# MOBILITY AND PERSISTENCE OF MODERN DAY PESTICIDES IN SOIL USED TO CONSTRUCT THE FAIRWAYS OF THE GUAM INTERNATIONAL COUNTRY CLUB GOLF COURSE

## 1. CHLORPYRIFOS

Gary R.W. Denton
H. Rick Wood

Water & Energy Research Institute of the Western Pacific
University of Guam

&

James McConnell

College of Agriculture and Life Sciences
University of Guam

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# ABSTRACT

A combination of laboratory and field-based investigations were carried out to identify the mobility and persistence of the organophosphorous insecticide, chlorpyrifos, in a local soil used to build the fairways of the Guam International Country Club golf course (GICC). This facility lies directly over the island's sole-source aquifer and is regarded by some to represent a potential threat to the integrity of the underlying groundwater with respect to agrochemical contamination. Chlorpyrifos is one of several pesticides used at GICC to control troublesome weeds and insect pests.

The results of our laboratory investigations indicate that chlorpyrifos is rapidly taken up by the soil, with a sorption equilibration time in the order of 30 minutes. Sorptive partitioning between the soil and water was determined by batch equilibrium. The soil-water partition coefficient ($K$), determined from the Freundlich adsorption isotherm, was around 70 picomol/g suggesting a relatively strong affinity for the soil phase. However, the desorption data implied that the adsorptive mechanisms operating were relatively weak since only 20% of the pesticide remained on spiked soil after 4 desorptive rinses.

Degradation half-lives of chlorpyrifos in unsterilized and sterilized soil samples, held at 26°C, were estimated at 6 and 12.5 days respectively, indicating that both biotic and abiotic factors determine decay rates in this soil. Losses of chlorpyrifos from groundwater samples (dechlorinated tap water), spiked either before or after passage through unsterilized soil columns, further highlighted the importance of microbiological degradation processes, with half-lives in the order of >4 weeks and <1 week for each treatment respectively.

The field-based experiments were conducted in an outdoor setting using packed lysimeters. "Worst case scenario" conditions were approximated with respect to chlorpyrifos application rate, surface vegetation, and seasonal moisture regimes. To this end, two single application experiments were conducted in which the presence/absence of turf-grass was the primary variable. In the first experiment, Bermudagrass vs. bare soil was irrigated with sufficient groundwater to simulate a dry season high watering regime (1.25 cm/day). In the second experiment, Zoysiagrass was selected as the turf-grass representative and both treatments were watered to excess with deionized water (5 cm/day) in an attempt to simulate extreme wet season conditions.

During the first experiment, detectable levels of chlorpyrifos (3.5-9.6 ng/l) occurred in effluent drainage water from 4 of 24 lysimeters on days 4-7 and were coincident with the passing of a tropical cyclone. Thereafter, levels were below a detection limit of 1.5 ng/l for the duration of the experiments. Chlorpyrifos was not detected in any effluent drainage water during the second experiment despite the increased hydraulic loading. However, the breakdown products 3,5,6-trichloro-2-pyridinol (TCP) and 3,5,6-trichloro-2-methoxy pyridine (TMP) were detected from the second week onwards in both treatments.

Soil analyses indicated that chlorpyrifos was predominantly confined to the upper 2-cm portion of the soil column and was undetectable below a depth of 10-20 cm, depending upon hydraulic loading. The half-life of chlorpyrifos was in the order 3 days for bare soil treatments, in both

experiments. Dissipation rates were about the same for the Bermudagrass turfed treatments but decreased markedly with Zoysiagrass to produce a half-life of around 7 weeks. In this particular instance, residual amounts of chlorpyrifos (up to 1.2% of the initial amount) were detected in the upper 2-cm soil section 24 weeks after application.

The implications of the data are clear. The high propensity of chlorpyrifos for GICC fairway soil, coupled with its relatively rapid degradation rate, greatly reduces the chance of it being appreciably leached into the underlying aquifer, except, perhaps, in very shallow soils (<10 cm), immediately after application under conditions of prolonged, heavy rain. The possibility of this pesticide ever becoming a serious drinking water contaminant on the island, therefore, seems very unlikely under normal turf-grass management practices. However, the potential impact of the more mobile degradation products remains to be evaluated.

