprayers may be sprayed on fence rows or dumped at the preparation site. This research was conducted to determine if a low cost pesticide disposal system for farmers was feasible. The system included a rinse collection area, raised soil filled steel collection vessels residing on a concrete slab and walls to contain any spills. Rinse water was applied on a weekly basis to each soil filled steel vessel. Besides the pesticides entering from the farm operation, seven pesticides were applied to each vessel over two years and monitored for dissipation. The monitored pesticides were carbaryl, simazine, alachlor, chlorpyrifos, endosulfan I and II, and captan. Over two growing seasons from May through October a total of 390 g a.i. of each of the pesticides were applied to each of six steel research vessels containing a locally obtained soil. To monitor the dissipation of the selected pesticides, air and soil samples were analyzed for the parent compound and

the major metabolite. At the end of the second growing season the following amount of compounds remained from the 390 g a.i. applied: carbaryl 20.3 g or 5.2%; simazine 139.6 (35.8%); alachlor 40.6 g (10.4%); chlorpyrifos 70.6 g (18.1%); endosulfan I 92.4 g (23.7%); endosulfan II 71.4 g (18.3%) and captan 16.0 g (4.1%). Volatilization accounted for greater than 50% of the loss for each of the following: chlorpyrifos; endosulfan I and II; alachlor; and captan. Carbaryl and simazine were near the 30% range for airborne losses. Carbaryl appeared to be primarily degraded by chemical and/or microbial action. Simazine loss was nearly equal between volatilization and soil degradation. Overall the system appeared to work effectively to dissipate the monitored pesticides over the 17 month period. The system was able to dissipate approximately 4800 gallons of pesticide rinse water in the first year. In the second year more than 5200 gallons or 97% of the second years grand total volume was dissipated.

Dedicated To Robin, Thomas, Kathryn And My Parents,

Leila and Milton Dickmann

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REVIEW OF LITERATURE

INTRODUCTION

Clean water in the United States is a natural resource that has been used with little forethought because of the vast abundance of lakes, rivers and groundwater. Initially the United States had few demands on the large reservoirs of water. But as the population has grown the demand for water has greatly increased. Recently the population growth has occurred rapidly. In the first USA census of 1790, the population per square mile of land was 4.5 and in 1970 it was 57.4 (World Almanac, 1981). In 1997, the population density has grown to 76.2 people per square mile(U.S. Census Bureau, 1998).

With an ever burgeoning population, a limited resource such as water will eventually become a scarce commodity. The lack of water has caused water rights litigation in the Southwest United States (Ridenbaugh, 1998) and has a potential to start wars such as between the countries of Sudan and Egypt (Egypt Economics, 1998).

It has been estimated that four trillion gallons of

rain fall on the United States every day which refill the lakes and streams and recharge the aquifers. It is also estimated that the total water usage in the U.S. everyday is approximately 300 billion gallons or 7.5% of the recharge rate (Lewis, 1996). 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 source of drinking water for half of the U.S. population. According to the U.S. Geological Survey of 1980, 89 billion gallons of water are pumped from wells each day and of this tremendous volume 64.5 billion gallons are directed toward agricultural use (Solley, 1983).

The uses of water range from drinking and industrial/ agricultural processes to wastewater treatment. So when speaking of water quality one must also specify the intended use of the water. For example, while dissolved calcium and magnesium produce hard water which cause scale and problems in cleaning, these same ions are necessary to provide a healthy fish population. Water high in nitrates is good for the production of corn, but is harmful and possibly deadly for infants. Therefore, one must first note the intended use of water to determine if the water quality is appropriate for the application (Michigan Water Resources, 1987).

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Safe drinking water is a primary concern of all people. It is well documented that health problems arising from low level contaminants in drinking water or in food may not present themselves until much time has elapsed since their use. The pathogenic effects of pesticide tainted water may be presented in a variety of ways: acute/chronic poisonings; immunological changes; allergic reactions; and/or mutagenic/ teratogenic/carcinogenic effects. For example, after only a few years of using organochlorines it was discovered to accumulate in the adipose tissue and blood of humans who had no known occupational exposure. This was especially alarming in the case of newborns and infants which had high levels of DDT and DDE. (Spynu,1989)

Over 95% of the rural population in the United States is dependent upon groundwater for household use. In 1986, 19 pesticides were found to have entered the groundwater in 24 states as a result of agricultural practices. Atrazine has been identified in the groundwater of Pennsylvania, Iowa, Nebraska, Wisconsin, Maryland and Minnesota at concentrations ranging from 0.3 to 3.0 ug/L (Cheng and Koskinen,1986). In Kansas, atrazine has been found in the groundwater at 1.5 to 14.0 ug/L (Carney *et al.*, 1989). A statewide rural well-water survey conducted in Iowa, showed nearly 13.6% of rural drinking wells to be contaminated with

one or more pesticides (Selim and Wang, 1994). Based on these studies, it would be prudent to institute methods to minimize both agricultural inputs and movement of pesticides in the environment when they are deemed necessary.

Examination of the movement of pesticides from and within the soil has revealed a dynamic process which takes many paths which are dependent on what physical or chemical pressures are exerted at a specific point in time. These various pathways include: volatilization; adsorption to soil organic matter or clay; microbial, chemical and photochemical degradations; transportation by erosion/runoff to surface waters; plant uptake; movement to lower soil depths (vadose zone); and leaching into groundwater(Chesters *et al.*, 1989).

The ability of compounds to leach into the groundwater is related to a number of factors which permit or retard the pesticides passage through the root and vadose zones. These factors include: soil texture; soil organic matter; tillage methods; depth to groundwater; temperature; amount of compound applied; precipitation/irrigation; relative humidity; and bulk density, pH, and ion exchange capacity of the soil. Each of these properties will interact with the compound and the type of effect is based on the structure and properties of the compound (Chesters *et al.*, 1989).

Adsorption is the intermolecular force between a compound and soil mineral or organic surfaces which may involve high or low energy bonds. High energy bonds are either ionic or ligand in nature. There are many types of the low energy bonding and these are: charge-dipole; dipole-dipole; hydrogen bonding; charge transfer; Van der Waals or magnetic(Bailey and White, 1970).

Pesticides enter the atmosphere through spraying, accidental spills, release during normal handling, and volatilization from water, plant and soil surfaces. The volatilization of pesticides from soils is related to its physical and chemical properties such as saturated vapor pressure, solubility in water, and the compound structure which includes the kind, position(s) and number of functional groups. These chemical and physical properties of the pesticide will interact with the environment. This interaction has many components or modifiers and are listed as follows: soil water content; bulk density/porosity; clay and organic matter; adsorption site density; structure; temperature; surface wind speed; evaporation; humidity; and precipitation. Other modifiers which are based on human activities are the amount of pesticide used; the depth of incorporation; irrigation pattern and plant cultural practices (Jury and Valentine, 1987).

Any process which increases vapor diffusion such as an increased temperature or pesticide concentration will result in more volatilization. This volatilization from a surface causes a lowered pesticide concentration, which in turn causes a capillary or wicking action from the adjacent soil. The properties for diffusion and their rank of their importance are as follows: soil moisture > temperature >bulk density (Spencer, 1982).

Henry's law constant (K_h), provides a dimension less number (ratio of saturation vapor density to solubility) that represents the volatility of a compound. Chemicals with a value > 2.65×10^{-5} are considered highly volatile. There are two types of categories to describe volatility, category I is a group whose control of volatilization is in the soil (binds preferentially to the soil) and category III are those chemicals which are limited by the stagnant air boundary layer above the soil surface (less binding to the soil, potentially more volatile). Chemicals with a K_h > 2.65×10^{-5} are in category I because they volatilize to the soil atmosphere as rapidly as they are transported to the soil surface. The volatility of category I compounds decreases with time under all conditions whether water is evaporating or not (Jury *et al.*, 1984).

Conversely, a category III compound has a $K_h < 2.65 \times$

10^{-5} and the stagnant boundary layer acts as a partial barrier to transport causing compounds to accumulate at the surface. Hence, category III compounds concentrate at the soil surface under evaporative conditions and the volatilization rate will increase with time. However, category III compounds can have increased volatilization by wind action and soil moisture causing evaporation. This evaporation can lead to a 20 fold increase in dissipation of the compound when compared to minimal evaporation conditions (Jury *et al.*, 1984).

The primary concerns of pesticide use, after its efficacy, are the activity against nontarget species and the persistence of the residues. These are very complicated issues and studies may be contradicting. In biological degradation studies a number of problems may arise, such as the development of enrichment cultures. Enrichment cultures arise when a microbe degrades a compound or a similar compound more quickly on the next exposure because a microbes' enzymes are activated and ready to use the compound as an energy source. Another situation affecting degradation is the distinction between a nutrient poor environment and a nutrient rich environment. In a nutrient rich environment, the higher concentration of a nutrient may allow a microorganism to use this nutrient as an energy

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source instead of the pesticide because the nutrient is a more accessible substrate requiring the use of less energy (MacRae, 1989).

Another issue to address is do the metabolites observed result from cometabolism and if so, are there a series of microbes responsible for this phenomenon. After the determination of microbial action on a compound, another step is to determine the concentrations at which this degradation takes place. For example, do the microbes act on 1 ppm as well as 100 ppm of the substrate (MacRae, 1989).

An example of how important it may be to amend or assist nature is observed when Kearney *et al.*(1986) studied the combined activity of microbes and UV-ozonation in the degradation of coumaphos, an organophosphate. Kearney used the microbe, *Flavobacterium* sp. to cleave the phosphoro-thioate linkage, but no further oxidation of the benzene ring would occur. However, using a UV-ozonation method they were able to degrade the chloroferon produced by microbial activity. Other methods used to aid in degradation of pesticides include varying the pH; changing redox potentials *i.e.* going from aerobic conditions to anaerobic; amending the soil with compounds such as hydrogen sulfide or other microbes (MacRae, 1989).

Goldstein *et al.*(1985) have suggested reasons for

failing to degrade pollutants in natural environments. Their research determined that pesticide degradation was dependent on soil inoculation conditions which were the concentration of the pesticide in nature may be too low to support growth; the natural environment may contain inhibitory substances; added microbes may use the organic substrates in the environment rather than the pesticide; and the microbes may fail to move through soil pores to sites of the pollutant.

Microbial-pesticide interaction was also examined by Gaylor *et al.* (1983) when herbicide application to research plots of cotton caused a reduction in cotton yields when compared to hand weeded controls. The yield reductions were contributed to herbicide damage to the cotton plants or to adverse herbicide-microorganism interactions affecting the growth of the cotton plants.

Chlorpyrifos

Chlorpyrifos [0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate] is a broad spectrum insecticide formulated as emulsifiable concentrates(EC), granulars(GR), and wettable powders (WP). Chlorpyrifos has 2 major metabolites being: 3,5,6-trichloro-2-pyridinol (TCP) and 3,5,6-trichloro-2-methoxypyridine (TMP). In all metabolite studies for chlorpyrifos, it has been shown that TCP is by

far the more common metabolite from 6 to 33% of the degradation products, whereas TMP is 0.1 to 10% (Chapman and Chapman, 1986).

TCP has the unusual chemical property of being ionizable and has a pKa=4.55, whereas the parent, chlorpyrifos and its other metabolites are not ionizable. At a pH=2 the ratio of anion to neutral is .0028, at pH=5 the ratio is 2.82 and at pH=7 it is 28. As for volatility, the vapor pressure for the parent is 1.8×10^{-5} mm Hg @25 °C, the TCP anion is nonvolatile and the vapor pressure for the neutral TCP is 2.48×10^{-5} mm Hg. TMP has a vapor pressure of 9.68×10^{-3} mm Hg, which is 500 times more volatile than either chlorpyrifos or TCP. Thus, under laboratory conditions it is more often a significant metabolite, but under field study conditions it is often detected at lower concentrations (Racke, 1993).

Other pertinent physical data on chlorpyrifos indicate a K_{ow}=4.8 to 5.2 ml/g, M.W.= 350.6; water solubility of 2.0 ppm @ 24- 25 °C; K_d=13.4 to 1862 ml/g with a mean of 173 ml/g. Based on this data it would be assumed that chlorpyrifos having a non-polar nature would partition to soils/sediments and thus tend not to leach into the ground-water or runoff into the watershed (Racke, 1993).

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therefore likely to leach or runoff into streams. TMP is a liquid at room temperature, relatively nonpolar, and has a low water solubility= 20.9 ppm; so like its parent it would be less mobile. TCP on the other hand is water soluble= 117 ppm @ pH=3 and 49,000 ppm @ pH=7 (anionic). The mobility of TCP would be strongly influenced by environmental conditions and matrix pH (Racke, 1993).

Leaching studies from both laboratory soil column leaching assays and field studies indicated that leaching and runoff are of low potential for chlorpyrifos. Thiegs (1964) performed a leaching study with 5% granular formulation of ^{36}Cl-chlorpyrifos and added 15.24 cm of water for a leachate, which resulted in 86.9% of the radioactivity to remain in the upper 2.54 cm of soil and 6.4% exited the column. Iosson (1984) performed a similar study, where he added 20 cm of water to 28 cm column containing soil treated at 1 kg/ha. The leachate contained no parent compound and <0.05 ppm of TCP. Fermanich and Daniel (1991) conducted a radiolabeled study with intact 90 cm cores and simulated rainfall conditions. It was determined 99% of the total chlorpyrifos residues were in the top 2.5 cm of soil and TCP was the chief compound in the 2.5 - 10 cm layer and less than 0.12 % of the ^{14}C was found in the leachate.

Fontaine *et al.* (1987) conducted field experiments in

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Michigan, Illinois and California, and applied chlorpyrifos at a rate of 3.36 kg/ha. Soil samples were taken over the growing season down to 45.7 cm and residues of parent, TCP and TMP were found to be confined to the upper 30.5 cm. Hoffmann *et al.*(1991) did a field study in North Dakota and applied chlorpyrifos at 1.12 kg/ha and sampled the soil over the season to down to 1.2 m. Residues in the 0-7.5 cm soil layer were found at 10 ppm and at 37.5 cm the chlorpyrifos concentration was 0.01 ppm. No residues were found in the tile drains.

Alachlor

Alachlor [2-chloro-N-(2,6 diethylphenyl)-N-(2-methoxymethyl)acetamide] is a widely used chloroacetanilide herbicide. This pre-emergent herbicide is absorbed through the roots or the shoots of seedlings. Its mode of action is it inhibits root elongation. It has a MW=269.8, water solubility of 240 mg/L at 25°C, a vapor pressure= 2.2×10^{-5} mm Hg, Henry's law constant(K_H)=1.3×10^{-6}, and a K_{ow}= 430 (Chesters *et al.*, 1989).

Alachlor is used especially in the North Central U.S. and has been found in the streams and rivers of several states and Ontario, Canada. It is most likely to be observed at the time of application in the range of <1 ppb,

and usually in the part per trillion concentration. Runoff is the suspected source of entry into the surface waters which is dependent on rainfall amount, prior soil moisture, concentration of applied alachlor, and the proximity to water. Alachlor has not been detected in community water supplies that originate from the Great Lakes , but it has been detected in various rivers that feed into the Great Lakes bordering the states of Michigan, Wisconsin, Ohio and New York (USEPA, 1986).

The soil adsorption of alachlor is best described by the Freundlich adsorption equation rather than the Langmuir equation. Adsorption of alachlor to the soil occurs best at lower temperatures because adsorption is an exothermic reaction and Sethi and Chopra (1975) showed better adsorption of alachlor at 25 °C versus 35 °C. Chemical degradation is enhanced under the conditions of high soil moisture and high solar energy (Hargroves and Merkle, 1971).

Volatilization of alachlor from natural waters should be minimal as the Henry's law constant (K_h) =1.3 x 10^{-6}. In a study by Baker and Johnson (1984), 84 kg of alachlor was applied to a dilute pesticide waste disposal pit over a 2 year period and only 0.3% was volatilized in 40,000 l of evaporation of water. In an effort to significantly

increase alachlor vapor, an air flow of 1 cm^3/min was passed over the surface of soil against a no flow control at 0.0% RH, 25 °C. This resulted in an approximately 500 fold increase in evaporation of alachlor. When the air temperature was increased from 25 to 40 °C the alachlor to water ratio further increased three fold, up to 9.9 mg/l.

Although alachlor has a water solubility of 240 ppm, field studies have shown that leaching is much less likely than lab studies. So although it has a high water solubility, the soil adsorptive properties of alachlor are dominant (Peter and Weber, 1985). The field studies show less leaching into the ground columns than laboratory studies because under normal conditions large volumes of water do not occur after applications and runoff/erosion would carry the herbicide away. The erosion factor was evaluated by Chesters *et al.* (1989) and after reviewing many studies they discovered only a few large rainfalls accounted for most of the herbicide loss from erosion during the growing season. Most of the pesticide losses were associated with degradation and volatilization.

Alachlor is primarily degraded microbially and photolytically, and very minimally by chemical means. The major metabolites are 2,6-diethylaniline(2,6-DEA), 2-chloro-2',6'-diethylacetanilide and 2',6'-diethylacetanilide. The

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formation of 2,6-DEA is caused by photolysis (in laboratory studies), by soil fungus cultures and hydrolysis in flooded soils. The metabolites 2-chloro-2',6'-diethylacetanilide and 2',6'-diethylacetanilide are products of photolysis and fungus cultures (Chesters *et al.*, 1989).

Degradation of alachlor is more rapid under aerobic than anaerobic conditions, as nearly 30% was removed by anaerobic conditions versus 72% under aerobic conditions after 13 days. The rate of CO_2 production and disappearance of alachlor increased with temperature up to 30 °C and then declined due to enzyme denaturation. The temperature dependence noted found that for every increase of 10 °C the half life decreased by 2 fold. After 30 days, little CO^2 production or parent/metabolite products were found in a sandy loam soil as it was thought the parent and metabolites were tightly bound to soil organic matter(Chou, 1977).

Zimdahl and Clark (1982) found that for alachlor at 80,50, and 20% of field moisture content (FMC) and at temperatures of 30, 20 and 10 °C respectively , the half-lives ranged from 11 to 25 days in clay loam and 19 to 43 in sandy-loam soils. The highest degradation rates where at higher temperatures and FMC. Walker and Brown (1985) also demonstrated more dissipation of alachlor at higher temperatures and FMC.

Beestman and Deming (1974) studied alachlor dissipation in sterilized and unsterilized soils and found sterilized soils to be 50 times slower to degrade alachlor. In another degradation study of alachlor, the USEPA (1981) determined a sterile soil had a 4% loss of alachlor whereas a non-sterile soil had a 50% dissipation of alachlor. Other studies have shown degradation of alachlor on sterile soils to range from 28% in 13 days to 43-48% in 28 days but it was questioned if the soils were sterile (Chesters *et al.*, 1989).