# INTRODUCTION

Golf course development in Guam has mushroomed in recent years, with ten courses currently in existence and as many again proposed. Although the local business community generally supports golf course development, the average person in the street is not so favorably disposed. On the contrary, many view golf courses as high risk entities, because of the relatively large quantities of agrochemicals used to maintain the greens in optimum playing condition, and the potential threat such chemicals pose to human health and wildlife. This perception stems, to some extent, from well publicized accounts of problems encountered in Japan and the US in the 1970's and early 1980's, that linked golf courses to pesticide contaminated rivers, streams and groundwater resources (Duble *et al.* 1978, Cohen *et al.* 1990, Abrams 1994, McArthur 1994).

While there is no denying that such events certainly happened in the past, modern management practices have greatly reduced the risk of similar events occurring to day. It has been said, in fact, that correctly located and properly managed golf courses are chemically benign, from a contamination standpoint (Carlton pers. com.). Moreover, they provide wildlife habitats and frequently become an integral part of local conservation programs (Anon 1994). They also help reduce gaseous and particulate air pollutants, act as buffer zones against the spread of fires, reduce glare and background noise, and have a cooling effect on air temperature (Watschke 1990). The fact remains, however, that the general public has a very low tolerance for risks they have no control over and are easily frightened by recurring and often highly distorted statements by the media linking golf courses with the appearance of cancer causing chemicals in drinking water (Amsden 1989). As a consequence, new developments frequently encounter distrust and opposition from the general public rather than encouragement.

On Guam, for example, one such golf course, the Guam International Country Club (GICC) has met with strong public criticism since its inception in 1988. Covering some 205 acres, this development lies directly over the northern lens, a limestone aquifer that supplies the island population with most of its drinking water. The issue of prime concern and one that continues to be debated, both within scientific and public circles, centers around the possibility that pesticides used by GICC can infiltrate the lens system and contaminate the underlying groundwater (Birkland 1990, Anon 1991)

Proponents of the development argue that modern-day pesticides used by GICC, aside from being short-lived, are rapidly and tightly bound to the surface soil layers and thus rendered immobile. In addition, the impermeable plastic liners that GICC have placed under their greens, tees and lakes, provide an effective and permanent barrier against any downward migration of pesticide. The risk of groundwater contamination is, therefore, virtually non-existent. Those opposing the development are quick to point out that the fairways, which occupy an area one order of magnitude greater than all the greens and tees put together, and which are also subjected to periodic spraying, lack the protective liners. Claims of rapid pesticide biodegradability and immobility in local soils are also contested, on the grounds that such assumptions are based on tests conducted in temperate regions of the world, and may not be applicable to Guam given the poor soils and climatic extremes that prevail on the island.

In support of these counter arguments, it has been shown elsewhere that shallow soils, low or deficient in organic matter, like those of northern Guam, provide the least favorable environment for pesticide degradation and offer the least resistance to their downward migration (Miles *et al.* 1979, Sharom *et al.* 1980, Miles *et al.* 1983, 1984, Racke *et al.* 1990). It is conceivable, then, that local soil covering the fairways of GICC may, in fact, provide a relatively ineffective barrier against pesticide movement into the underlying aquifer.

Recognizing the need for careful monitoring of the behavior and fate of pesticides used over Guam's sole source aquifer, the Guam Environmental Protection Agency (GEPA) approached the Water & Energy Research Institute (WERI), at the University of Guam (UOG), to develop a research program that would identify which, if any, of the pesticides currently used by GICC posed a significant threat to the integrity of the underlying groundwater, from a leaching potential perspective. The project described herein is a direct outcome of that request and examines the mobility and persistence of the organophosphate insecticide, chlorpyrifos, one of the most commonly used pesticides on Guam and a major component of GICC's chemical arsenal (Sanchez and Carlton 1991).

Chlorpyrifos (*o,o-diethyl o*-(3,5,6-trichloro-2-pyridylphophorothioate) is sold on Guam as a general use, nonsystemic insecticide, under the trade name "Dursban". It is used by GICC to control sod web-worm and other insect pests that affect turf-grass. Chlorpyrifos primarily affects the nervous system of insects through cholinesterase inhibition, and is highly toxic to birds. It is moderately toxic to humans, causing death at concentrations of around 500 mg/kg body weight (TOXNET 1975-1986). Symptoms of acute poisoning in man include gastrointestinal problems, headache, loss of muscular coordination, dizziness, extreme weakness, muscle twitching, nausea, slow heartbeat (bradycardia) , buildup of fluid in the lungs (pulmonary edema), drowsiness, mental confusion, and sweating (USEPA 1984). There is no information on the affects of long-term, low level exposure of humans to chlorpyrifos, although liver damage is suspected (NJDOH 1986). There are also data gaps on the oncogenicity, mutagenicity and teratogenicity of this compound and it's degradation products (Hotchkiss and Gillett 1987).

Data describing the behavior of chlorpyrifos in soils from Guam, or any other island in Micronesia, was not available prior to commencing this study. A review of published information from studies conducted elsewhere, indicated that chlorpyrifos is strongly bound to soil particles (Kuhr and Tashiro 1978, Sharom *et al.* 1980, Oki *et al.* 1990) and, as a consequence, has a low 'leaching potential' (Abrams 1991). However, under certain conditions, related to soil type and hydraulic loading, its movement into deeper soil levels is facilitated (Kuhr and Tashiro 1978) resulting in groundwater contamination (Parsons and Witt 1988; Williams *et al.* 1988, Cohen *et al.* 1990). Likewise, the persistence of this compounds in the soil is generally reported to be short-lived with an environmental half-life in the order of a few days to a few weeks (Kuhr and Tashiro 1978, Walker *et al.* 1988, Elhag *et al.* 1989, Rouchaud *et al.* 1989) although longer half-lives ranging from several months (Racke *et al.* 1990) to several years (Wright *et al.* 1991) have been recorded.

Clearly then, the mobility and persistence of chlorpyrifos in one soil type cannot simply be inferred from its behavior in another. Prior consideration must always be given to the characteristics of the soil to which it is applied, in addition to past and present agronomic practices, prevailing climate and the nature of the underlying bedrock (Miles *et al.* 1979, Miles *et al.* 1983, Miles *et al.* 1984, Kurtz and Parizek 1986, Rouchaud *et al.* 1989, Deubert 1990, Racke *et al.* 1990). In the latter context, it is noteworthy that karst topography, such as the folded and faulted carbonate rocks that make up Guam's northern lens system, typically allows rapid recharge to the underlying aquifer (Barrett Harris and Associates 1982, Mink 1982) and is considerably more prone to pesticides leaching from overlying soil than areas of restricted drainage (Helling and Gish 1986).

In the current study, we focused our attention on the soil used to construct the fairways at GICC. The behavior of chlorpyrifos in this soil was determined by a combination of laboratory and field-based investigations. In the latter studies, "packed" lysimeters were used to evaluate the influence of turf-grass vs. bare soil on the mobility and persistence of this pesticide. Quantitative and qualitative differences in the hydraulic loading attempted to simulate the moisture regimes that could be encountered at GICC as a result of a) excess groundwater irrigation during the dry season and b) prolonged heavy rain during the wet season.

# MATERIALS & METHODS

## 1. TEST SOIL CHARACTERISTICS

The local soil used for sculpturing and top-dressing the GICC fairways is a reddish brown (2.5 YR 3/4) latosol of volcanic origin, derived from the slopes of Mount Santa Rosa in the north of the island. It was found to be slightly acidic (pH 6.7), contained very little organic matter (<0.5%) and, texturally, may be described as a silty, clay loam. Fairway depths of this soil (hereafter referred to as the "test soil") at GICC are generally around 15-30 cm, although shallower depths sometimes occur.

## 2. LABORATORY INVESTIGATIONS

A series of laboratory experiments were carried out with chlorpyrifos and the test soil to determine sorption equilibrium times, the soil-water partition coefficient (K), desorption characteristics, pesticide persistence in both soil and water, and the relative importance of inherent biotic and abiotic soil degradation processes. Details of each investigation are outlined below.

### *2.1 Soil Adsorption/Desorption Characteristics:*

To determine the sorption equilibration time for chlorpyrifos, 2.5 g of test soil were added to 500 ml of deionized water (MilliQ), spiked with 25 µg of the pesticide (in 25 µl of methanol), in duplicate 1 L glass jars. The jars were sealed with Teflon-lined, screw caps and shaken on an orbital shaker at room temperature (26°C) for 6 hours. Following a settling period of 3 minutes, 7 ml of soil suspension were removed from each jar after 30 minutes, 1 hour and hourly thereafter for the remainder of the experiment. The samples were placed in 10 ml Teflon centrifuge tubes and centrifuged at 15,000 g for 5 minutes. Five-ml aliquots of the supernatant were than extracted with 1 ml of hexane, on a vortex mixer for 1 minute prior to analysis by gas chromatography (GC).