Alachlor shows low acute mammalian toxicity by rat LD_{50}=0.93 g/kg and dermal exposure of LD_{50}=13 g/kg. Oncogenicity from rat feedings occurred and presented the following tumors: lung; stomach; thyroid; and nasal turbinate. Teratogenicity and immunosuppression did not appear to be a problem, however these limited studies indicate further testing is needed (Chesters *et al.*, 1989).

The Environmental Protection Agencies (EPA) from Delaware, Maryland and several Midwestern states conducted a sampling survey for atrazine and cyanazine in the surface waters of 245 communities that use those waters as a source for drinking . In the Ohio study seventy (70) communities were sampled, and based on the federal drinking water standards limit of 3.0 ppb, only one community exceeded the standard- Sardinia, OH had atrazine at 3.66 ppb. Of the

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Ohio communities involved in the survey , 54% had concentrations of alachlor ranging from 3.66 to 0.28 ppb (Bennish, 1997).

As a result of this survey a controversy has risen in Dayton, Ohio. The Environmental Work Group, a Washington based environmental organization, has promoted a stricter standard of 0.15 ppb for atrazine which is based on the Food Quality Protection Act passed by Congress. This action was supported by both the American Water Works Association and the Association of Municipal Water Agencies. As a result of this coalition, many citizens are questioning the safety of their water supplies (Bennish, 1997).

Simazine

Simazine, 2-chloro-4,6-bis(ethylamino)-s-triazine, is a widely used selective herbicide whose primary mode of action is as a photosynthesis inhibitor. It is used for the control of broadleaf weeds and annual grasses, especially in corn and citrus, but may be used as a non-selective herbicide for vegetation control in non-cropland. It is applied as either a spray or in granular form prior to weed emergence. It has little or no foliar activity and must be absorbed by plant roots. Simazine is solid at room temperature with a melting point of 225 to 227 °C. The molecular weight is

201.7, water solubility = 5 ppm @ 20 °C, vapor pressure = 6.1 x 10^{-9} mm Hg @ 20 °C, the pK_a = 1.7 @ 20 °C (Kearney and Kaufman, 1975).

Due to the location of the nitrogen atoms in simazine the ring has less aromatic character because of the electronegativity of the nitrogen atoms. With this type of configuration, the electron withdrawing chlorine and substituent amino groups form the degradation product of 2-hydroxy-4,6-bis-(ethylamino)-s-triazine or aka 2-hydroxy simazine. The 2-hydroxy derivatives represent one of the main degradation products of the triazines in soil, and these are more basic than the parent compounds. Herbicidally active dialkylamino-s-triazines behave as weak bases in aqueous solution as protonation occurs on the ring nitrogen atoms (Esser *et al.*, 1975).

Weber (1970) reviewed simazine studies which indicated a slow hydrolysis in the region of neutrality, but showed an increase in either increasing alkalinity or acidity. In a study by Harris(1967), approximately 30 to 50% of the simazine applied converted to the hydroxy form in eight weeks @ 30 °C. Formation of hydroxy compounds occurred in much greater amounts in the soil versus the aqueous solutions. It was suggested that the soil catalyzed a non-biological hydrolysis reaction (Harris, 1967).

Non-biological degradation of simazine to hydroxy simazine has been confirmed by soils sterilized by sodium azide and heat. Several factors were found to increase this hydrolytic degradation: increasing temperature and moisture; low pH; and high organic matter. Other than the low pH these conditions are also favorable for microbial growth (Esser *et al.*, 1975).

Triazine ring cleavage has been confirmed by the production of $^{14}CO_2$ from ^{14}C- side-chain labeled simazine. However, this can be a slow process as it may take one to four months from application for 10% of the ring labeled $^{14}CO_2$ to be evolved. Ring cleavage can be enhanced when glucose is added to the soil and conversely, when the soil was sterilized at 120 °C for 20 minutes on 3 consecutive days or placed under anaerobic conditions no $^{14}CO_2$ was produced. These results indicated that microbial action was involved with the ring cleavage (Esser *et al.*, 1975).

Early studies have shown that s-triazines irradiated with UV and sunlight on surfaces or in solutions had undergone photolytic decomposition producing the metabolite 2-hydroxy simazine. However, most degradation occurred at UV wavelengths of 220 and 254 mu which are not representative of field conditions. Likewise field studies have indicated photolysis of simazine will occur, but its

importance for dissipation of simazine appeared to be low (Jordan *et al.*, 1975).

Persistence of triazines herbicides in soils varied greatly dependent upon the weather, soil and management practices. Methoxy-triazines are more persistent than chloro or methylthio triazines. Decomposition was the slowest in cool, dry climates, and conformed to a first order reaction. The interaction of triazines herbicides with other pesticides has not demonstrated an important influence on their activity or soil carryover. Microbial degradation of triazines provided a variable degree of activity but probably has major significance in dissipation (Lebaron, 1975).

Carbaryl

Carbaryl, or 1-naphthyl N-methylcarbamate, is a widely used carbamate insecticide and is used on citrus, pome, stone and berry fruits; forage, field and vegetable crops; nuts; lawns; poultry and pets. It is formulated as baits; dusts; granules; wettable powders; flowables; and aqueous dispersions (Union Carbide Fact sheet, 1984).

Carbaryl has not been shown to be oncogenic, teratogenic or a reproductive hazard, but it is mutagenic. The allowable exposure limits for carbaryl are 5 mg/m^3 for both

threshold limit value (TLV), time weighted average(TWA) and permissible exposure limit (PEL). It has a health hazard rating of high and requires personal protection (Rhone-Poulenc AG Company, 1987).

The following are some of chemical and physical properties of carbaryl: melting point 142 °C; Molecular .Wt. 201.22; K_{ow} = 2.36; water solubility = 40 ppm @ 30 °C; vapor pressure = 1.36 x 10^{-6} mm Hg at 25 ^{0}C and an estimated K_H = 1.28 x 10^{-8} at 20 °C. On a dry soil surface carbaryl has a photolysis half-life of 4 days and increases to 28 days on saturated soils. Hydrolysis occurs more rapidly in neutral and basic soils, and more slowly in acidic soils. Carbaryl biodegrades significantly in soil and has been shown to undergo 80% mineralization in 4 weeks. Carbaryl has the potential to be moderately mobile and may leach into groundwater (Howard, 1991).

Somasundaram *et al.* (1990) did a study on the mobility of pesticides and their hydrolysis metabolites in soil. They used soils with a wide range of clay (8 to 34%) and organic matter from 0.7 to 6.1 %. The results showed the hydrolysis products of the four studied organophosphorus insecticides were significantly more mobile than their parent compounds, but the metabolites of carbamates (1-napthol metabolite of carbaryl included), s-triazines and

phenoxy herbicides were less mobile than their parents. In the cases where soil effects were observed the greater the level of organic matter, clay, CEC and water holding capacity (at 1/3 bar) the lower the mobility of the compound was observed. In the cases of pH, the highest mobilities were seen at pH > 8. The K_{OW} values were a better predictor of mobility than the water solubilities. Finally, no direct relationship was found between the pK_a of the chemicals and their mobility.

Carbaryl has been found to inhibit soil respiration in a sandy loam with or without glucose, but to a lesser extent when glucose was added. The study showed CO_2 production was reduced by 6.5 and 19.5% at 150 and 1500 ppm, respectively when no glucose was added; however, when glucose was added the reductions were only 3.5 and 11.5%. Furthermore, carbaryl can reduce CO_2 production for four days at 25 ppm, ten days at 125 ppm, and 15 days at 1250 ppm. Similarly, the 1-napthol metabolite caused a respiration reduction for 27 days at 125 ppm and a 40 day reduction at 1250 ppm (Rajagopoal *et al.*, 1984).

Carbaryl was adsorbed more quickly in acid soils than neutral or alkaline soils, and even more readily in dry soils. It is believed that the sorption of carbaryl in a soil-aqueous system is achieved by van der Waal forces.

When carbaryl is placed in a soil-aqueous system with organochlorines, the organochlorines were most strongly sorbed by all the soils tested(Rajagopal *et al.*, 1984).

Sorption of carbaryl and 1-napthol was greater in soils with high organic matter, and 1-napthol is more strongly absorbed than carbaryl on acidic soils. The Freundlich K value for carbaryl is 2.20 and does not appear to be as highly mobile as expected. The lack of movement of carbaryl through the soil column or run off, is associated with the organic matter content of the soil (Rajagopal et al., 1984).

The half-life of carbaryl has been reported from 1 to 16 weeks. A field study was performed on Norfolk sandy loam soil with carbaryl applied at 1.5, 4.5 and 14.5 ppm. The carbaryl was incorporated into the soil resulted in half-lives of approximately 8 days (Mount and Oehme, 1980).

Caro (1974) reported the 95% mineralization of carbaryl after 135 days when applied to a Coshocton silt loam. Some areas of the field had persistent concentrations of carbaryl for 25 to 116 days longer but then rapidly decomposed. This lag period was stated to indicate the degradation was primarily microbiological.

Enhanced degradation of carbamates occurred in soils with a prior history of carbamate use. This increased rate of degradation has been found to be up to three times faster

in these types of soils(Rodriguez and Dorough, 1977). A study by Racke and Coats (1988) showed soils with prior field exposure to carbofuran, cloethocarb or a mixture of carbamates, stimulated specific populations of microbes able to degrade carbofuran. But, carbaryl and cloethocarb were most rapidly degraded only in soil with prior exposure to several carbamates or cloethocarb. Thus, although cross-adaptation for enhanced degradation is present with carbamates, structural similarity plays a role in this process.

In the case of mixtures of pesticides, it was found that carbaryl inhibited the degradation of linuron and monolinuron and chlorpropham. Carbaryl caused an extended lag phase to chlorpropham when applied at 1 ppm. (Kaufman and Blake, 1970).

Carbaryl is known to be chemically unstable at pH >7, but it is difficult to separate microbial hydrolysis from chemical hydrolysis. Mount and Oehme (1980) found the rate of carbaryl hydrolysis increased with temperature in all of the soil concentrations from 10 to 40 ppm with a pH of 7.3. After eight days at 28 °C, 93% of the carbaryl had been hydrolyzed as compared to only 9% at 3.5°C.

Flooded soils contain microbes that are capable of degrading carbaryl. The bacteria, *Pseudomonas* cepacia, was

isolated from flooded carbofuran exposed soils. It was found to degrade both carbofuran and carbaryl in a mineral salts medium (Venkateswarlu *et al.*, 1980). The study also indicated carbaryl was more persistent in sterile soils than in non-sterile soils.

Evidence from Bollag *et al.* (1980) indicated the role of microorganisms in the degradation of carbaryl and 1-napthol played a strong role in soil ecosystems. In neutral pH soils, the major means of degradation of carbaryl is likely microbial, whereas in alkaline soils degradation is primarily by chemical means and secondarily microbial.

Endosulfan I,II

Endosulfan is a broad spectrum insecticide and acaricide, composed of two isomers; 70% alpha (endosulfan I) and 30% beta (endosulfan II). The molecular formula for endosulfan is $C_9H_6Cl_6O_3S$ and the MW= 496.95. The mode of action for endosulfan is as a non-systemic contact and stomach insecticide against aphids, thrips, beetles, foliar feeding larvae and mites. It is formulated as emulsifiable concentrates, wettable powders, dust, and granules (Goebel *et al.*, 1982).

The following is a synopsis of the physicochemical properties of endosulfan. Endosulfan is stable in storage

and against sunlight. Alpha is more soluble in water than the beta isomer, 530 ug/l vs 230 ug/l respectively, and the low water solubility is reflected in the K_{ow} = 3.83. The Henry's Law Constant (K_h) is an estimated average of alpha and beta isomers and is 1.12 x 10^{-5} atm-m^3/ moles (Howard, 1991). Alpha has a melting point of 109 °C vs 213 °C for beta. The vapor pressure was determined to be 1 x 10^{-5} mm Hg at 25 °C.

Vapor phase endosulfan released into the air will react photochemically with hydroxyl radicals resulting in a $t_{1/2}$ =1.23 hr (Howard, 1991). Rao and Murty (1980) conducted a study that showed the persistence of endosulfan for 60, 100 and 160 days when applied to dry soil plots at 125, 250 and 1000 ml/acre of a 35% emulsifiable concentrate. The primary metabolite in all but the highest application rate soils was endosulfan sulfate.

A study was performed with a Gezira soil from Sudan which was amended with a carbon based growth medium and spiked with 280 ppm of endosulfan. The soils were then incubated at 37 °C for 100 days. After 100 days endosulfan recoveries in the experimental samples were 43% for alpha and 69% for the beta isomer, and the control recoveries were 55% for alpha and 91% for beta. Thus, ammending the soil with an additional carbon source increased the degradation

rate of endosulfan. In a subsequent study with the Gezira soil, the investigators spiked the soil with endosulfan at 125 ppm at 37 °C for 42 days, but no amendments were added and one soil was sterilized. The endosulfan recoveries were 50.6% for alpha and 29.7% for beta on the control, whereas the sterilized soil recoveries were 63.8% for alpha and 65.3% for beta (El Beit, 1981). This study was conducted in the dark, thus photolysis was not factor.

Under aerobic conditions the primary metabolites of the endosulfan isomers in soil are endosulfan sulfate,30-60%, endodiol, 2.6%, and endolactone, 1.2%(Goebel *et al.*, 1982). When specific microorganisms were exposed to endosulfan I and II it was found that 17 of 28 soil fungi, 15 of 49 soil bacteria and 3 of 10 actinomycetes had metabolized >30% of ^{14}C labeled endosulfans. Endosulfan sulfate was the major metabolite of fungi, and endodiol was the primary product of bacteria(Goebel *et al.*, 1982). In a study by Miles and May (1979a), endosulfan was applied to a sandy loam soil and the major metabolite produced was endosulfan sulfate(11-22%) and the next major metabolite was endodiol (approximately 3%).

Based on soil adsorption/mobility studies, both alpha and beta endosulfan seldom leached through the soil columns. The low probability for leaching is confirmed by the K_{oc} values for the alpha and beta isomers, 3.46 and 3.83,

respectively. The cases where it was found to leach, were under the conditions of high water volumes and low organic soil content (sandy soils). The circumstances in which leachate was observed, more beta than alpha endosulfan was recovered (Howard, 1991).

In a 1975 survey of 11 agricultural watersheds in Southern Ontario, Canada, 81 pesticides were found to be applied on farms and rights-of-ways. Another study, conducted from May 1975 to April 1977 on streams draining the 11 watersheds were analyzed for 61 of the 81 listed pesticides, plus 4 isomers, 13 metabolites and 2 industrial organic pollutants. The only pesticides found to be present in the streams throughout the year were atrazine, endosulfan and simazine. Five compounds exceeded the water quality criteria established by the International Joint Commission for lake and stream waters entering the Great Lakes. Endosulfan was noted to be one of the five compounds exceeding the water quality criteria and was involved in 14% of the cases where water quality was exceeded (Frank *et al.*, 1982a).

Captan

Captan, N-[(trichloromethyl) thio]-4-cyclo-hexene-1,2-dicarboximide, is a fungicide used on fruit and nut crops.

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Captan is practically insoluble in water (0.5 ppm at 20°), but soluble in acetone, ethanol and chloroform. Captan is easily hydrolyzed to 4-cylhexene-1,2-dicarboximide (phthalimide) via very unstable intermediates. The K_h for captan is 5.9×10^{-6}, which is moderately volatile. Captan is not expected to leach into the soil, but evaporation from soil surfaces may be significant (Howard, 1991).

The half-life of captan varies from 1-12 days depending on soil mositure and pH. Captan can be easily hydrolyzed under alkaline conditions. Koivistoinen *et al.* (1965) found captan to be rapidly hydrolyzed and disappear in 7 days post crushing of grapes even at a pH of 3. Frank *et al.* (1985b) reaffirmed that captan will degrade when it is not stored properly by as much as 39% in 7 days at 20°C.

Groundwater

Concerns of minimizing the possibility of contaminating the environment from spills and overuse of pesticides is addressed by Fawcett(1989) in *Farm Chemicals Magazine*. The magazine articles provided practical advice which attempted to inform the farmer of good stewardship practices to reduce the use of chemicals and the risks they would encounter if not followed.

In the *Farm Chemicals Magazine* (1989) the USGS provided

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information on how groundwater enters an aquifer (the process of hydraulic conductivity). This process may take only days if there are quick access points such as improperly sealed wells, disturbed soil columns or sink holes (caverns or holes in the ground where the karst or carbonate rocks dissolve). Some aquifers may take many years (up to thousands) to regenerate the groundwater depending on the strata (clay, rocks) separating the point of entry to the depth at which the aquifer begins. One idea presented is that water flows underground (hydraulic gradient- high pressure to low pressure, less resistance concept), however the idea was not specifically addressed that this means their farming practices affect other people with the same hydraulic gradient. But contamination on their farm may filter to neighboring areas for which they may be legally liable if well sampling could prove them as the source. Conversely, if they are aware that a neighboring farm is improperly using/disposing chemicals, this activity could affect them if underground flow is toward their property. (USGS, 1986)

There are other sources of contamination besides those related to agricultural such as: improper septic systems; surface impoundments; injection wells; and urban runoff. There are also natural contaminants which include: bacteria;

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metals; radon; and the lesser but undesirable conditions of hard water and bad odor (Fawcett, 1989).

In setting up a containment facility it is important to sample the soil prior to building to establish a history of the sight should litigation ever develop. The typical requirement is for concrete containment of 110 to 125% of the expected volume. The tanks should be raised to allow inspection for leaks and secured to prevent floating in cases of substantial leaks. Underground plumbing currently in use at some facilities to carry the rinse waters is not suggested for new installations since any leaks would be difficult to detect. Above ground plumbing is preferred and that it have secondary containment as well (Broder, 1989).

It is estimated to take 190 to 300 L of water to rinse a sprayer hopper or holding tank and the plumbing, which may contain 15 to 38 L of field strength mix. It is recommended that rinsate storage tanks be able to hold 1130- 2270 L and be composed of either polyethylene or fiberglass so the contents can be seen from the outside (Noyes, 1989).

Objectives

The research described in this dissertation was designed to assist the farmer in providing a safe disposal system for excess pesticide sprays/rinses that occur after a

crop or field was sprayed. The use of a disposal system would prevent contamination of nearby streams and wells that would occur if the operator was to just drain the excess onto the ground or spray it on a fence row. The disposal system uses soil in above ground tanks, placed on a concrete floor allowing one to monitor the tank for leaks. The following parent compounds and major metabolites were analyzed in the above ground tanks: alachlor and 2,6 diethyl aniline(2,6-DEA); captan and phthalimide; simazine and hydroxy-simazine; carbaryl and 1-napthol; endosulfan I,II and endosulfan sulfate; and chlorpyrifos and 3,5,6-trichloro-pyridinol. The **hypothesis** for this study is H_o: Pesticides from farm sprays and rinses will significantly dissipate/degrade in a soil disposal system within 1 year of application and thus be an acceptable disposal method. Alternatively, H_1: Some or all of the pesticides will not dissipate/degrade but accumulate and therefore not be an acceptable disposal method.

Additional research was conducted to check the efficacy of a product called Super Bugs^R, which claims to be capable of degrading a wide variety of chemically contaminated soils, ponds/ditches and holding tanks. SuperBugs^R is a proprietary mixture of microorganisms that was amended into soils in which alachlor, captan, carbaryl and chlorpyrifos

were applied. The hypothesis for this study is H_o: Superbugs^R, as an amendment to soils containing selected pesticides, will degrade the selected pesticides significantly faster than an unamended soil. Alternatively, the null hypothesis is H_1: there is no significant difference between pesticide degradation ability of the Superbugs^R amendment and the endigenous microbial population of the soil in the study.

MATERIALS AND METHODS

MATERIALS

Field Research Site:

Field research was conducted at the Clarksville Horticultural Experimental Station (CHES), located at Clarksville, MI, and operated by Michigan State University. This facility is located approximately 40° N latitude and 84 ° W longitude, and is approximately 45 miles west of Lansing, MI. CHES is a 440-acre station dedicated to fruit and vegetable research.

Research Containment Vessels:

Two 3000 gallon underground steel storage tanks were cut in half, longitudinally, and epoxy-coated. The resultant four 1500 gallon tanks were further split in half (by welded steel dividers) forming 8 equal research units of 750 gallons. Six of the units were filled with a locally obtained sandy-loam soil and the remaining two units were used for collection and application of pesticide rinses (figure 1). Each storage tank was 18 feet long and 64 inches in diameter. Each of the soil filled units contained approximately 1993 kg of soil.

All vessels were supported by steel frames, setting on

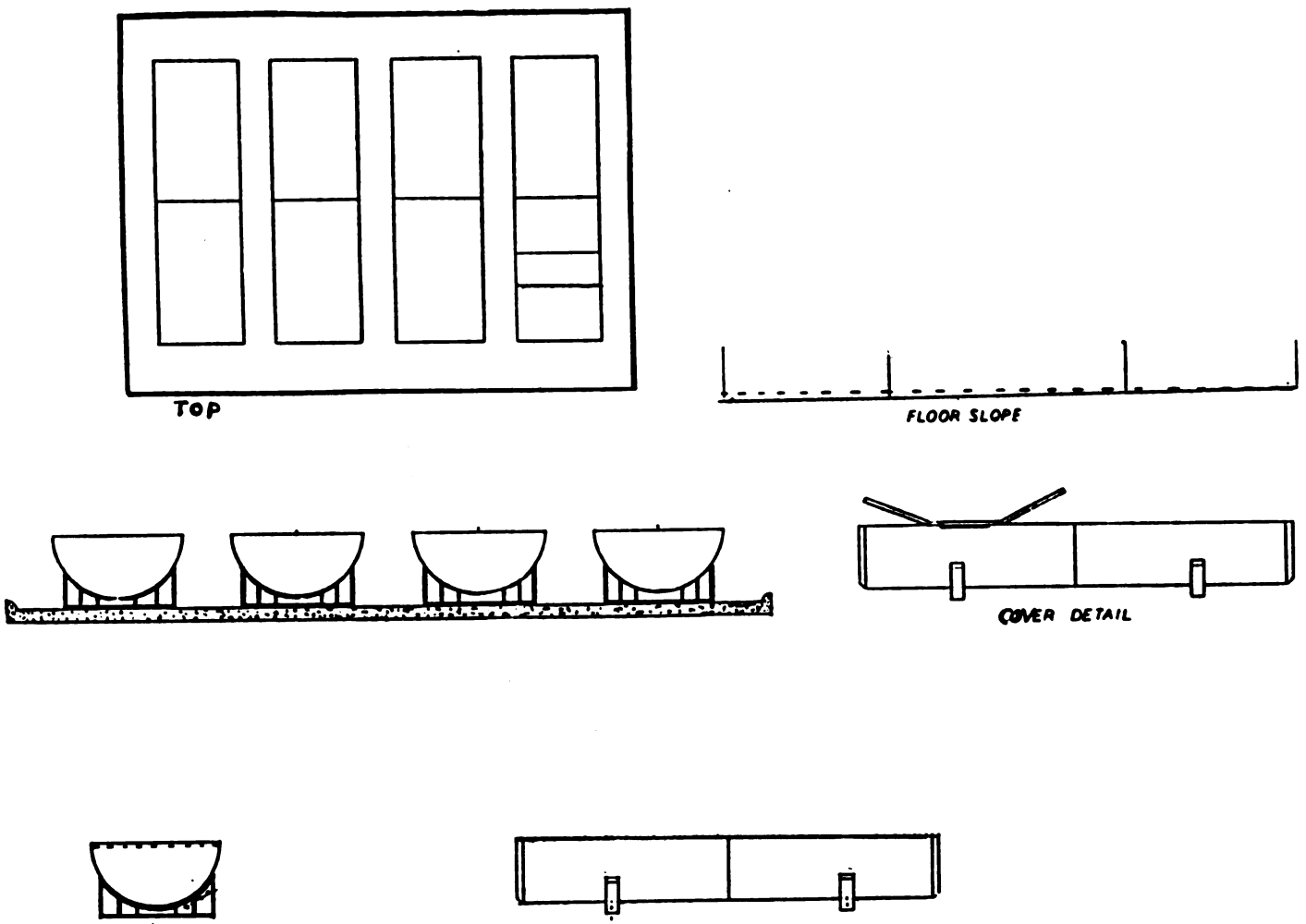


Figure 1 Research Vessels

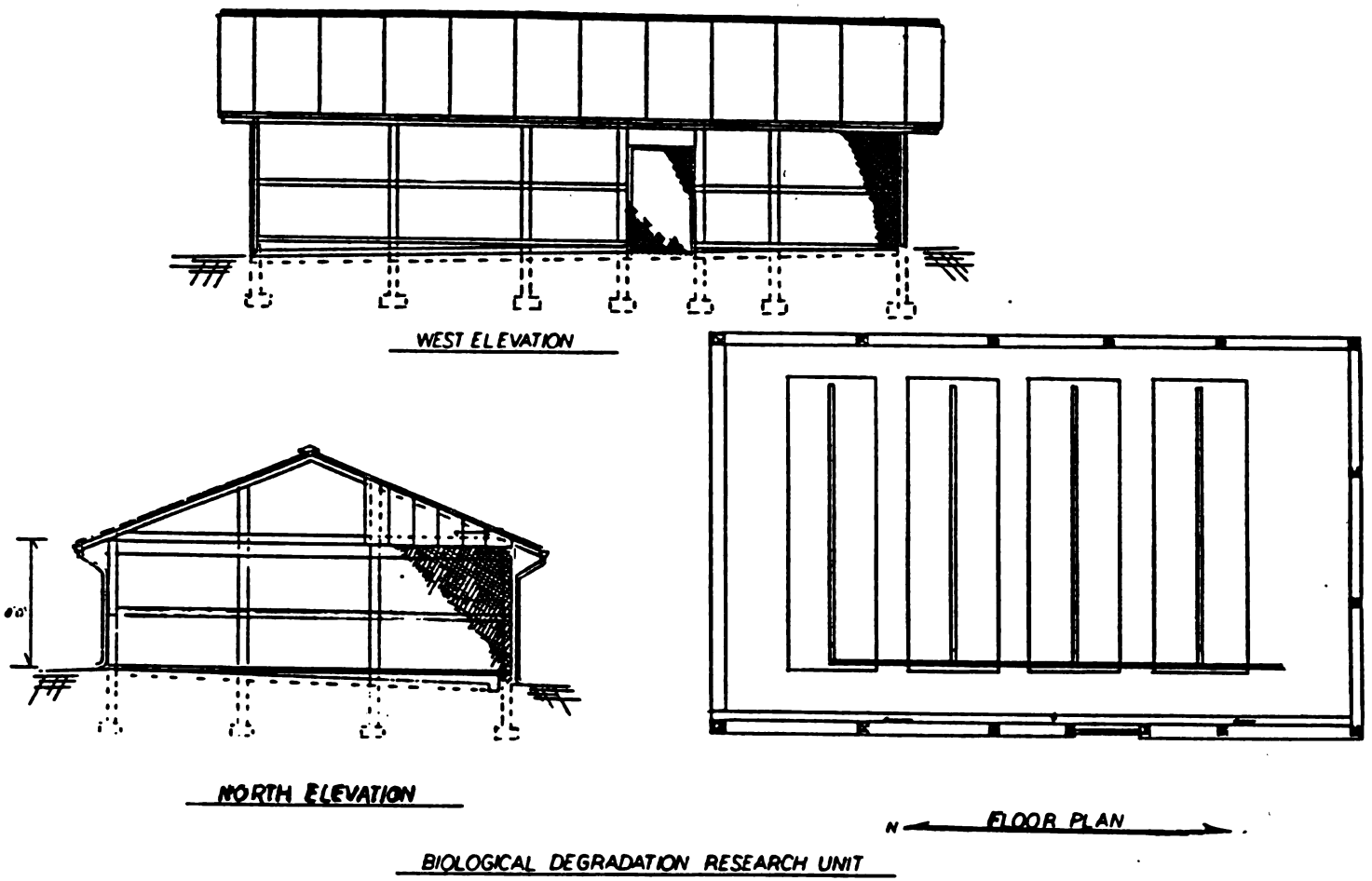


Figure 2 Research Unit

a concrete floor which permitted visual inspections for leaks (figure 2). The roof was covered by Lascolite^{R} panels, these transmitted visible light, but transmission cut off was at ca. 320 nm. The concrete floor was sloped slightly into a collection channel and had raised sides for containment purposes. This channel (trough) had a ball joint operated tee valve that could be opened as needed to remove collected mud or rain. Two sides of the facility were recessed into the ground and driving rains could allow mud to enter through the chain-link fence as happened initially until the landscape was leveled. The facility was enclosed by a chain-linked fence, a door with a lock, and electrical outlets for the mixing/pumping of rinsates (pesticide rinses) and operating the compressors.

Two vertical tanks were used for storage of pesticide rinses (rinsates), one was 1100 gallons and the other was 5000 gallons. These were premium Snyder Industry tanks composed of a crosslinked polyolefin with ultra violet inhibitors. The 1100 gallon tank was the primary tank used for application on the soils and the larger tank was used in times of excess volume. Soils were to have water applied on a weekly basis from the reservoir tank. The pesticide rinses were collected in one of the 1500 gallon research vessels via an underground 6 inch diameter PVC pipe draining from the loading/ rinsing pad approximately 50 yards away.

Reagents:

All solvents were analytical HPLC grade and were used as received. The solvents used were from Mallinckrodt Chemicals and were acetone, methanol, petroleum ether, ethyl ether (anhydrous), hexane and methylene chloride. All mobile-phase solvents used for HPLC analyzes were degassed by vacuum, and filtered through 0.7 um glass fiber filters.

Chemicals:

All chemicals were of analytical grade quality and were anhydrous sodium sulfate (granular), pesticide grade florisil 60-100 mesh activated at 135 °C for 48 hours, 0.01 M KH_2PO_4, and 18 M H_3PO_4. Reference standards were from EPA Research Triangle Park, N.C.(all standards > 99% purity) and were Lasso^R EC (alachlor 45.1% a.i.), Lorsban^R EC (chlorpyrifos 40.7% a.i.), Princep^R 80W (simazine 80% a.i.), Sevin^R 50W (carbaryl 50% a.i.), Captan^R 50-WP(captan 50% a.i.), and Thiodan^R 50WP (endosulfan I, II, 50%).

Miscellaneous Items for Part I:

The following is a list of items used for "The Fate of Selected Pesticides in Above Ground Disposal Vessels": boiling chips; silanized glasswool; Whatman (25 mm x 80 mm) Soxhlet cellulose extraction thimbles; polyurethane foam plugs (PUF's) 4.5 cm diameter x 5 cm length procured from Jaece Industries, Inc. Tonawanda, NY; two B&G vacuum pumps,

1/3 HP, 1725 RPM with six flow controllers on each pump; 10 ml disposable pipettes; Little Giant submersible pump (circulation rated at 500 gallons/hour @ 1 foot); water meter calibrated at 0.1 gallon increments; hand held Omega pH meter, Model PHHH-80 and Zymark Turbovap evaporator.

Miscellaneous Items For PART II:

A sandy-loam soil was obtained from Plant Sciences Greenhouse. The soil was analyzed and did not contain any detectable levels of the following pesticides/metabolites: carbaryl/1-napthol; captan/phthalimide; alachlor/2,6-DEA and chlorpyrifos/3,5,6-TCP. Sixteen (16) kg of soil was added to each of 12 ten gallon aquariums (12" H x 12" W x 23" L). The following items were also used: J&W SPE Silica cartridges (500 mg x 3 cc, particle size 40 microns; pore size 60 angstroms) and J&W SPE manifold; celite; 125 ml flasks; mechanical shaker; Superbugs^{R}; fertilizer (nitrogen 9%, available phosphoric acid 3%, sulfur 2%, soluble potash 1%, iron 0.5%, manganese 0.5%, zinc 0.5%, copper 0.0025%, and boron 0.01%; and a temperature controlled chamber set at 21°C $\pm$ 2.

Methods

Soil characterization:

The sandy-loam soil was mechanically characterized at the Crop and Soil Sciences Building at Michigan State University by Dr. Mokma. Soil volume was approximately 150 cubic feet (ca. 1990 kg) for each research unit (1 of 8 units). The soils were further characterized for organic matter content and soil pH (McLean, 1982). The cation-exchange-capacity (CEC) were performed by the Soils Testing Laboratory at Michigan State University (centrifugation method by D.D. Warncke, 1980). Soils used were analyzed for selected pesticides and were determined to be below detectable limits (0.01 ppm).

Meteorological data was collected daily which included air and soil temperatures; wind speed; relative humidity and pan evaporation.

All laboratory equipment was cleaned by soaking and scrubbing in hot, soapy water, followed by a triple rinse of hot water and distilled water. A final rinse of acetone and/or hexane was performed prior to placement in a drier oven (methlyene chloride/acid washes were used as needed).

The pesticide rinse holding tank 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. A

submersible pump was operated in the holding tank for 90 minutes prior to application to the research units to promote uniform concentrations. After mixing, a non-submersible pump was attached to the outlet faucet with a forty foot garden hose that had an in line water meter and a particulate filter.

Equal volumes were uniformly applied to all soils by surface application. When pesticide rinses are applied to each tank,the volume delivery was checked once by a polyethylene measuring pail for accuracy. Four liters of this application was collected to determine if the holding tank rinse water contained any compounds currently being analyzed. After this standing volume was applied the seven pesticides of interest were applied to the soils by a 2.5 gallon hand held polyethylene spray tank to allow for an even distribution of pesticides on the soil surface.

Holding Tank Rinse Water Samples:

Analysis was performed on the rinsates according to the multi-residue method of the EPA. One L of rinse was extracted with methylene chloride in a separatory funnel, run through sodium sulfate and concentrated on the turbovap to ca. 10 ml. Florisil micro column clean up was performed as needed. Micro columns were prepared by adding a small amount of silanized glass wool to a disposable pipette. PR

with 1 cm of anhydrous sodium sulfate. Columns were rinsed with 20 ml of pet ether and 50 ml of 50% ethyl ether / pet ether was used to collect the pesticides of interest. Quantitative analysis and confirmation were performed on a Waters Wisp HPLC system and a ECD/NPD Hewlett-Packard Gas Chromatograph with HP Chemstation software. Parameters used are listed at the end of methods section.

Soil Sampling and Analysis of CHES Soils:

Research vessel soils had each of the selected pesticides (captan; endosulfan I, II; simazine; alachlor; chlorpyrifos, carbaryl) applied at three intervals: June 4; August 6; and September 10 in 1990. Applications for 1991 were made on May 28, July 15 and September 5. The selected pesticides were added to the soils after an application of the pesticide rinse water. This was done to provide a greater dilution volume that would allow for a more even distribution of the added pesticides to the soil surface. The first year 210 g of active ingredient (equivalent to 105.4 ppm, based on 1993 kg/tank) was added to each tank and the second year had 180 g (90.3 ppm) of active ingredient added to each tank.

Soil sampling was performed by a stainless steel soil corer. Core samples were 40 x 4 cm. The sample cores did vary from approximately 16 to 28 inches in depth. Three

vary from approximately 16 to 28 inches in depth. Three samples were taken from each research unit, one sample was always taken from the center region and one sample from each of the lateral regions. Each soil sample was mixed throughly and a sub-sample was taken for analysis. After obtaining the sub-sample, the remaining soil was returned to the sample site and a dated test tube was inserted to denote the sampled spot. Soil samples were placed in glass, air tight screw top bottles and transported in a cooler. Upon arrival at the laboratory, the samples were place in walk-in freezer at -20 °C until analyzed. Soil samples were collected on a weekly basis, prior to application of pesticide rinses in the holding tank.

Soils were allowed to thaw at room temperature before pesticide extraction was performed. The extraction procedures for the following parent compounds and metabolites: endosulfan I, II/endosulfan sulfate; carbaryl/1-napthol; chlorpyrifos/3,5,6-trichloro-2-pyridinol (TCP); alachlor/2,6-diethylaniline (2,6-DEA); captan/phthalimide; simazine/hydroxy-simazine were based on those of the Pesticide Analytical Manual (1986), Wright et al. (1991), Miles et al (1990b), Racke and Coats (1988). Each core was thoroughly mixed and three sub-samples were taken. Sub-samples were 20 to 30 g and weighed into a extraction thimble and placed in a soxhlet apparatus.

Duplicate 10 g samples were taken at this time to be oven/vacuum dried (110 °C and -15 mm Hg for 30 minutes) for the determination of the dry weight calculations. The selected pesticides were detected on a gas chromatograph-(ECD and NPD) or by HPLC, and confirmation of pesticides were by mass spectrometry.

The thimble was extracted with 50 ml acetone:50 ml hexane 50 ml methanol in a flat bottom flask with boiling chips for 8 hours at ca. 10 cycles/hour. The extract was quantitatively transferred/filtered through ca. 10-12 g of anhydrous sodium sulfate (filter rinsed with 2 five ml portions of hexane) and evaporated to approximately 5 ml by evaporator. This was filtered with a Gelman Acrodisc CR (PTFE membrane, pore size 0.2 to 1 um, retention <100 ul with air purge) on an as needed basis and an additional 0.5 ml was sent through the disc. This volume was quantitatively transferred to a florisil micro column. The column was packed with 10 g of activated florisil (130° C for 16 hours) which was placed upon a small plug of silanized glass wool. A 3 g top layer of anhydrous sodium sulfate was added and followed by 50 ml of hexane to wash/wet the column. The extract was transferred to the column and eluted with 75 ml of ethyl ether (E.E.)/ hexane. The eluent was then concentrated to 20 ml and adjusted as needed for injection into a GC or HPLC.