Subsequently, the soil-water partition coefficient for chlorpyrifos was determined by adding 200 ml of deionized water, spiked with 0.2, 0.66, 2, 6.6, and 20 µg of chlorpyrifos (in 2-20 µl of methanol) to 1 g of moist test soil in 250 ml glass jars (in triplicate). The jars were sealed with Teflon-lined screw caps and placed on an orbital shaker for 1 hour. Extractions were carried out as described above.

In the desorption studies, four successive water extractions of adsorbed pesticide were performed (in duplicate) on 0.5 g of moist test soil, spiked with 2 µg of chlorpyrifos (in 20 µl of methanol). After allowing a 30-minute period for the carrier solvent to evaporate, the soil samples were shaken in 40-ml Teflon centrifuge tubes with 25 ml of deionized water for 1 hour. Following centrifugation, 5-ml aliquots of the supernatant were removed from each tube and extracted with hexane as described above. The remaining supernatant was carefully discarded and a further 25-ml of deionized water added for the next extraction cycle.

### *2.2 Soil Abiotic and Biotic Degradation Rates:*

To determine the degradation rate of chlorpyrifos in the test soil, and identify the influence of biotic and abiotic factors, 5-g samples of moist soil were weighed into 25-ml glass vials. The vials were loosely capped and sterilized by autoclaving at 121°C for 1 hour. Sterilization was confirmed by the absence of growth in Tryptic Soy Broth (Difco) maintained at 35°C. Upon

cooling, the samples were spiked with 10 µg of chlorpyrifos (in 10 µl of ethanol), sealed and incubated at 28°C in the dark for a 3-week period. Unsterilized soil samples were treated similarly, as were glass-fiber filters (13 mm), which served as the control. Duplicate samples from both treatments and control, were removed at regular intervals for analysis. Pesticide extractions were facilitated by the addition of 5 ml of methanol to each vial and shaking for 1 hour. Corrections for water content of the soil were made during the final calculation of results.

### *2.3 Degradation Rates in Groundwater:*

To determine the degradation rate of chlorpyrifos in Guam's groundwater, under simulated field conditions, dechlorinated tap water (sterile) was inoculated with microorganisms by passing through columns of unsterilized test soil (15-cm diameter x 75 cm length). The drainage water was collected in 1 L Pyrex Fleakers. Replicate (4) 500-ml volumes of the microbiologically activated water were then spiked with 0.2 µg of chlorpyrifos (in 20 µl of methanol), sealed with Teflon film and incubated at 26°C for up to 30 days in the laboratory. At zero time and at regular intervals thereafter, 30-ml samples were extracted with 1 ml of hexane, on a vortex mixer, for 1 minute, prior to analysis by GC. Spiked dechlorinated tap water that was not subjected to the microbiological activation process served as the control.

### *2.4 Gas Chromatographic Parameters*

All qualitative and quantitative measurements of chlorpyrifos, during this phase of the study, were made using a Perkin Elmer (Sigma 300) gas chromatograph fitted with an electron capture detector, using a glass column (2 mm (id) x 1.83 m) packed with 1.5% OV-17/1.95% QF-1 on 100/120 Chromosorb W HP. The injector, oven and detector temperatures were maintained at 225°C, 200°C, and 325°C respectively. Nitrogen flow rates through column and detector were 30 ml/min and 60 ml/min respectively. The instrument detection limit was 0.3 pg. Method detection limits were approximately 100 pg/g for soil and 1.5 and 9 pg/ml for the groundwater and MilliQ aqueous extractions respectively.

## 3. FIELD-BASED INVESTIGATIONS

Two field-based experiments were set up to evaluate the mobility and persistence of chlorpyrifos in the test soil under two distinct watering regimes and in the presence or absence of turf-grass coverage. Packed lysimeters were used to maintain control over all water percolating through the soil profile during this part of the study. They were considered to provide a method of evaluation that was not too far removed from reality considering that the integrity of GICC fairway soil had already been disturbed.

### *3.1 Apparatus:*

The lysimeters used during the course of this study were constructed out of stainless steel. They were identical in design and dimension to that described by Bowman (1988, 1990, 1991). In essence, they were composed of two parts, an upper section (75 x 15 cm) that contained the soil and a lower support unit (15 x 15.5 cm), with a built in funnel, that channeled drainage water into an underlying collection vessel. The two sections, when fitted together, were held in place by duct-tape. A fine screen was attached to the bottom of the support unit funnel, the internal space of which was filled with a bed of fine silica sand to enhance core drainage.