Superbugs Bench Study

Twelve 10-gallon aquariums were filled with 16 kg of sandy-loam soil (with non-detectable residues for alachlor, captan, carbaryl and chlorpyrifos). Six of the aquarium soils were steam sterilized at the Plant Sciences Greenhouse on the campus at Michigan State University. The aquariums were divided into two groups of six; 3 sterilized and 3 non-sterilized soils. One group of six was amended with Superbugs^{R}, another group without the Superbugs^{R} amendment.

A fertilizer was applied (issued by the manufacturer-see under Materials Section) to all aquariums and was applied at a rate of 7 lbs per thousand sq ft. The pH of the sandy-loam soil was 7.3 based on 3 air dried samples (McLean, *1982)*. The following four compounds and stated concentration was applied to each of the aquariums: 3.2 g a.i. (200 ppm) of alachlor, chlorpyrifos, carbaryl, and captan. Soil moisture content was at 1/3 bar field moisture capacity (Buckman and Brady, 1962). Air temperature was maintained at 21° C and the lighting was fluorescent.

Sample collections were performed after the initial application (day 0) and the following days: 2, 3, 5, 7, 10, 14, 30 and 60. The sampling intervals were based on the half-lives of alachlor 10 days, captan 3 days, carbaryl 7 days, and chlorpyrifos 30 days (SCS Water Quality Workshop

Manual, 1988; Howard, 1991). Three recoveries were performed with each batch run and a standard was run every 12 samples unless a problem determined a standard run was necessary.

After the twelve aquariums were spiked with the four pesticides, each of the soils were sampled to establish initial soil concentrations of the pesticides. Three soil sample cores were collected by pushing an 166 mm test tube into the soil. After each sampling, a clean test tube was placed in the sample area as a marker. After mixing the core sample, a 20 g sample was placed in a 125 ml flask and 20 ml each of methanol and acetone were added (EM Separations, 1993). A 10 g sample was also taken to calculate percent moisture. The flask was then placed on a wrist action shaker for 20 minutes, the supernatent was decanted through an 11.0 cm circle of Whatman #4 filter paper covered with approx. 1/4 inch celite into a 250 ml filter flask. This procedure was repeated for a second time. A third extraction was performed as well but with 10 ml of 2% acidified methanol (Szafranski and Kontz, 1995). The collected volumes were passed through anhydrous Na_2SO_4 and reduced to 4 ml by the Zymark Turbovap. The final volume was filtered with a 0.45 PTFE Gelman Acrodisc as needed to remove particulate matter.

Solid phase extraction (SPE) was then performed using

a J&W manifold to hold and provide suction to the 500 mg silica SPE cartridges. The suction placed on the cartridge was set at approximately 6 inches Hg. The cartridges were then wetted with 3 ml of hexane and then eluted with 8 ml of methanol and collected in a test tube. The eluate was then diluted as needed for the appropriate chromatography (J&W instruction sheet No. 830-4000, 1989).

Detection of Air, Soil and Wastewater

The detection and confirmation of the selected pesticides and their major metabolites were by gas chromatography (GC),both ECD and NPD detectors, high performance liquid chromatography (HPLC)with a UV detector, and a mass spectrometer (Nermag R10-10C quadrapole MS with Technivent software).

Chromatographic Conditions

ECD-Gas Chromatograph. A Hewlett-Packard Model 5890 Series II gas chromatograph was used under the following parameters for the detection of endosulfan I and II; endosulfan sulfate; chlorpyrifos; simazine; captan; carbaryl; and alachlor.

Column: DB-5 fused silica capillary column (60 m x 0.25 mm i.d.) with 0.25 micron phase thickness (J&W

Scientific).

Injector temperature: 225 ° C

Oven temperature: programed from 170 ° C, isothermal for 15 minutes, then 2 ° C up to 224 ° C, and 10 minutes isothermal at this temperature.

Detector temperature: 285 ° C

Carrier gas: He at 30 psi

Make-up gas: N_2 at 20 psi

Integrator: Hewlett-Packard Chemstation Software

NPD-Gas Chromatograph. A Hewlett-Packard Model 5890 Series II gas chromatograph was used to confirm the pesticides: chlorpyrifos, simazine, captan, carbaryl, alachlor and 2,6 DEA. Detection was performed under the following conditions:

Column: DB-5 fused silica capillary column (30 x 0.25 mm i.d.)

Injector temperature: 240 ° C

Oven temperature: 170 ° C

Detector temperature: 250 ° C

Carrier gas: He at 20 psi

Gas flows: Air 60 ml/min; H_2 30 ml/min

Integrator: Hewlett-Packard Chemstation Software.

High performance liquid chromatography (HPLC) was used for metabolites 3,5,6-TCP, hydroxy-simazine, phthalimide, 1-napthol, and 2,6 DEA. The autosampler used was a Waters 712 WISP and the sample carousel temperature was set at 5 °C. The pumps were a Waters Model 510 and a Bischoff. The detector was a Milton-Roy variable.

Column: u Bondapak C_{18} 300mm x 4.0mm

Injection: 250 ul

Mobile Phase: Solvent A: 0.05 M KH_2PO_4 (pH = 3)

Solvent B: MeOH

Flow rate: 1 ml/min initially, then 1.5 ml/min @ 20 min

Gradient Conditions: initially 60% A: 40% B to 60% B in 20 min, then to 100% B in 10 min; and ramp back to 60%A:40% B in 12 min

The mass spectrometer used in these studies was a Nermag R10-10C, positive mode at 70eV, with Technivent software interfaced to a Di 700 Delsi GC equipped with a 60 m DB-1 column (J&W Scientific), 0.24 mm ID and 0.25 um film thickness and a flow rate of 3 ml/min.

CHES Soil Characteristics

Table 1. The following CHES soil characteristics were performed at Michigan State University's Soil Testing Laboratory.

soil type	sandy-loam
organic matter	1.9 %
Cation Exchange Capacity	6.5 meq/100 g
soil pH	6.5

Greenhouse Soil Characteristics:

Table 2. The following soil characteristics were determined by the Michigan State University Soil and Plant Nutrient Laboratory and this soil was used in the Superbugs^{R} study.

Soil type	sandy loam
organic matter	2.0 %
Cation Exchange Capacity	8.0 meq/100 g
soil pH	6.5
nitrate-NO_3	132 ppm
phosphorus	0.2 ppm
potassium	13 ppm
calcium	229 ppm
magnesium	49 ppm
sodium	9 ppm
chloride	39 ppm

Table 3. Results of the determination of 0.3 bar field moisture capacity using pressure plates for the Superbugs study, from a Turf Grass Laboratory at Michigan State University.

Sample	1	2	3	Avg
Bulk density:	1.33	1.46	1.43	1.40 ± 0.09
water retention @ 0.3 bar:	13.6	13.5	13.4	13.5 ± 0.01
porosity (1):	50.0	45.0	46.1	47.0 ± 2.62
porosity (2):	42.1	48.2	45.3	45.2 ± 3.05

PART I: FATE OF SELECTED PESTICIDES IN ABOVE GROUND DISPOSAL VESSELS.

RESULTS AND DISCUSSION

CHES Soil Recovery Studies

Four CHES soils (25 g) each were spiked with 20 ug of each of the following pesticides and their major metabolite: alachlor/2,6 diethylaniline; simazine/hydroxy simazine; carbaryl/1- napthol; chlorpyrifos/3,5,6-tri-chloro-pyridinol (TCP); captan/phthalimide; and endosulfan I, II/endosulfan sulfate. The samples were placed in the lab air flow hood until dried. The samples were run in triplicate and analyzed according to the CHES protocol. The selected pesticides were detected on a gas chromatograph-(ECD and NPD) or by HPLC, and confirmation was by mass spectrometry or a different GC detector.

Table 4. Recoveries of parent pesticides and the associated metabolite from CHES soil.

Pesticides	Avg. Recovery ±SD
alachlor	87± 5
2,6-DEA	77± 9
simazine	73± 6
hydroxy-simazine	74± 6
captan	81± 8
phthalimide	76± 7
chlorpyrifos	88± 6
3,5,6-TCP	77± 8
endosulfan I	85± 5
endosulfan II	82± 4
endosulfan sulfate	83± 7
carbaryl	84± 8
1-napthol	75± 6

Soil Freezer Stability Study

The method for analysis was the same as that for the afore mentioned CHES soils. The samples remained at -20 °C for 90 days until analyzed. The results of analysis are seen in Table 5.

Table 5. Recoveries of the parent pesticide and the

associated metabolite after 90 days of storage in the freezer at -20 °C.

Pesticide	Avg. Recovery ±SD
alachlor	84± 7
2,6-DEA	71± 7
simazine	72± 8
hydroxy-simazine	70± 7
captan	74± 6
phthalimide	73± 7
chlorpyrifos	77± 8
3,5,6-TCP	70± 9
endosulfan I	86± 8
endosulfan II	79± 6
endosulfan sulfate	78± 8
carbaryl	73± 6
1-napthol	71± 9

Air Analysis:

Evaporative losses of pesticides from the soils were trapped in polyurethane foam plugs (PUF's). The PUF's were 4.5 cm in diameter and 5 cm long. The PUF's were rinsed with distilled, deionized water in a Nalgene pipet washer for six hours followed by a Soxhlet extraction with 500 ml hexane for six hours. The PUF's were then vacuum dried, wrapped in hexane rinsed aluminum foil and stored in a screw

cap jar until the sampling period. PUF's cleaned under these conditions resulted in no detectable residues of the compounds of interest. Trapping efficiency was determined by placing two PUF's in tandem, which resulted in no detection of residue in the second PUF. This method is based upon those of *Compendium of Methods for the Determination of Air Pollutants in Indoor Air*(1990), Glotfelty *et al.* (1984) and Wright *et al.*(1991).

Air sampling was started within 2 hours of application for a 24 h period and then each week thereafter for 24 hr period. The air flow rate was approximately 8 l/min and was calibrated with a rotameter at the start of sampling. After the sampling period has been completed, the PUF samples are wrapped in hexane rinsed aluminum foil and placed in a glass screw top bottle. The samples were then taken to the lab for a 8 h soxhlet extraction (30-40 cycles) with 160 ml of methanol. The extracts were filtered through anhydrous sodium sulfate and evaporated with a Zymark Turbo evaporator to 10 ml. The extract was filtered with a Gelman Acrodisc CR (PTFE membrane, pore size 0.2 to 1 um, retention <100 ul with air purge) on an as needed basis and an additional 0.5 ml methanol was sent through the disc.

Air PUF Recovery Studies

Air recoveries were performed in triplicate by injecting 2.0 ug of the standards (alachlor; simazine; captan; carbaryl; endosulfan I, II; and chlorpyrifos) into the center of the PUF's. The plugs were then air dried and extracted as under the air analysis section. The selected pesticides were detected on gas chromatographs (ECD and NPD) or by HPLC, and confirmation was by mass spectrometry or another type of GC detector.

Table 6. Air Puf recoveries of parent pesticides at CHES.

Pesticides	Avg. Recovery	±SD
alachlor	93	± 5
simazine	84	± 4
captan	85	± 4
chlorpyrifos	90	± 4
endosulfan I	93	± 5
endosulfan II	90	± 6
carbaryl	85	± 6

Recovery Study for Superbugs[R]

Table 7 on the following page has the results of recovery for the Superbugs[R] study.

Table 7. Extraction recoveries were determined for the Superbugs[R] soils for the four compounds and major metabolites.

Pesticides	Avg. Recovery ±SD
alachlor	89± 4
2,6-DEA	75± 5
captan	87± 5
phthalimide	75± 6
chlorpyrifos	86± 7
3,5,6-TCP	82± 9
carbaryl	87± 5
1-napthol	78± 6

The weather data is presented below so it can easily be referenced for all of the compounds. The next issue addressed will be the problem of collecting large volumes of rinse water. Then the pesticides and their metabolites will be discussed in the following sequence: endosulfan I, II, carbaryl, simazine, alachlor, chlorpyrifos, and captan.

The weather data that was obtained was tabulated and placed in Table 8.

Table 8. Weather data used to calculate evaporation of pesticides due to wind and provide insight into which parameter aided the dissipation of the pesticides.

YEAR	AVG WIND MPH	AVG TEMP HIGH/LOW (°C)	AVG PAN EVAPORATION INCHES/Day	% RELATIVE HUMIDITY HIGH/LOW
1990	7.0	24.7/11.7	0.06	97 / 53.3
1991	8.2	26.1/12.2	0.12	92.9 / 48

The soil temperatures were taken in each of the 6 vessels, at two randomly chosen central locations in the vessels and averaged each week from June through October. The following table indicates the results.

Table 9. Average soil temperatures of research vessels during the soil sampling period from May through October.

YEAR	AVG SOIL TEMP	MAXIMUM TEMP	MINIMUM TEMP
1990	19.9 ± 5.5 °C	27.5 ° C	10 °C
1991	22.9 ± 5.2 °C	32.0 ° C	14 °C

The resultant weather data would indicate that 1991 was overall warmer, more windy, and less humid. When these factors are combined with the warmer soil temperature, this situation would be expected to increase evaporation from the research vessels and probably increase microbial activity in the soil in the second year as compared to the dissipation of the pesticides in the first year's application.

Large volumes of water were collected initially at the start of this disposal system which was alarming. For

instance, the rinse water collection logbook recorded 6057 L (1600 gal) was input into the system, but over 17,034 L (4500 gal) was actually collected. Most of the unrecorded volume was due to rain, so removable curtains were installed on the rinse pad to be used on rainy days to reduce rain water collection, and this reduced the volume. In addition to the rain curtains.

Inputs were difficult to monitor and reduce, thus an attempt was made to more rapidly reduce the volume acquired. By using the same trickle pads to increase humidity as those in the Crops and Soils Greenhouses at Michigan State University, a submersible pump was operated to run rinse water over the surface of the pads (10 sq. ft. surface area) and reduce the excess volume. This apparatus evaporated ~59 L/day (15.5 gal/day) for 152 days in 1990, for a grand total of ~8918 L (2356 gal). On 21 Sep 1990, a fan was suspended from the rafters approximately six feet from the pads to increase air flow over the pads and therefore increasing evaporation. It was operated for 7 to 8 hours per day over 47 days and evaporated ~ 106 L/day (28 gal/day), for a total of 4982 L (1316 gal). The total volume applied to the soils was ~4542 L (1200 gal), or 227 L/application(60 gal/ application). Thus the total volume of rinse water through the system was 18,443 L (4872 gallons), with another 7362 L (1945 gal) remaining. The following year, over the same

period of time more than 18927 L (5000 gal) was dissipated by evaporation (>13,630 L) and soil application (>4500 L).

CHES applied the same pesticides as used in the study, the rinse waters had to be analyzed to adjust, if necessary, the input of the pesticides in the study. Results indicated few detections (low ppb) and at <0.002% of the total active ingredients applied (210 mg to each vessel year one: 180 mg in year two), thus they are considered insignificant. Analysis of the soils prior to the start of the study revealed all compounds were below 1 ppm except simazine at 1.03 ppm.

Endosulfan I and II

Endosulfan I and II will be examined together as they are isomers of each other, alpha and beta. They were applied as Thiodan^{R}, which has an averaged K_h (for endosulfan I and II) of 1.12×10^{-5} and a vapor pressure of 1×10^{-10} mm Hg.

In the first year 210 g a.i. of endosulfan I and II was added and 180 g a.i. was added in the second year. The dissipation graphs (figures 3, 4, 5, 6) for these compounds

Figure 3. Endosulfan I concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i. of endosulfan I

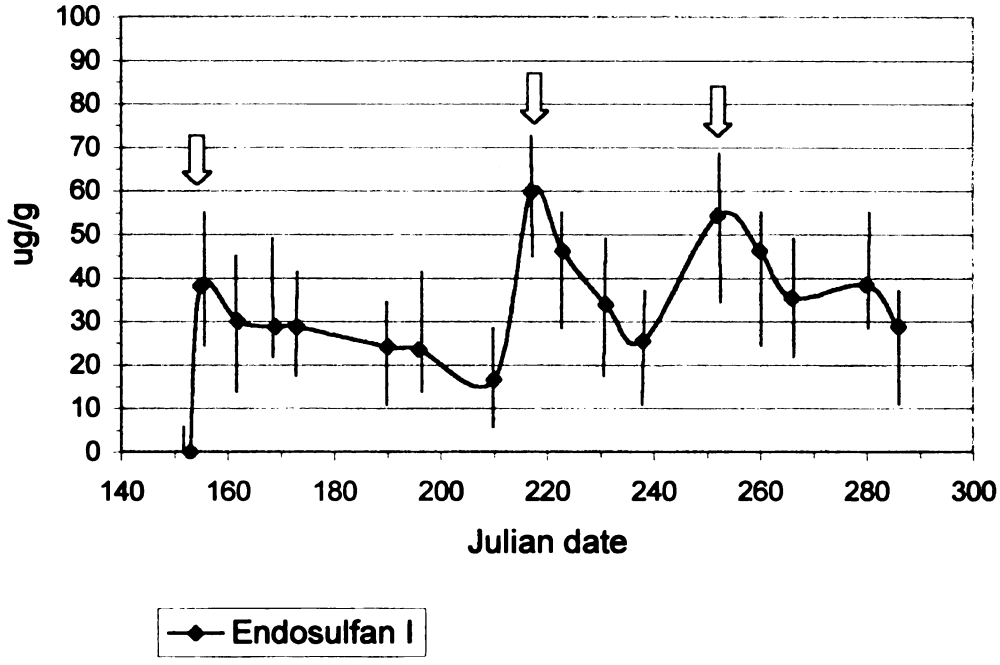


Figure 4. Endosulfan I concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of endosulfan II.

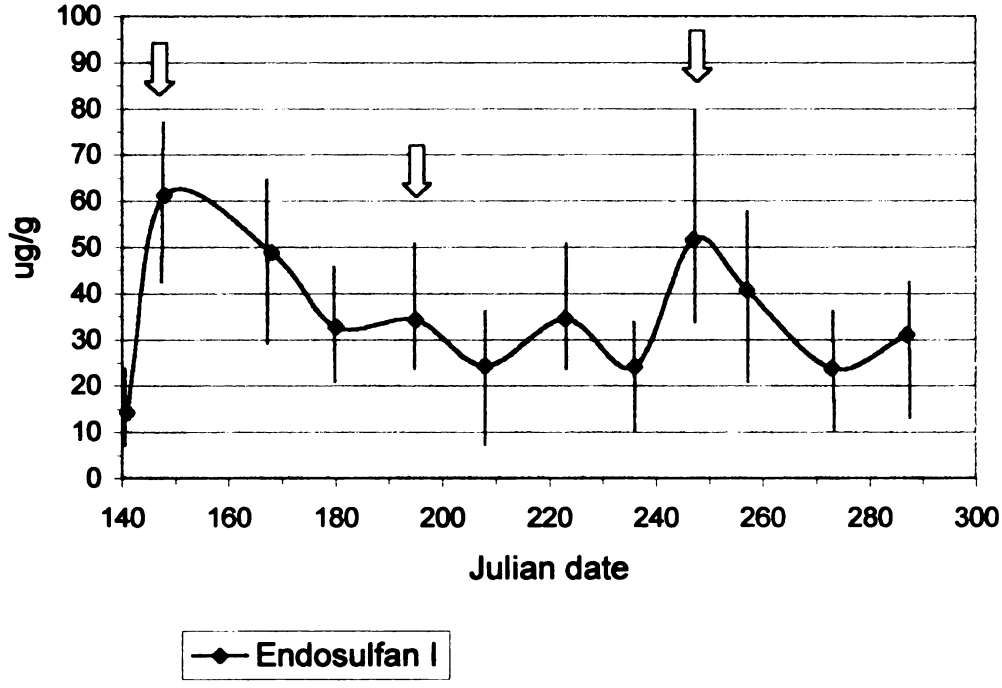


Figure 5. Endosulfan II concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i of endosulfan II.

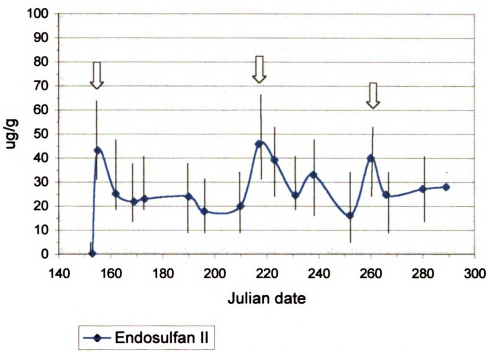
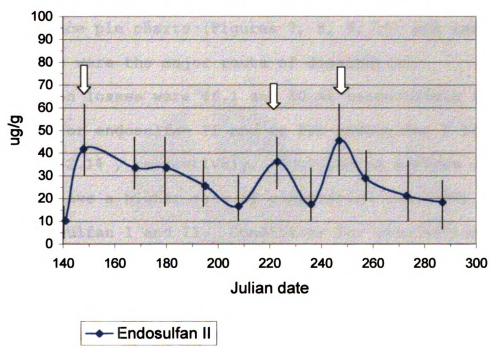


Figure 6. Endosulfan II concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of endosulfan II.



were similar as was expected because they are isomers. They each had three spikes as seen on the graphs representing the 3 soil applications.

At the end of the 1990 sampling period, endosulfan I had 57.6 g a.i. remaining, or 27.3% of the original soil concentration. Endosulfan II had 42.1 g a.i. as a residual or 20% of the initial concentration. In 1991, the concentration of endosulfan I at 47 g was at 17% of the first year's residual, and this value was 22.6% of the original soil concentration. As for endosulfan II, 38.1 g a.i. remained at the end of 1991, this was 9.3% lower than the prior year.

Since the endosulfans have high Henry's Law Constants, evaporation would be expected to be the prime mode of dissipation. The results of air sampling, as seen on the mass balance pie charts (Figures 7, 8, 9, 10) did indicate air losses were the major route of dissipation. Evaporation losses were 66.1 and 60.4% respectively in 1990 and 1991 for endosulfan II and as for endosulfan I it was 89.2 and 82.1% , respectively. Confounding matters was why did 1990 have a higher rate of evaporation than 1991 for both endosulfan I and II. Conditions for evaporation, as explained earlier, were more favorable for 1991 and so it should have had higher evaporative losses. It should be noted that endosulfan I in both 1990 and 1991 had average

Figure 7. Relative ratios for endosulfan I in 1990.
1=Residual Parent 2=Evaporative losses
3=Microbial/Chemical Degradation

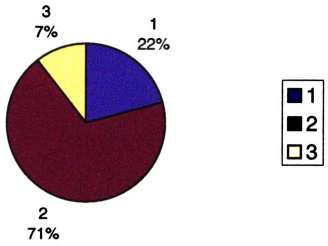
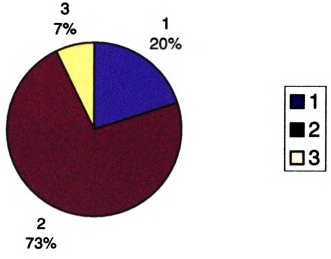


Figure 8. Relative ratios for endosulfan I in 1991.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation



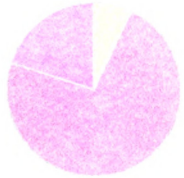


Figure 9. Relative ratios for endosulfan II in 1990.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation

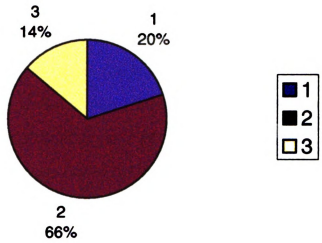
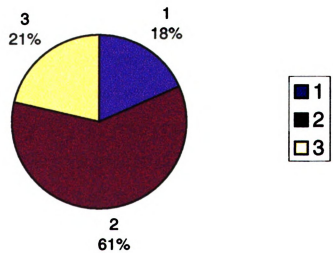


Figure 10. Relative ratios for endosulfan II in 1991.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation



mass balance percentages >100%, the results were 124.9% and 112.3%, respectively. These results suggested an overstatement of one of the components of the pie chart, probably the air sampling (due to once a week sampling).

The mass balance accounting for endosulfan II was not >100% in either year when air losses and residual parent were added together, unlike endosulfan II. The mass balance was determined for endosulfan II in 1990 by adding airborne losses (66.1%,calculated from PUF's); the residual balance of the parent pesticide, 20% (42.1 g in soil); and the maximum metabolite level achieve was 17.7 g or 8.4% of the total applied to the soil. The sum of this is 94.5%. Since the mineralization of the metabolite was not followed, one cannot state how much metabolite was formed over time, only the maximum. Due to not having a 100% accounting for of the parent compound, the balance to achieve 100% will be assumed to be due to chemical degradation or some other metabolite not monitored. In this case 5.5% would be attributed to chemical degradation/other metabolite formation.

The same problem occurred in the following year, 1991, residual parent was 18.3%; evaporation was 60.4%; and metabolite was 8.1%. To get 100%, 13.6% was added to the metabolite degradation for possible chemical degradation or some other metabolite formation. So, overall examination of endosulfan II evaporative losses for the mass balance show

that the second year was again lower than the first year. Based on the data at hand a plausible explanation may be that more frequent air monitoring may have presented better results.

The data on endosulfan sulfate applies to both endosulfan I and II, as it is the major degradation product for both compounds. The rate of mineralization of endosulfan sulfate was not monitored but it has been reported that it takes >20 weeks for 50% degradation of endosulfan sulfate (Howard, 1991).

The graph (Figure 11) for endosulfan sulfate, for 1990, shows many peaks which were not anticipated. But it showed an additive-stair step appearance, so the general trend was increasing throughout the sampling period. In 1991 (Figure 12), 3 peaks were observed for endosulfan sulfate as one would expect and the mean concentration was higher (4.3 ppm in soil) versus the 3.36 ppm observed in 1990.

Figure 11. Endosulfan sulfate (metabolite of both endosulfan I and II) concentration in CHES soils in 1990. Arrows indicate 70 g a.i. of endosulfan.

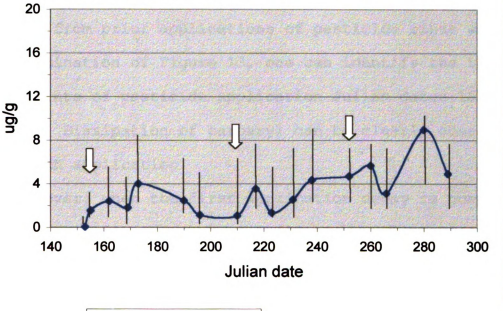
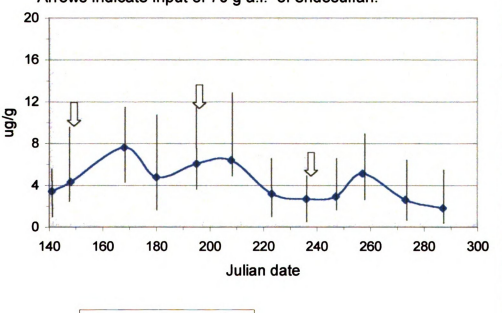


Figure 12. Endosulfan sulfate (the metabolite of endosulfan I and II) concentration in CHES soils in1991. Arrows indicate input of 70 g a.i. of endosulfan.



Carbaryl

On June 2, 1990, carbaryl (210 g a.i.) was applied to soils that were previously analyzed containing 0.23 ppm of carbaryl from prior applications of pesticide rinse waters. Upon examination of Figure 13, one can identify the three major points of pesticide application Julian dates 153, 217 and 252. Dissipation of carbaryl can be clearly observed after each application.

However, when the first application decay is compared to the decay after the second application (Figure 14), one can note that the first decay took nearly two weeks longer to go to a concentration below 10 ppm. One explanation for the more rapid loss in the second application is that prior applications enhanced the microbes that degrade carbaryl as proposed by Racke and Coats (1988) and others. The initial time lag seen with the first application of the pesticide but not observed in successive applications, is an indication that cometabolic processes are involved. This shows microbes require some time to adjust to utilize the compound. The slower dissipation seen with the third application of pesticides is because it is later in the year and this means lower soil/air temperatures and thus lower microbial degradation activity and evaporation is expected.

The graph (Figure 15.) of the metabolite, 1-napthol,has

Figure 13. Carbaryl concentration in CHES soils in 1990. Arrows indicate inputs of 70 g a.i. of carbaryl.

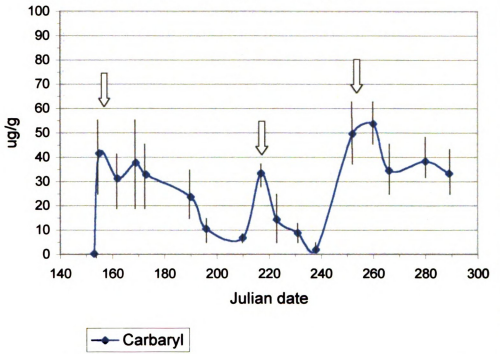


Figure 14. Carbaryl concentration in CHES soils in 1991. Arrows indicate inputs of 70 g a.i. of carbaryl.

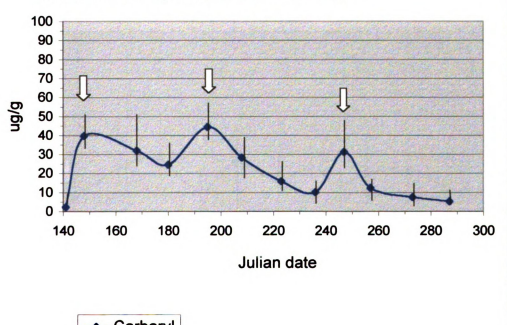


Figure 15. 1-napthol (carbaryl's metabolite) concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i. carbaryl.

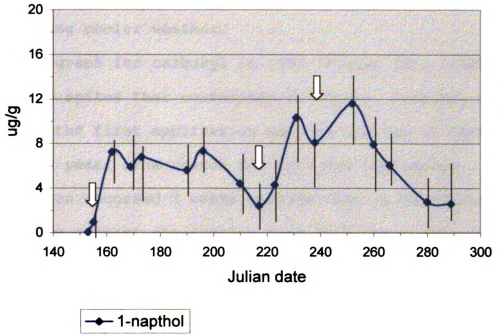
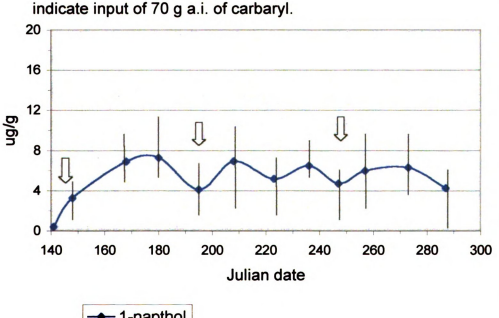


Figure 16. 1-napthol (carbaryl's metabolite) concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of carbaryl.



3 general peaks that generally correspond to the application periods of the parent. The lower concentration at the end of the graph is likely due to the development of the approaching cooler weather.

The graph for carbaryl in 1991 (Figure 16), likewise had three spikes that correspond to inputs, however, the decay of the first application was not similar to that of the prior year. The reason for this was the second application occurred 3 weeks earlier than in the second year. The general observation from both years data is that in 4 to 6 weeks post application, under the environmental conditions for these two years, the parent was found to be present at 10 ppm or less. Under these conditions the containment tanks appeared to function satisfactorily as vessels of containment and dissipation.

The graph for 1-napthol in 1991 (Figure 16), appeared to fluctuate at first as the sine wave appearance has 4 peaks and one would only expect 3 to correspond to the number of applications. It could be concluded that the peak at day 236 was unrepresentatively high because the parent carbaryl concentration was at a very low concentration. Another possible explanation is day 223 was erroneously low and microbial activity was still generally high at that time. It should also be noted that the second year does have fewer sample dates, and with more sampling one could

better determine what the microbial activity was at that time. Overall, the level of 1-napthol was at a generally higher level than in 1990 and less fluctuations.

The vapor pressure of carbaryl is 1.36×10^{-6} mm Hg, but the Henry's Law Constant (K_h) states it is 1.28×10^{-8} (Howard, 1991). This means the volatility of carbaryl is not expected to be as high as endosulfan I and II, which have a combined K_h value of 1×10^{-5}. The results of the air sampling in the first year showed 58.8 g evaporated, 28% of the applied (Figure 17). The second year was warmer, drier and more windy and 62.8 evaporated, an increase to 34%(Figure 18). The microbial/chemical degradation of carbaryl was determined by subtraction, as continuous monitoring of parent to mineralization was not possible. By adding the amount of parent material lost by evaporation to the residual amount of parent pesticide and subtracting it from the total amount in the original soil the balance remaining was attributable to the degradative processes.

In conclusion, 390 g a.i. of carbaryl was applied to vessel and only 10.4 g remained after 2 seasons. More degradation was noted in the second year, 60.8% vs. 39% in the first year. Evaporative losses were lower than microbial/chemical degradation in both seasons.

Figure 17. Relative ratios for carbaryl in 1990.
1=Residual Parent 2=Evaporative losses
3=Microbial/Chemical Degradation

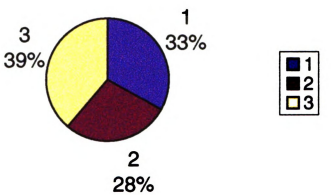
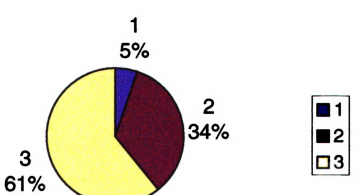


Figure 18. Relative ratios for carbaryl in 1991.
1=Residual Parent 2= Evaporative Losses
3=Microbial/Chemical Degradation



SIMAZINE

Simazine applications resulted in soil concentrations resembling a slowly rising scale as the applications appeared additive, no major dissipation was noted as in the case of carbaryl. But at the end of the sampling period in the first year the soil concentrations were still less than that of input, ~62% less, and at the beginning of the second year, it was seen that the concentration remaining was slightly less than 10% of the input (210 g AI.), see Figures 19 and 20.

In 1991, the graph (Figure 20) of simazine repeated the stair step additions of 1990. The input in 1991 was 180 g (85% of the first year) but its peak concentration was nearly 20% below that of the first year when standardized. For example, first year input = 210 g was the equivalent of 105 ppm in soil, the maximum concentration observed was 80 ppm in the first year so 80/105= ~76% versus 51/90=~57% for 1990.

Examination of the metabolite, hydroxy-simazine, see the graphs in Figures 21 and 22, illustrated a gradual rise in 1990, which could be mostly chemical degradation as it appeared to be a steady rise. But having a decline in metabolite at the end of both seasons indicated some substantial biological activity may have been present. Chemical hydrolysis is considered to be the major mode of

Figure 19. Simazine concentration in the CHES soils in 1990. Arrows indicate input of 70 g a.i. of simazine.

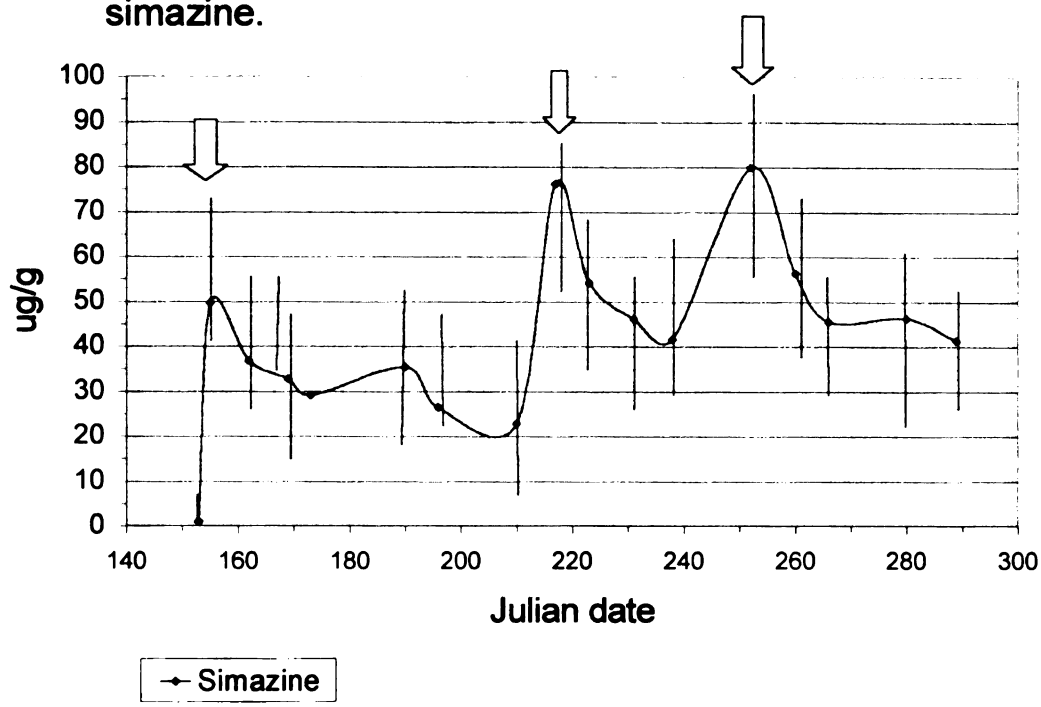


Figure 20. Simazine concentration in CHES soils in 1991. Arrows indicate 70 g a.i. of simazine.