Drainage was further improved by extending a fine wire (~5 cm long) from the center of this screen into the collection vessel beneath.

During the experiments, the lysimeters were placed in four insulated (10 cm thickness, polystyrene foam), plywood boxes (twelve per box) and maintained out-doors, in full sun. This arrangement simulated field conditions insofar as minimizing temperature fluctuations in the sub-surface soil layers while at the same time exposing the surface layers to the solar extremes encountered during the day. The boxes were mounted on wooden platforms, approximately 30 cm above ground to avoid flooding and provide ease of access to drainage water collection vessel housed in the lower section of each lysimeter.

Each assembled lysimeter was packed with coarse-screened (1-cm sieve), semi-moist test soil to within 2-3 cm of the top of the upper cylinder. Settling was facilitated by mechanically tapping the outside of the lysimeter during loading and by daily irrigation of the column for several weeks prior to pesticide application.

***3.2 Experimental Design:***

Both experiments were designed to assess the behavior of chlorpyrifos in the test soil under "worst case" scenario conditions with respect to turf-grass density, pesticide application rate, and seasonal moisture regimes. Thus, two treatments, comprising of twelve turfed and twelve bare soil lysimeters were evaluated in each experiment. Tiffway II Hybrid Bermudagrass and a local species of Zoysiagrass were used in experiments 1 and 2 respectively. Small runners of each were sprigged into the lysimeter soil, watered daily and periodically fertilized over a period of several weeks to encourage a dense turf and well established root system prior to starting the experiments. The grass in these lysimeters was regularly trimmed to promote thatch build-up and lateral growth of the leaders.

The daily watering regime was the primary factor that separated the two experiments. In the first experiment, the lysimeters were irrigated with dechlorinated tap water (groundwater: typically hard [200-250 mg $CaCO_3$/l] and mildly alkaline [pH 7.2-7.5].) at the rate of 1.25 cm/day. This was intended to simulate elevated irrigation rates at GICC (from their private wells) during the dry season. In the second experiment, deionized water (MilliQ: typically soft <1 mg $CaCO_3$/l] and mildly acidic [pH 5.6-6.5]) was added to each lysimeters at the rate of 5 cm/day, thus simulating high rainfall during wet season conditions. It should be noted here, that this volume is four times the 30-year average daily rainfall encountered on Guam during August (typically the wettest month of the year).

The pesticide application rate in both experiments were standardized at 6 lbs./1000 sq. ft. (a theoretical application of 8435 µg per lysimeter). This was four times that currently employed by GICC to control its most troublesome insect pests and was incorporated into the experimental design to account for accidental spills and over dosing. Pesticide behavior was evaluated by the collection and analysis of effluent drainage water and the sectioning of soil cores at regular intervals during the course of each experiment.

*3.3 Pesticide Application and Watering Regime:*
On the day preceding pesticide application, 1 L of water was added to each core, which was then capped to prevent evaporative losses. This ensured that the soil columns were fully saturated with water at the start of the experiment thereby making it easier to establish a water balance. A 10-ml aqueous suspension of 0.35% Dursban® 2E (DowElanco), containing 24.1% chlorpyrifos, was applied to each lysimeter starting 1 cm away from edge of the cylinder wall and working towards the center in a spiral fashion. Immediately following application, the pesticide was gently washed into the surface soil layers/grass thatch with a deionized water spray. After a further 24 hours, and daily thereafter, the columns were irrigated with 250 ml of dechlorinated tap water in experiment 1 and 1 L of dionized water (MilliQ) in experiment 2. The lysimeters also received water from natural rainfall in both experiments.

*3.4 Effluent Drainage Water Extractions:*
Water draining through each soil column was collected in a 1 L Pyrex Fleaker, housed in the bottom section of each lysimeter. The flasks were easily accessed via trap doors in the base of each insulated box. Water was removed for analysis on a daily basis for the first 2 weeks after commencing the experiments and at 2-3 day intervals thereafter. Aliquots of 30 ml were placed in 50 ml Teflon centrifuge tubes and extracted with 0.5 ml of n-hexane on a vortex mixer for 1 minute. Following a standing period of approximately 5 minutes, the upper hexane phase was removed for direct analysis by GC. Recoveries of spiked effluent water samples were close to 100% by this method.