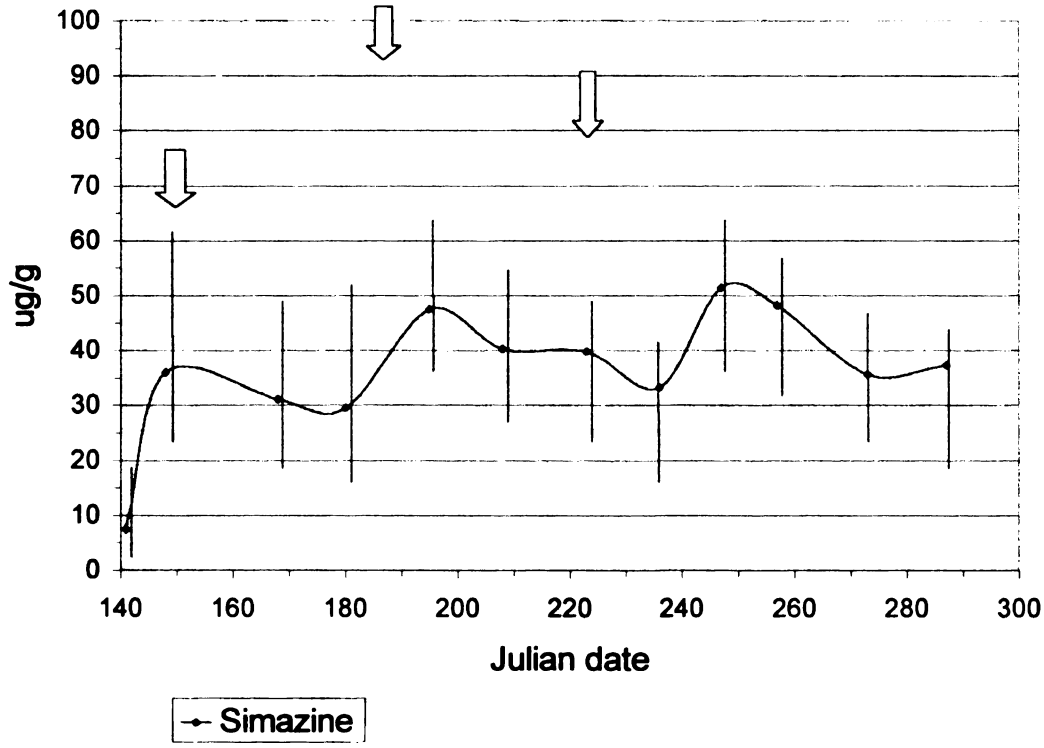


Figure 21. Hydroxy-Simazine (Simazine metabolite) concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i. of simazine.

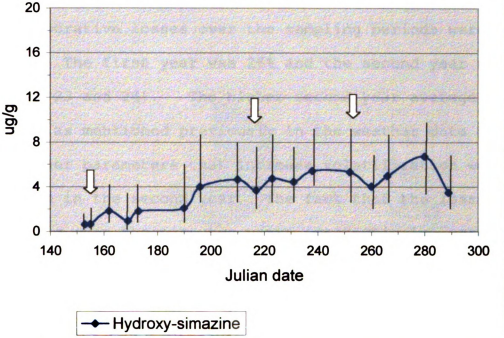
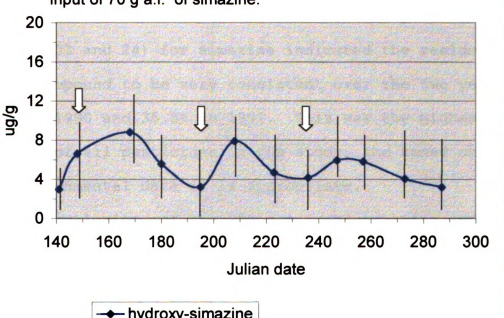


Figure 22. Hydroxy-Simazine (Simazine metabolite) concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of simazine.



detoxification of chloro-s-triazines, but soil microbes are noted to degrade the herbicides with varying degrees of activity (Kaufman and Kearney, 1970).

Evaporative losses over the sampling periods were very similar. The first year was 26% and the second year was 30% (Figures 23 and 24). The higher second year average was expected as mentioned previously in the weather data that all weather parameters that increase volatilization were increased in the second year. The fact that the loss of 54g and 56.1 g over the past two years, respectively, were even lower than carbaryl, is that the K_h (Henry's Law Constant) was even lower than carbaryl's. The K_h of simazine is 4.62 x 10^{-10} and its vapor pressure is 6.1 x 10^{-10} mm Hg. Since simazine is not very water soluble, 2 ppm (Dubach, 1970) and the K_h is likewise low, low volatility is expected.

Further examination of the mass balance pie charts (Figures 23 and 24) for simazine indicated the residual parent compound to be very consistent over the two years, 41.3% in 1990 and 35.8% in 1991. This was the highest residual of all pesticides in the study, and based on all of the environmental data it is appropriate.

In conclusion, of the 390 g a.i. of simazine applied to each tank over the two years, an average of 71.4 g remained, or 18%.

Figure 23. Relative ratios for simazine in 1990.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation

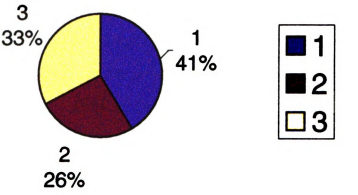
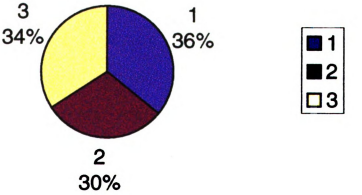


Figure 24. Relative ratios for simazine in1991.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation



Alachlor

Graphs of alachlor's dissipation over the two year period resembled that of carbaryl, (Figures 25 and 26). Both years distinctly show rapid pesticide dissipation. The amount of a.i. remaining in 1990 was 31.9 g or ~15.1% of the original. At the end of year 1991, 27.9 g remained or ~15% remained, even with lower input. Based upon the information in the literature review, no unexpected results occurred in evaluating the parent concentrations in the soil.

Alachlor's primary metabolite in this study, 2,6-DEA, had widely varying concentrations in 1990 (Figure 27) attributable to both sampling variation and initial induction of microbial enzymes. There was the general trend of increasing concentration throughout the 1990 sampling period. However, the highest concentration of metabolite occurred just prior to the last application date Sep 5, Julian date 247 (Figure 28). This is unexpected and may be the result of sampling variation. But, there was a trend of increasing concentrations of 2,6-DEA up to this point and the concentration of the parent was still approximately 15 ppm. It has been reported that alachlor is expected to be degraded three times more quickly by microbes than by chemical means, and alachlor is degraded 50 times more slowly in sterile soils than non-sterile (Beetsman and

Figure 25. Alachlor concentration in CHES soils in 1990.
Arrows indicate input of 70 g a.i of alachlor.

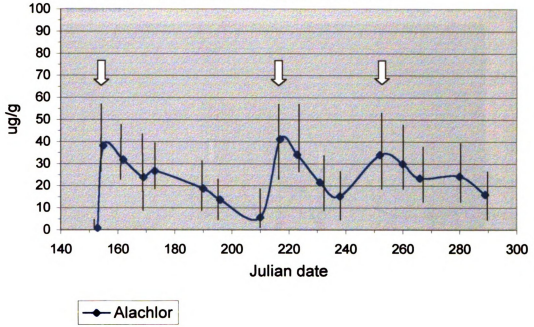


Figure 26. Alachlor concentration in CHES soils in1991.
Arrows indicate input of 70 g a.i. of alachlor.

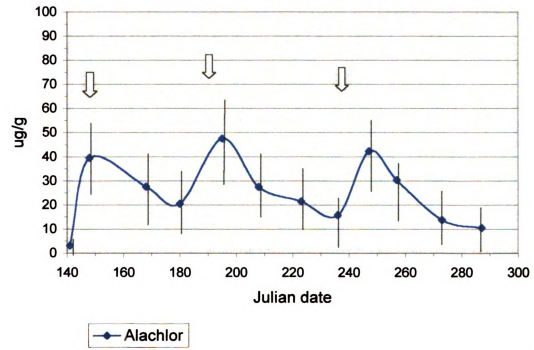


Figure 27. 2,6-DEA(alachlor metabolite) concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i. of alachlor.

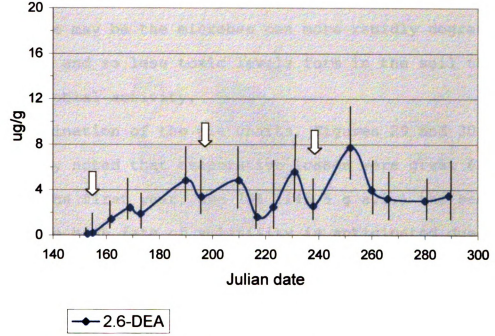
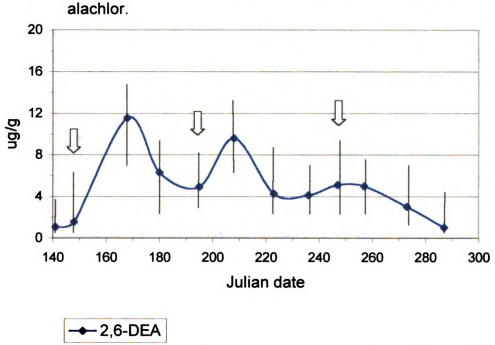


Figure 28. 2,6-DEA(alachlor metabolite) concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of alachlor.



Deming, 1974). In the second year there are 3 inflection points that correspond to the 3 applications of the parent. The reason for less variation in the second year of the metabolite may be the microbes can more rapidly degrade the compounds and so less toxic levels form in the soil that slow microbial activity.

Examination of the pie charts, Figures 29 and 30, it is distinctly noted that evaporative losses were great 62% (130 g a.i.) the first year, and 78% (145.5 g a.i.) the second year. The high rate of volatility is anticipated due to the relatively high $K_h = 1.3 \times 10^{-6}$ and a vapor pressure of 2.2×10^{-5} mm Hg. Based on the results of air losses and the residual parent compound in the soil, the amount of microbial/chemical degradation was assumed to account for the remainder of the active ingredient.

Figure 29. Relative ratios for alachlor in 1990.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation

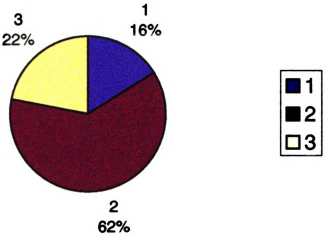
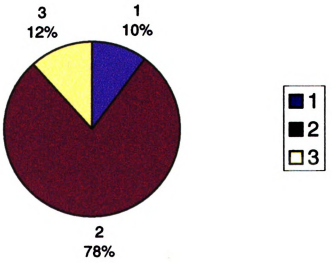


Figure 30. Relative ratios for alachlor in 1991.
1=Residual Parent 2= Evaporative Losses
3=Microbial/Chemical Degradation



Chlorpyrifos

The graph for the first year of chlorpyrifos (Figure 31) showed an incremental build up of chlorpyrifos. Three distinct inputs of the parent are evident and dissipation was observed. At the end of 1990, 23.2 ppm (46.2 g) was found in the soil, or 21.8% of the original amount was still present. This can be compared to 36.1 g remaining at the end of the second season (Figure 32), which was 19.3 % of what was placed on the soil in the second year. The overall reduction over the two years was 90.8%.

The major metabolite, 3,5,6-TCP, is present soon after the initial application of the parent. The metabolite concentration increases throughout the summer and then tapers off at the end of the year (Figure 33). The initial high presence of the metabolite may have been the beginning of a quick microbial breakdown of the initial application, Julian date 169 did not fit expectations and was due to sampling variation and was too low in this circumstance. The slow rise over the next two applications may have occurred because it is known that 3,5,6-TCP has bioactive properties against several fungi which aid in the breakdown of the parent (Felsot and Pedersen, 1991). Thus, the second and third applications may have created a toxic condition that later resolved. As for the slowing down at the end of

Figure 31. Chlorpyrifos concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i. of chlorpyrifos.

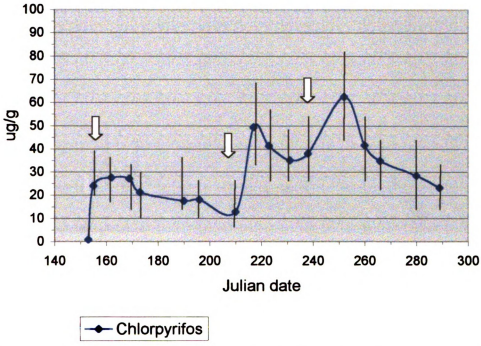


Figure 31. Chlorpyrifos concentration in CHES soils in 1991. Arrows indicate input of 60 g a.i. of chlorpyrifos.

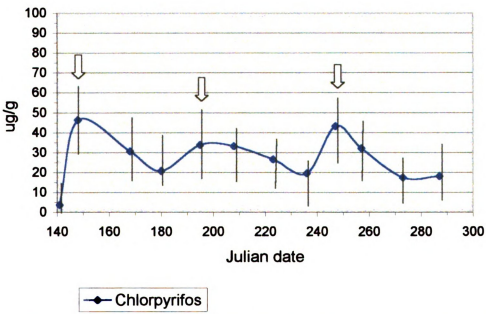


Figure 33. 3,5,6-TCP (Chlorpyrifos metabolite) concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i. of chlorpyrifos.

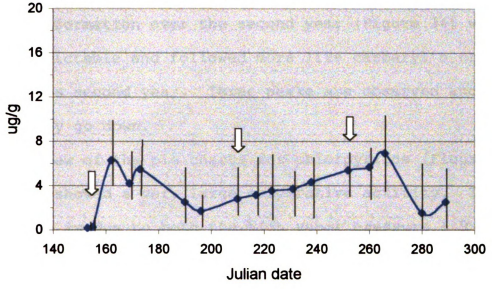
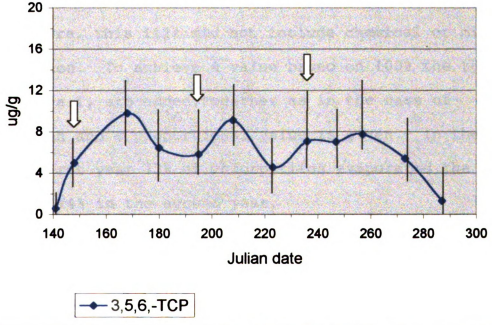


Figure 34. 3,5,6-TCP (Chlorpyrifos metabolite) concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of chlorpyrifos.



the year, it is likely due to the development of colder weather slowing down microbial activity and less substrate (lower concentration of parent compound).

TCP formation over the second year (Figure 34) was much more predictable and followed more like carbaryl's or alachlor's second year. Three peaks are observed and found to rapidly go down.

Review of the pie charts for chlorpyrifos (Figures 35 and 36), showed a very large evaporative activity. This condition is due to both the high vapor pressure 1.9×10^{-5} mm Hg and a $K_h = 7.8 \times 10^{-5}$. At the end of 1990, ~172 g a.i. of chlorpyrifos may have been lost through airborne processes. This was a potential reduction of 81.9%. The word potential was used because based on air losses and the residual amount of parent in the soil, in combination with a high of 6.9% 3,5,6-TCP present this adds up to 112%. Furthermore, this 112% did not include chemical or microbial degradation. To achieve a value based on 100% the total grams of a.i. are added together as in the case of endosulfan and a proportional value is given. In the case of the first year 73% of chlorpyrifos evaporated the first year and 74% in the second year.

Figure 35. Relatvie ratios for chlorpyrifos in 1990.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation

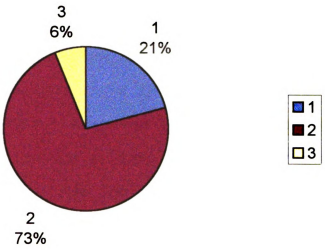
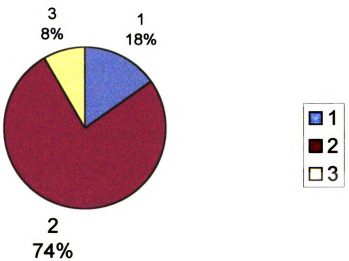


Figure 36. Relative ratios for chlorpyrifos in 1991.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation



Captan

The graphs for captan concentrations in CHES soils for 1990 and 1991 are very much alike over both years (Figures 37 and 38). Captan in these soils degraded rapidly and approached the detection limit in all but the first application in 1991. Captan is degraded primarily by chemical hydrolysis and little is degraded by microbial action (Howard, 1991). A reason for its lack of breakdown for the first application in 1991 may be that the soil pH was lower than other times and was not favorable for hydrolysis. There were sufficient applications of pesticide rinse water over this period of time so the lack of water did not reduce hydrolysis. Studies have shown wettable powder formulations for captan have appeared more stable than other formulations (Howard, 1991), and that is what was used in this study. But, it was used in all applications so that does not explain the slower degradaition rate. Sampling variability is a likely possibility, as the coefficient of variation was 55%.

The amount of captan which remained at the end of year one was7.6 g a.i., or 3.6% of the applied amount (Figure 39). The second sampling period had 8.2 g a.i. of captan at the end of the season and this represents 4.5% of the captan input over the second sampling period (Figure 40).

Figure 37. Captan concentration in CHES soils in 1990. Arrows indicate input of 70 g a.i. of captan.

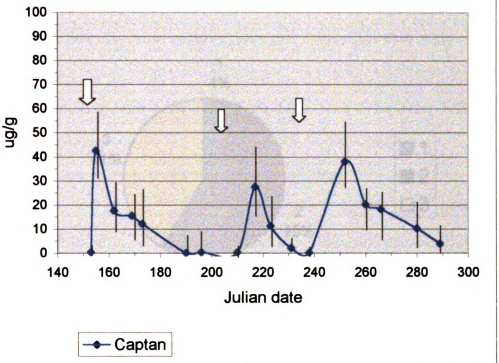


Figure 38. Captan concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of captan

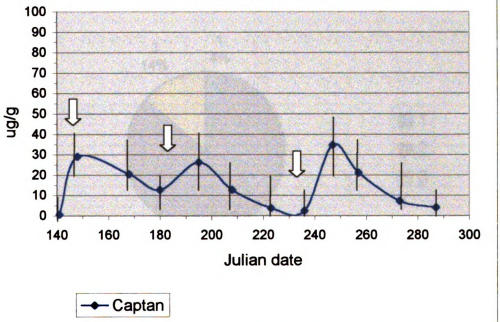


Figure 39. Relative ratios for captan in 1990.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation

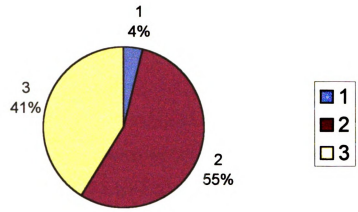
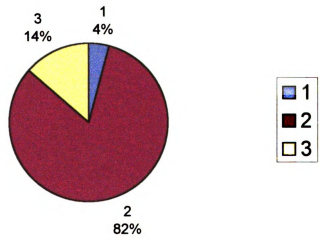


Figure 40. Relative ratios for captan in 1991.
1=Residual Parent 2=Evaporative Losses
3=Microbial/Chemical Degradation



Phthalimide, the primary metabolite in this study, was observed to have three peaks in 1990 and two in 1991. Since degradation of captan is primarily a chemical process, a gradual rise in the appearance of phthalimide was anticipated. The dip occurring at day 200 through 220 musst be the result of a change in the soil conditions, negatively affecting chemical and/or microbial hydrolysis.

From the pie charts (Figures 39 and 40), nearly the same amount of parent remained at the end of both seasons, 7.6 g and 8.2 g a.i., respectively. The modes of their disappearance were different, in 1990, the chemical degradation (41.2%) was similar to the rate of evaporation. But, 1991 had an increase in airborne loss as it increased to 82.2%, a nearly 29% gain. This was an increase from 115.9 g of a.i. lost to the air to ~150 g becoming airborne, or a 29% increase. As in all previous cases, the containment vessels were able to dissipate the pesticides when applied at the following rates of ~105 ppm the first year and ~90 ppm the second.

Figure 41. Phthalimide (captan metabolite) concentration in CHES soils in 1990. Arrows indicate 70 g a.i of captan.

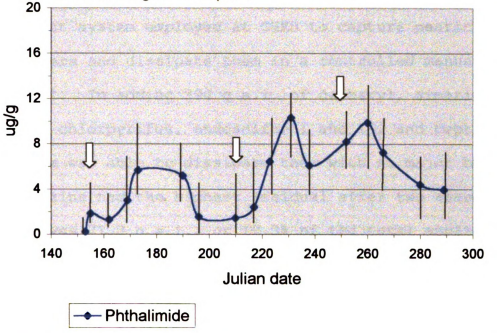
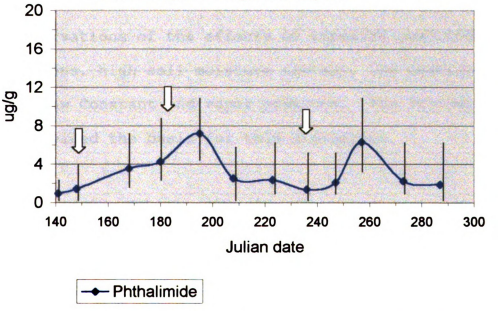


Figure 42. Phthalimide (captan metabolite) concentration in CHES soils in 1991. Arrows indicate input of 70 g a.i. of captan.



CONCLUSION AND SUMMARY

Based on the results of this study over 2 seasons, the containment system employed at CHES to capture pesticide waste waters and dissipate them in a controlled manner, was successful. In adding 390 g a.i. of carbaryl, simazine, alachlor, chlorpyrifos, endosulfan I and II, and captan, the system was able to dissipate them with no major build up. Simazine had the highest residual after two seasons and this was 71.3 g a.i., or 18.3% of the total applied.

From a graph of a concentration of parent pesticide in a soil, a linear regression can be performed on the slope to determine the half-life ($t_{1/2}$) of the pesticide. In this study six total applications were performed thus six half-lives can be determined. The resultant half-lives will be compared to a published average half-life value and one can make observations of the effects of repeated pesticide applications, high soil moisture content, the pesticides' Henry's Law Constant and vapor pressure. The following table provided the basis for this discussion.

Table 10. Comparison of the effects of Henry's Law Constant and vapor pressure on the evaporative losses and half-lives ($t_{1/2}$) of selected pesticides over a two year period.

Pesticide		predicted $t_{1/2}$ (days)	actual $t_{1/2}$ (days) 3 applications 1	2	3	Henry's Law Constant	Vapor Pressure (mm Hg)	Evap Loss (%)
carbaryl								
	year 1	10	32	12	26	1.28×10^{-8}	1.36×10^{-6}	28
	2	--	35	17	10	-------	-------	34
simazine								
	year 1	60	55	31	49	4.62×10^{-10}	6.10×10^{-9}	26
	2	--	50	44	38	-------	------	30
alachlor								
	year 1	15	22	13	25	1.30×10^{-6}	2.20×10^{-5}	62
	2	--	24	18	17	-------	-------	78
chlorpyrifos								
	year 1	30	46	27	34	7.80×10^{-5}	1.90×10^{-5}	73
	2	--	28	34	22	-------	-------	74
endosulfan I								
	year 1	50	42	37	40	1.12×10^{-5}	1.00×10^{-5}	71
	2	--	40	33	33	-------	-------	73
endosulfan II								
	year 1	50	44	41	38	1.12×10^{-5}	1.00×10^{-5}	66
	2	--	47	34	36	-------	-------	61
captan								
	year 1	3	11	7	10	5.90×10^{-6}	7.50×10^{-6}	55
	2	-	20	10	13	-------	-------	82

The most apparent observation from the table is that all half-lives were generally greater than the published values (Wauchope *et al.*, 1992). The three compounds with lower half-life values than their predicted values were simazine 60(days) and endosulfan I,II (50 days), the three longest half-lives. In review of the actual half-lives, the sequence did basically follow the predicted order being captan, carbaryl, alachlor, chlorpyrifos, endosulfan I,II and simazine.

The half-life values are closely related to volatility and microbial/chemical degradation. The increased volatility seen in the second year is explained when Table 8 is reviewed. The increased wind speeds, warmer temperature, lower humidity and doubled rate of pan evaporation all would predict higher evaporation.

Higher air temperatures would indicate warmer soil temperatures and this would especially be reflected with the research vessels being above ground. Table 9 shows the second year of the study was warmer by 3°C on average and also had the higher maximum temperature by 5°C. This tranlates into an environment which is more conducive for microbial activity.

Microbial activity is important in the degradation of

simazine, alachlor and chlorpyrifos. Microbial degradation of carbaryl can also be important if chemical hydrolysis conditions of high alkalinity and soil moisture are not met.

In reviewing the metabolites for these compounds the general appearance for the first year is a gradual climb in concentration and a lowering at the end of each season. It would appear that it takes time to induce the enzymes in the soil microbes at the beginning of each summer. Then at the end of the season the effect of lower soil temperatures and less parent compound available to degrade lowers the metabolite concentration.

The highest concentration of metabolite occurs in the middle and latter part of the year when the soil temperatures are warmer and probably the microbial enzymes are more active (enzyme activity not monitored). The combination of high microbial activity, because of repeated exposure and warmer mid summer temperatures, and increased volatility, also due to higher temperatures, cause the half-lives to be the lowest of the year in 9 of 14 instances.

Metabolite concentrations were higher with additional applications of pesticides and in the second season, metabolite production increased sooner which might indicate increased microbial activity. Therefore based on this observation it would seem likely that a third year would

observation it would seem likely that a third year would show higher microbial activity sooner as seen in higher metabolite concentrations occurring sooner. Over time one would expect that the microbial population would be optimized to degrade the compounds that are frequently input into the disposal system.

The compound with the highest soil residual, simazine, was the compound with the lowest Henry's Law Constant (HLC) and the longest half-life. Therefore, simazine has low volatility and low microbial/chemical activity. The compound with the second lowest HLC (carbaryl) had the next to the lowest evaporative loss as would be expected. But carbaryl did have the second lowest soil residual. The reason for it degrading so quickly was that it readily under goes chemical and microbial hydrolysis.

A second issue that needed to be addressed was the high volumes of water collected. Again, the system was able to handle >4800 gallons the first season and over 5000 in the second. Especially when the evaporative fans were operated, approximately 6 to 7 hours a day, 5 days a week.

There are future problems that could arise, such as how long can such a system effectively work? Also are there pesticides or combinations of pesticides and/or metabolites that could harm any beneficial bacteria in the system and

shorten or halt degradation; and would it be necessary to devise separate tanks for herbicides, insecticides and fungicides?

In some circumstances the most volatile compounds may achieve levels in the air that are above the recommended airborne limits. This may especially occur with alachlor, chlorpyrifos, endosulfan I,II, and captan which all had evaporative losses >50%, and captan had an evaporative loss of 82% in the second year. But, under normal farming conditions the concentrations of the pesticides used would be much lower than the elevated levels used in this study.

Another concern is that a disposal system would be time consuming and involve a start up cost which most farmers would not institute unless required.

PART II:LABORATORY INVESTIGATIONS IN THE USE OF SUPERBUGS[R] TO ENHANCEN PESTICIDE DEGRADATION IN A SOIL SYSTEM

RESULTS AND DISCUSSION

The purpose of the Superbugs[R] study was to examine the claims of Chemical Specialities Intl. of Cameron Park, CA, that its product called Superbugs[R] would return the environment back to nature in 60 days, with a current success rate of 100%. It was said to be a safe, economical way to dispose of hazardous wastes in loading and spill areas, as well as ponds and ditches with no odors or noxious gases. Superbugs[R] is a proprietary mixture of bacteria, enzymes, and microbial nutrients stated to degrade insecticides, fungicides, herbicides or petroleum products (waste oil, diesel fuel, gasoline, or solvents).

Alachlor

The ANOVA results for the study of alachlor indicated that their was no significant treatment difference between the sterile soil (SS) alone versus the other three soils; sterile soil with Superbugs[R] (SS+SB); soil (S), and soil with Superbugs[R] (S+SB) at the 0.05 level. The coefficient of variation was 37%, this high variability was expected, based on previous experience of analyses from similar types

of extractions performed at CHES. The variability in sampling may also be observed from figure 43, rather than finding continual dissipation of the compounds one occassionaly finds higher concentrations at later sample dates.

The $t_{1/2}$ (half -life) for the SS group, by linear regression, was 39 days (Figure 44), and from the data available the expected value was ~10-14 days for non-sterile soils. Thus, the greater half-life was expected, but some accounts, as will be discussed shortly stated very little degradation would occur in sterile soils for 60 days. So the $t_{1/2}$ was lower than anticipated, yet half-lives are quite variable as seen by large variations in published material.

Felsot and Dzantor (1990) showed that alachlor was stable for at least 28 days at 1,000 mg/kg, at 100 mg/kg alachlor had degraded by 24% in 28 days and concentrations at 10 mg/kg had degraded by 75% in the same period. In 1995, Felsot and Dzantor amended soils with cornmeal and noted that the alachlor at 10 mg/kg degraded by 99% after 14 days and 54% of the 1000 mg/kg alachlor had dissipated. In the unamended soils, 49% of the 10 mg/kg alachlor soil degraded after 21 days, whereas in the 250-1000 mg/kg concentrations nominal degradation occurred. Organic amendments were used because alachlor was observed to be

Figure 43. Superbugs study with alachlor at 1/3 bar field moisture capacity and 21° C, under 4 diffferent soil conditions.

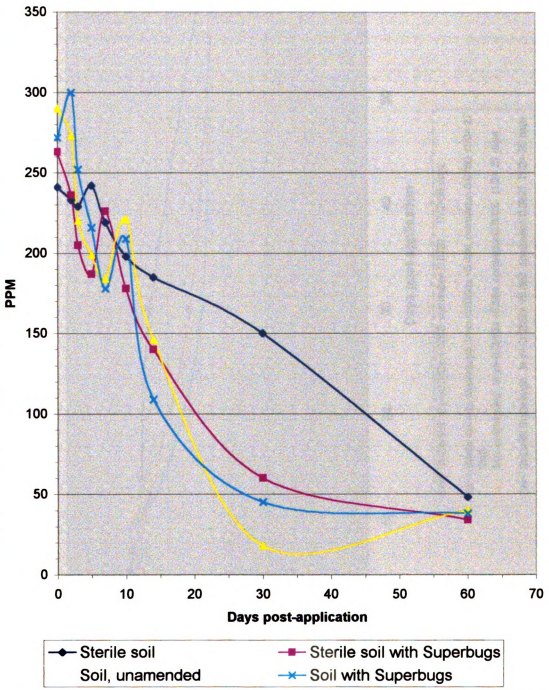
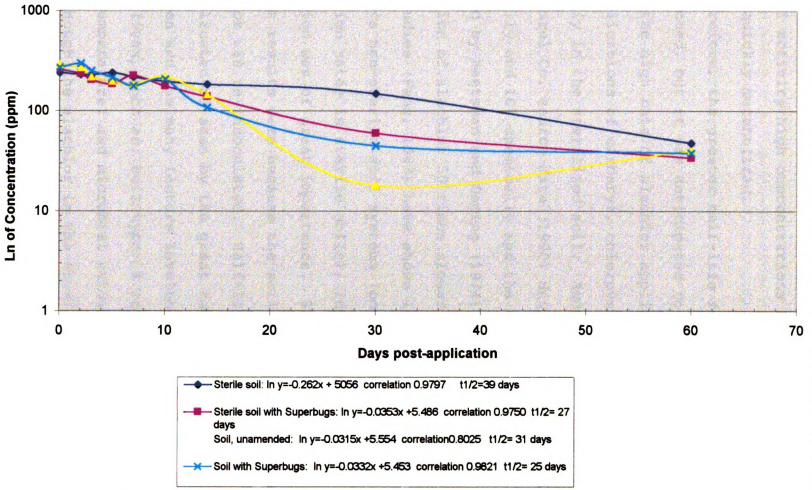


Figure 44. Superbugs study with linear regressions of alachlor at 1/3 bar field moisture capacity and 21°C and 4 different soil conditions.



cometabolized in the soil, so by generally increasing microbial activity high concentrations of alachlor may also be more quickly metabolized.

Therefore, the greater half-life for the sterile soil was expected, but it was anticipated to be much greater due to both the high rate of alachlor application in conjuction with applications of carbaryl, chlorpyrifos and captan; and especially in the sterilized soil. According to Monsanto^{R} Agricultural Co. source data (1990) degradation occurs 90% microbially and 10% chemically and the Monsanto^{R} data is confirmed by Beetsman and Deming (1974), who found degradation of alachlor 50 times slower in steriled soil. Other studies (Fang, 1983) have shown less difference in sterile vs non-sterile soil systems (only 10-15% lower degradation rates in sterile soils), indicating chemical degradation was of great importance. Some believe the different results were because the soil was not completely sterile or was re-innoculated. Half-life determinations are complicated as seen by the great range of published half-lives and the many factors involved in the estimation of half lives, such as: soil type; % soil organic matter; % water; temperature; and microbial cultures/ activity.

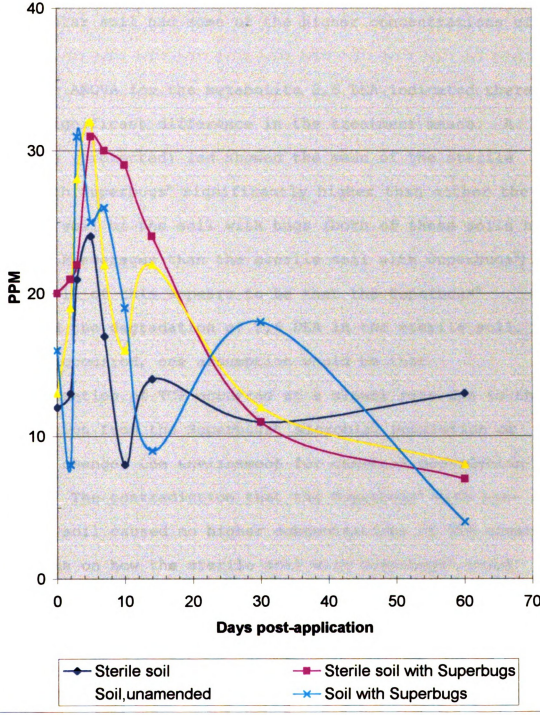
Although the alachlor in the sterile soil was not significantly different from the other soils (alpha=0.05),

it was generally higher than the other three soils (Figure 43). The fact that it was supposed to be sterile and had no rapid degradation would indicate that alachlor can be sufficiently degraded by chemical means in combination with volatilization. The other possibility could be that it was not completely sterile and microbial activity occurred slowly initially and increased over the study. Figure 44 shows the linear regression of the treatments and the natural log of the concentration to be relatively linear.

The graphs of alachlor (Figure 43) for the various soils would confirm the suspicion there was no difference between the treatments since they appeared so similar. The sterile soil was more linear than those of the other three soils but was not statistically different (alpha =0.05).

The formation of the metabolite, 2,6-diethylamine (2,6 DEA) in figure 45 was rapidly seen at the start of the first week with the sterile soil showing the lower rate of conversion. Although some general random spikes are evident the trend was that the formation of 2,6 DEA in all the soils were similar. The high intial presence of 2,6 DEA may be present due to application of older formulations being applied that were degrading prior to application. The large variability of 2,6, DEA in the soil is seen on the graphs, but generally show a crescendo by day

Figure 45. Superbugs study of 2,6 diethylaniline, at 1/3 bar field moisture capacity and 21° C, under 4 different soil conditions.



7 and fall of to a level concentration after 30 days. The high appearance of 2,6-DEA at day 0 does correspond to the degradation of its parent. Generally noted is that the metabolite was the lowest overall in the sterile soil and the regular soil had some of the higher concentrations of 2,6 DEA.

The ANOVA for the metabolite 2,6 DEA indicated there was a significant difference in the treatment means. A Fisher's (protected) lsd showed the mean of the sterile soil with Superbugs^R significantly higher than either the sterile soil or the soil with bugs (both of these soils had lower TCP averages than the sterile soil with Superbugs^R). The result of this appears to be that the Superbugs^R retarded the degradation of 2,6 DEA in the sterile soil. If this occurred, one assumption would be that mineralization of TCP occurred at a slower rate due to the competition from the Superbugs^R microbial population or else it changed the environment for chemical degradation to occur. The contradiction that the Superbugs^R with non-sterile soil caused no higher concentrations of TCP creates a dilemma on how the sterile soil with Superbugs^R could cause the difference. The coefficient of variation for 2,6-DEA was 35%, again one sees a large variation.

Chlorpyrifos

The results of the ANOVA for chlorpyrifos in the soils showed no significant difference between treatment means (the four different soil conditions, at the 0.05 level). The coefficient of variation was 45%, again this was high as it was in the case of alachlor due to a large variation in sampling. Literature has indicated that chlorpyrifos was less likely dependent on microbial degradation than alachlor (Racke, 1993) and this may explain the similar curves seen in the sterile as well as the regular and Superbugs amended soil treatments in figure 46. Another explanation for the sterile soil having degraded alachlor at a faster rate than anticipated would be again the soil was not totally sterile or was re-innoculated at some point. The graphs (Figure 46) have shown the regular soil to generally have the lowest chlorpyrifos concentration after 60 days and the sterile soil was somewhat higher on average versus the other three soils.

The half-lives (Figure 47) under the various soil conditions were as follows: 36 days for sterile soil; 30 days for sterile soil with Superbugs^{R}; the non-sterile or unamended soil was 8 days; and the half-life for the soil with Superbugs^{R} was 28 days. These results compare to an

Figure 46. Superbugs study with chlorpyrifos at 1/3 bar field moisture capacity and 21° C, under 4 different soil conditions.