*3.5 Soil Extractions:*
Two lysimeters were removed from each treatment after 1, 2, 4, 8 and 16 weeks in the first experiment, and 1, 2, 4, 8, 16 and 24 weeks in the second experiment. They were capped, placed in plastic bags, labeled, and stored horizontally in a chest freezer at -80°C. When required for analysis, a propane torch was used to warm the stainless steel tubes sufficiently to eject the frozen cores. Each core was quickly wrapped in aluminum foil, labeled and refrozen to facilitate sectioning. The first few cores examined from the first experiment were sectioned at 10-cm intervals using a geological diamond disc saw. Because of the restricted movement of the pesticide down the soil column, all subsequent cores in both experiments were sectioned at 2-cm intervals. In the second experiment, soil sectioning was facilitated with a band saw, which proved to be far more convenient.

Once sectioned, the frozen samples from experiment 1 were placed on aluminum plates and allowed to thaw at room temperature, a process that took about 1 hour for the thicker 10-cm sections. They were then crumbled with a metal fork, refrozen and pulverized prior to homogenization in a Waring blender. Upon thawing, duplicate sub-samples of moist soil (~100g) were weighed into 250 ml screw-cap, glass jars and extracted with 100 ml methanol on a orbital shaker for 3 hours. Upon settling overnight, a portion of the extractant solution was withdrawn for direct GC analysis.

A slightly different approach was taken the second experiment. Here, the frozen 2-cm sections were immediately sliced into three equal sectors after removal of a small portion for water content determination. Each sector weighed around 100 g (± 10-15g) and was individually

extracted as described above. By this method, the precise amount of pesticide present in all three sectors was calculated and used to estimate the pesticide content of the entire section.

### *3.6 Gas Chromatographic Parameters:*

The GC parameters for experiment 1 were identical to those described above for the laboratory studies. Soils from experiment 2, however, were analyzed using a newly acquired Varian 3400 instrument equipped with an electron capture detector, and a megabore (0.53-mm i.d.) SPB-5 column (Supelco). Injection and detector temperatures were set at 225 °C and 300 °C respectively. The oven was held at a post-injection temperature of 125 °C for 2 minutes and then ramped at 15 °C/minute to 260 °C. Carrier gas (nitrogen) flow through the column was set at 8 ml/minute with a 22 ml/min make up through the detector. The instrument detection limit was in the order of 0.1 pg while the method detection limits were approximately 0.5 ng/l and 30 ng/kg for drainage water and soil samples respectively.

**Plate 1: Lysimeter Components**
One of 24 stainless steel lysimeters used during the study. Essential components, from left to right are: silica sand; test-soil; drainage water retention vessel; upper and lower sections of lysimeter; stainless steel screens; duct-tape.

**Plate 2: Lysimeter Assembly, Step 1:**
Fine silica sand is poured into the built-in funnel of the lower support unit until level with the outer crimping. A fine screen at the funnel outlet keeps the sand in place.

**Plate 3: Lysimeter Assembly, Step 2:** Two stainless-steel screens are positioned, on top of the silica sand bed, to support the upper section of the lysimeter and facilitate water drainage through the test-soil column.

**Plate 4: Lysimeter Assembly, Step 3:** The upper section of the lysimeter is carefully inserted into the lower support unit and pressed firmly into place.

**Plate 5: Lysimeter Assembly, Step 4:** The upper and lower sections of the lysimeter are held firmly in position with several winds of commercial duct-tape.

**Plate 6: Lysimeter Assembly, Step 5:** The lysimeter is packed with coarse-screened (1-cm sieve), semi moist test-soil to within 2-3 cm of the top of the upper cylinder. The outer wall of the lysimeter is periodically tapped during this process to facilitated settling.

**Plate 7: The Outdoor Set-Up**
Once assembled, the loaded lysimeters were positioned in an out-door setting in four insulated boxes (6 per box). The boxes were mounted on platforms approximately 30 cm above ground.


**Plate 8: Lysimeter Irrigation**
Following application of chlorpyrifos, the desired moisture regimes were maintained by hand irrigating of the lysimeters on a daily basis.

**Plate 9: Drainage Water Collection**
Water passing through the test-soil core was collected in a 1 liter, glass vessel housed in the lower support unit of each lysimeter. The vessels were accessed through trap doors located on the underside of the insulated boxes.