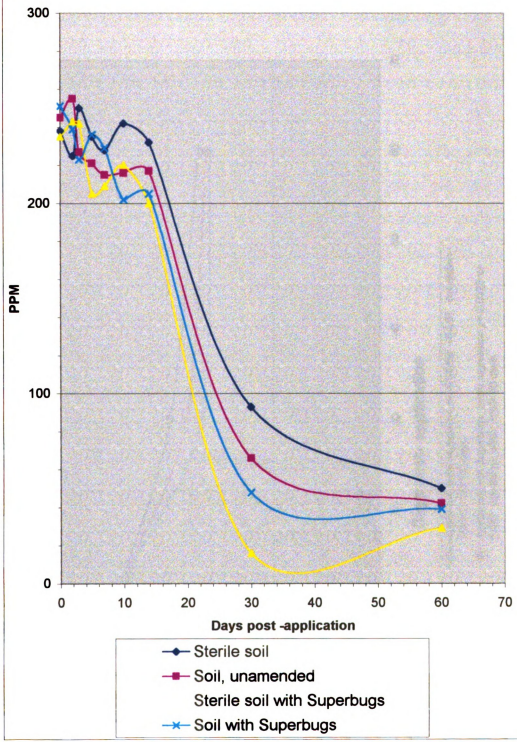
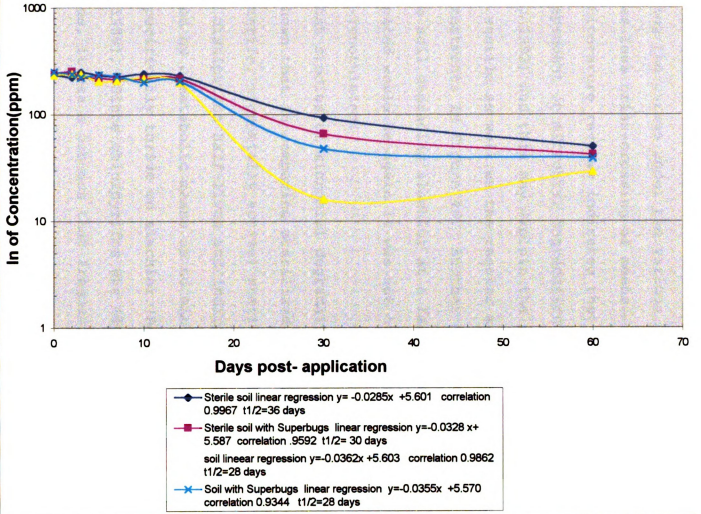


Figure 47. Superbugs study with chlorpyrifos at 1/3 bar field moisture capacity and 21°C, under 4 different soil conditions.



expected half-life of 30 days, thus little difference was noted in the rate of dissipation which would indicate that under the conditions of this study chemical degradation was likely very important. The graphs for chlorpyrifos were much less erratic than those of alachlor, in that by following the curves under the various soil conditions one observes less criss-crossing of means.

Literature reviews indicated that chlorpyrifos is less dependent on microbial degradation than alachlor (Racke, 1993) and this may explain the similar curves seen in the sterile as well as the regular and Superbugs amended soil treatments in Figure 46. Another explanation for the sterile soil degrading alachlor at a faster rate than anticipated would be again it was not totally sterile or was re-innoculated.

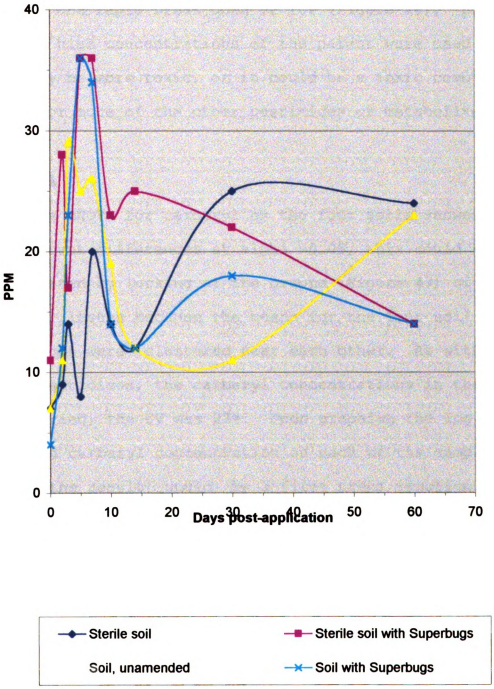
Most studies of microbial degradation of chlorpyrifos have shown that in comparing sterilized vs natural soils (non-sterile, microbially active) sterile soils had much longer dissipation half-lives and indicated alachlor was degraded by cometabolic means as no microbes were isolated that specifically thrive on alachlor (Racke and Coats,1988). Since chlorpyrifos was metabolized slowly by microbes, it was a concern that frequent pesticide applications may result in accumulation (Pozo et al, 1995).

Results from Pozo et al (1995) found that concentrations up to 10 ppm in soil enhanced overall bacterial populations and did not affect fungal microflora. However, N_2-fixing bacteria were reduced at concentrations applied at 10 ppm. Based on the results of this study (Figure 46), it appeared that there was a short period of inhibition to dissipation, with a substantial loss of chlorpyrifos between days 14 and 30.

The ANOVA for TCP indicated significant differences in treatment means of the four soils at alpha= 0.05. According to Fisher's (protected) LSD, the sterile soil with Superbugs^R again was significantly different from another soil, the sterile soil, which had the lowest average TCP concentration. With this repeated occurrence, Superbugs^R alone may preferentially increase the degradation transformation of chlorpyrifos to TCP, but inhibits TCP's mineralization. The coefficient of variation was 27%.

Unlike chlorpyrifos, the 3,5,6-trichloro-2-pyridinol (TCP) metabolite has been found to be readily degraded and mineralized by soil microorganism (Racke et al., 1988). It was reported that 65-85% of the TCP applied (5ppm) to several soils was mineralized within 14 days. In a follow up study Racke and Robbins (1991) tested 25 soils for

Figure 48. Superbugs study of 3,5,6-Trichloro-pyridinol (chlorpyrifos' metaboliite) at 1/3 bar field moisture capacity and 21° C, under 4 different soil conditions.



microbes that could degrade TCP and only 2 of the 25 exhibited significant degradation within 21 days. The results obtained from the soils used with Superbugs^{R} did not exhibit the rapid break down of TCP (Figure 48), possibly because high concentrations of the parent were used and this may be more toxic, or it could be a toxic combination of one or more of the other pesticides or metabolites.

Carbaryl

The ANOVA for carbaryl on the four soils showed no significant differences at alpha =0.05, this could have been stated by looking at the graphs (Figure 49) of carbaryl losses because the means for the four soil conditions were clustered near each other. As with the prior pesticides, the carbaryl concentrations in the soils were varied, the CV was 27%. Upon graphing the log of the averaged carbaryl concentration on each of the sampling dates, the result would be a first order reaction. The observed half-lives of carbaryl were in a range of 8 to 13 days (Figure 50), which followed the expected half-life of approximately 7 days when applied at recommended rates. Since this was a high concentration and there was little difference from the expected norm in the sterile soil without Superbugs^{R}, it is likely degradation took place

Figure 49. Superbugs study with carbaryl at 1/3 bar field mositure content and 21° C, under 4 different soil conditions.

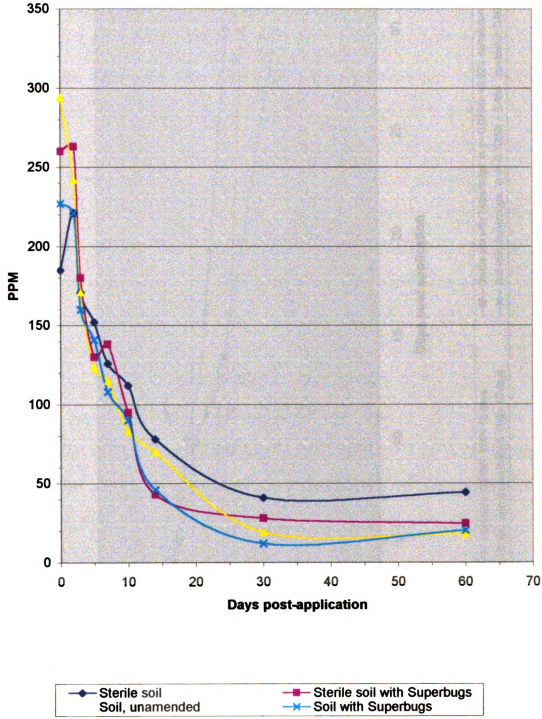
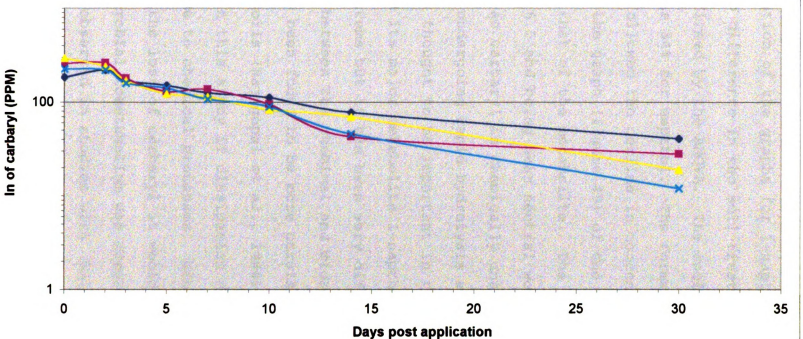


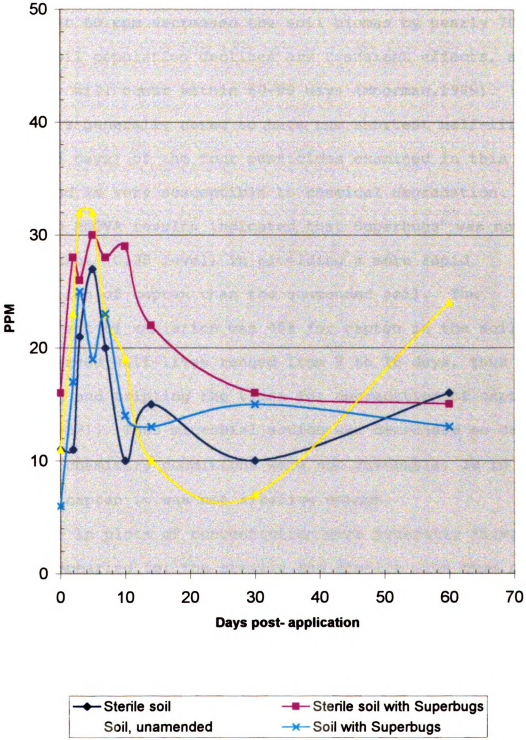
Figure 50. Superbugs study with linear regression of carbaryl at 1/3 bar field mositure capactiy and 21°C , under 4 different soil conditions.



primarily by chemical and/or volatilization processes.

Examination of the graphs for 1-napthol (Figure 51), suggested no difference in the soil treatment means and this is confirmed by the ANOVA. The coefficient of variation was 34% for napthol. The formation of the metabolite followed the decline in concentration of the parent when the graph (figure 49) of the parent are compared to that of the metabolite. The soil for the study had a pH =~ 6.5 and being near neutral would promote degradation as carbaryl is chemically unstable in alkaline conditions, undergoing rapid hydrolysis at pH > 7.0. Microbes are thought to be important in the degradation of carbaryl and its major metabolite 1-napthol in soil and water ecosystems but it has been very difficult to distinguish between the chemical and microbial roles. Carbaryl has been found to be more persistent in sterile vs nonsterile soils (Rajagopal *et al.*, 1984), thus under the conditions in this study if dissipation occurred it would mainly be due to chemical processes. Since no lag time occurred in the loss of carbaryl it would be claimed that no major microbial cometabolism was observed (if present at all) as was observed in studies with Rajagopal *et al.*, 1984.

Figure 51. Superbugs study of 1-napthol, at 1/3 bar field moisture capacity and 21° C, under 4 different soil conditions.



Captan

The effects of fungicides on soil microbes is a major concern because studies have shown soil concentrations of captan at 50 ppm decreased the soil biomas by nearly 70%. These soil population declines are transient effects, and recovery will occur within 60-80 days (Moorman,1989). Captan is generally noted to have the shortest half-life (~3 to 5 days) of the four pesticides examined in this study and is very susceptible to chemical degradation.

The ANOVA results indicated that Superbugs^{R} was not significant (0.05 level) in providing a more rapid degradation of captan than the unamended soil. The coefficient of variation was 45% for captan in the soil. The observed half-lives ranged from 8 to 16 days, thus doubling and tripling the times for degradation of captan (Figure 52). Thus microbial action was decreased on captan or soil chemistry conditions were not favorable, *ie* in the case of captan it was not alkaline enough.

The ln plots of concentration were generally first order appearing for the sterile and sterile plus bugs soil. The nonsterile soils had a slight lag time of 10 to 12 days, and then decreased slightly more rapid than the sterilized soils. The degradation graphs (Figure 53) of captan under the four soil conditions look very similar.

Figure 52. Superbugs study with linear regression of Captan at 1/3 bar field moisture capacity and 21° C, under 4 different soil conditions.

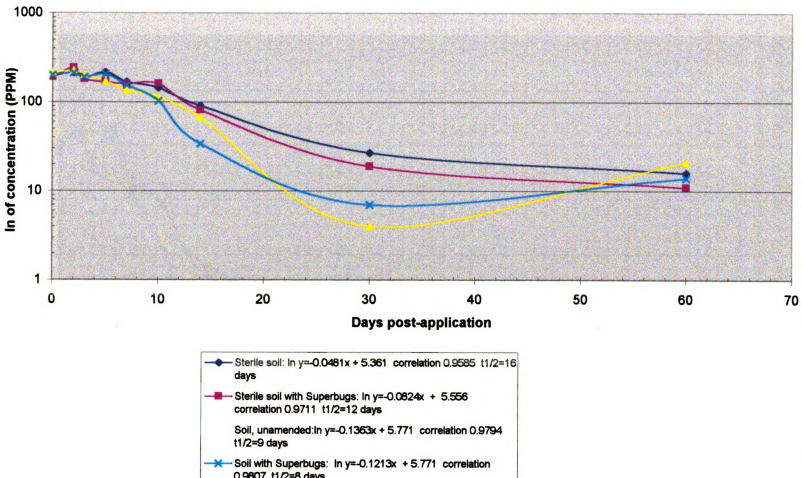
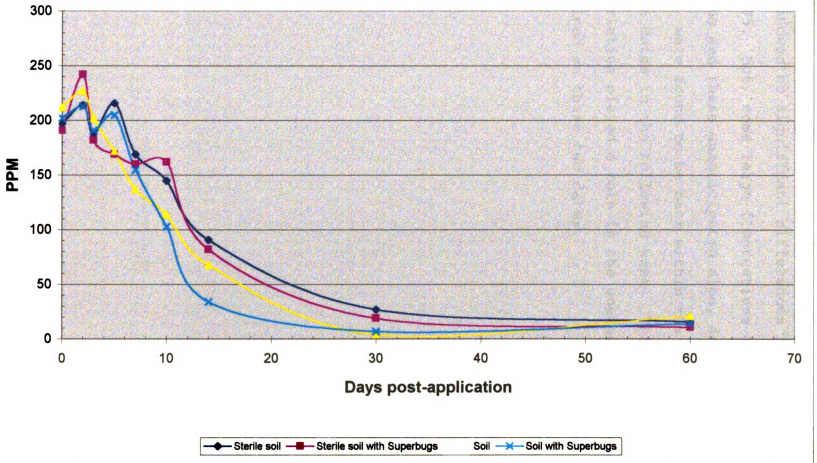
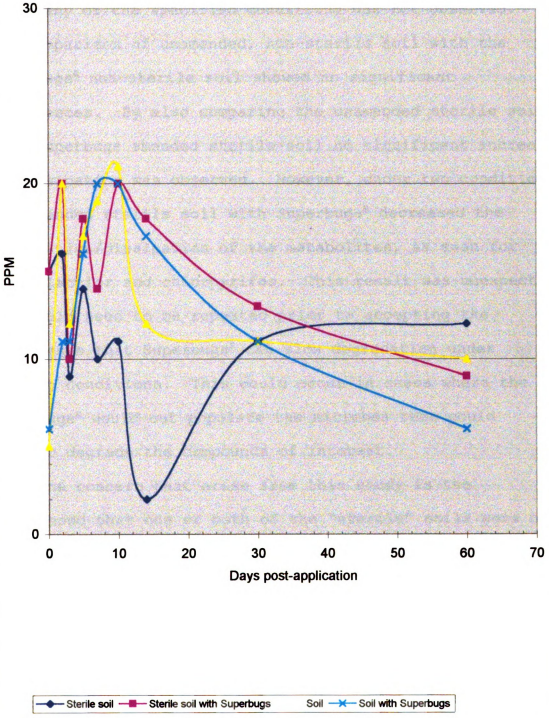


Figure 53. Superbugs study with Captan at 1/3 bar field moisture capacity and 21°C, under 4 different soil conditions.



Phthalimide residues (Figure 54) in the soils used for the ANOVA, showed no significant differences in degradation at alpha=0.05. But, some large fluctuations are observed on the graphs and these unanticipated dips, as seen on days3 and 7, were found to be back within the range of the other sample dates in the following week. This indicated sampling variation played a role in the unexpectedly low values obtained on these two dates.

Figure 54. Superbugs study of phthalimide, at 1/3 bar field moisture capacity and 21° C under 4 different soil conditions.



SUMMARY AND CONCLUSIONS

The use of Superbugs[R] as an amendment to increase the degradation of alachlor, chlorpyrifos, carbaryl and captan under any of the specified conditions was not observed. The comparison of unamended, non-sterile soil with the Superbugs[R] non-sterile soil showed no significant differences. By also comparing the unamended sterile soil with Superbugs amended sterile soil no significant increase in dissipation was observed. However, under two conditions the amended sterile soil with Superbugs[R] decreased the degradation/dissipation of the metabolites, as seen for both alachlor and chlorpyrifos. This result was unexpected and would need to be repeated prior to accepting the hypothesis that Superbugs[R] can slow degradation under certain conditions. This could occur in cases where the Superbugs[R] would out populate the microbes that could beetter degrade the compounds of interest.

One concern that arose from this study is the likelihood that one or both of the "sterile" soils were not sterile or became re-inocculated. This idea presented itself because the results obtained were expected to show a much longer degradation rate (half-life) in the sterile soil than all the other soils. In the amended sterile soil with Superbugs[R], the degradation rate was expected to

be higher than the sterile, unamended soil if the microbes worked, but it was found to do no better to degrade the compounds than the sterile soil. The soils used for this study did remain in a storage room, covered/taped with thick, black plastic prior to being used in this study and could have been re-inocculated during the 1 week storage.

Captan, alachlor and carbaryl either doubled or tripled their anticipated normal $t_{1/2}$ values, whereas chlorpyrifos did not appear to change much at 200 ppm. The observation of only a slight change in the half-life of chlorpyrifos was expected as it has been already found to be generally toxic to microbes and its disappearance is due to chemical degradation volatilization and photolysis.

The results indicated Superbugs^{R} did not perform any better than natural soil,but under different connditions or on some other compounds it may be more effective.
Finally, an area of future research would be to explore the response of microbes to the high pesticide concentrations in this study by monitoring the soil biomass or enzyme activity.

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