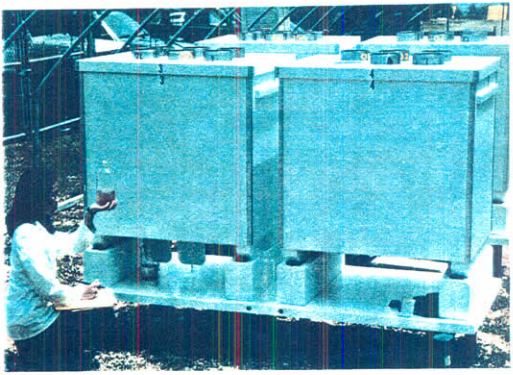


**Plate 10: Leachate Measurments**
The volume of water passing through the test-soil cores was measured on a daily basis. Sub-sample (~100 ml) were periodically taken for pesticide analysis.

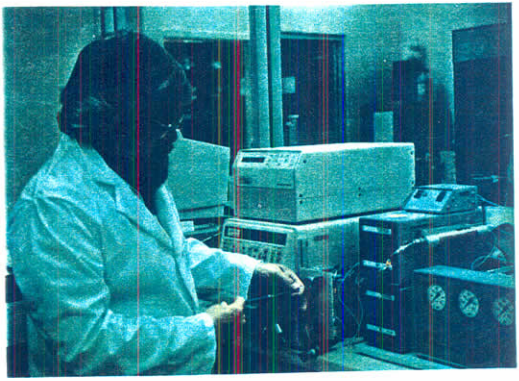


**Plate 11: Chemical Analysis**
All pesticide analysis of water and soil samples were undertaken by the WERI Water Quality Laboratory under the direction of Mr. Rick Wood.

# RESULTS AND DISCUSSION

The data collected over the entire study period are summarized in this section and discussed in relation to other relevant reports found in the literature.

## 1. LABORATORY INVESTIGATIONS

### *1.1 Adsorption/Desorption Characteristics:*

Linear plots, of the % total amount of chlorpyrifos adsorbed by the test soil vs. time, revealed that the adsorption equilibrium was rapidly established within the order of 30 minutes (Fig 1). Sorptive equilibration times given in the literature for this pesticide vary considerably from a few minutes (Macalady and Wolf 1985) to several hours (Sharom *et al.* 1980). Bowman and Sans (1985) speculated that chlorpyrifos adsorption to soil organic matter proceeds at a slower rate than adsorption to the mineral component. Thus, the sorptive equilibria is expected to be reached faster in soils deficient in organic matter, like the one examined here, compared with organic rich soils.

The soil-water partition coefficient for chlorpyrifos with our test soil was derived from the adsorption isotherm shown in Fig 2. In this instance, values of $x/m$ vs. $C$ were plotted on log-log scale according to the empirical Freundlich relationship:

$$x/m = KC^{1/n}$$

where $x/m$ is the amount (pmol) of chlorpyrifos adsorbed per unit weight of soil (g), and $C$ is the equilibrium concentration of chlorpyrifos in solution (pmol/ml). The constants $K$ (soil-water partition coefficient) and 1/n were obtained by least squares regression analysis of the log-log plot as the value of $x/m$ at 1 pmol/ml equilibrium concentration and the slope of the line respectively.

The $K$ value obtained here indicates that, under the conditions of our experiment, the test soil adsorbed 70 pmol/g of chlorpyrifos from water containing 1 pmol/ml of the pesticide. Thus, chlorpyrifos has a strong tendency to favor the sorbed rather than the dissolved state. This seems to be the general finding throughout the literature and is expected, considering the nonpolar nature of the pesticide, and its correspondingly low water solubility of around 1-2 µg/l (Bowman and Sans 1979, Racke 1993). However, sorption affinities reported for chlorpyrifos vary greatly between soils and can be explained, at least in part, by variations in organic matter content. For example, Sharom *et al.* (1980) reported sorption coefficients ($K$ values) of 18, 118, 139 and 1862 (pmol/g) in 4 soils containing 0.7, 2.5, 2.8 and 75.3% organic matter respectively.

The results of the desorption experiment (Fig. 3) demonstrate the capacity of the test soil to retain adsorbed chlorpyrifos and directly reflects the pesticide's potential for leaching through the soil profile. Chlorpyrifos is generally thought to have a low leaching potential and was placed in the soil transport category of "immobile" by McCall *et al.* (1980). In the present work, however, it appears that the adsorption mechanisms operating in our test soil are relatively weak, since 80% of the pesticide was removed in the fourth desorptive rinse. This is considerably higher than the 30% loss reported for a sandy loam by Sharom *et al.* (1980) using

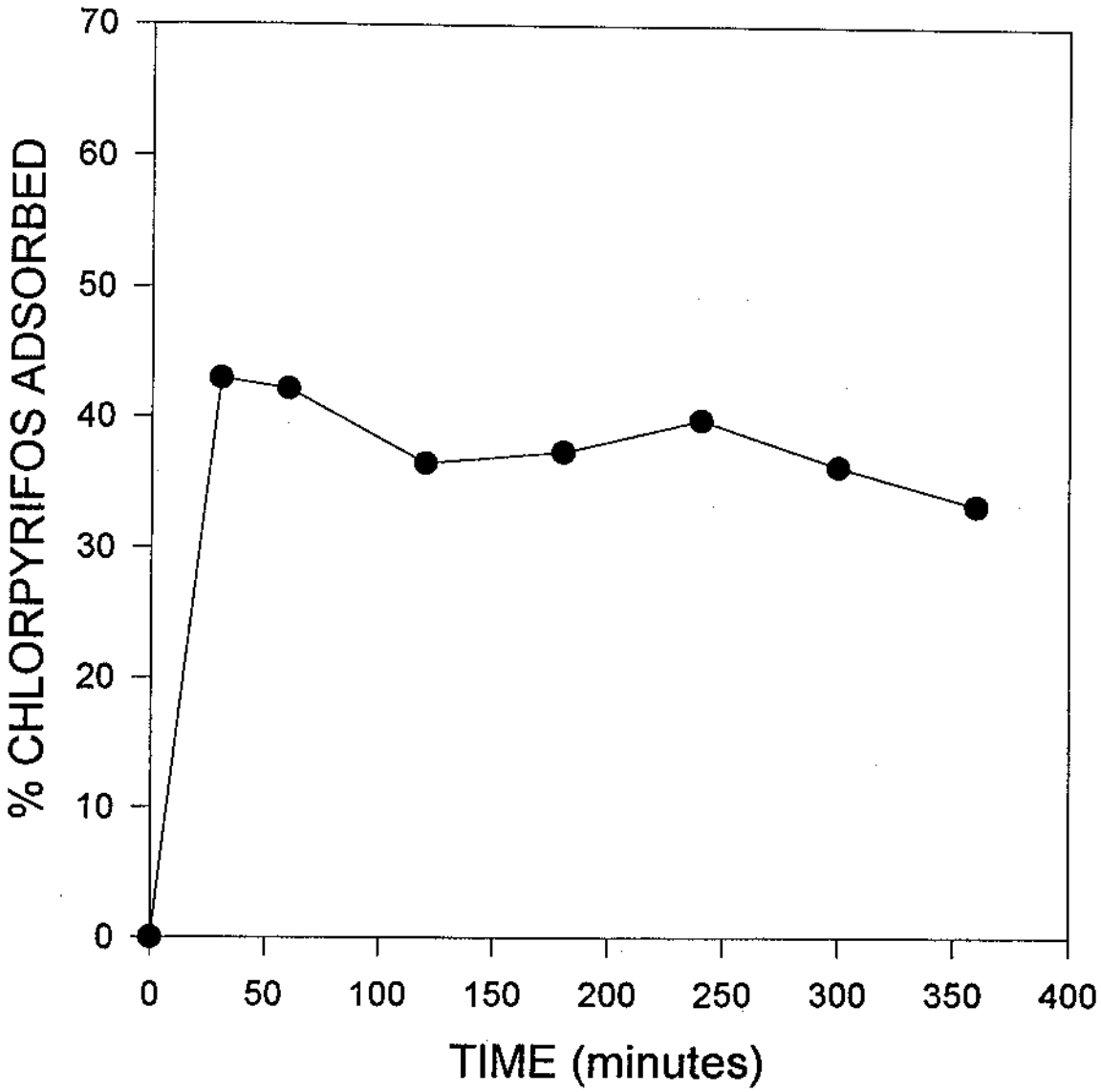



**Fig. 1:** Determination of adsorption equilibrium time for chlorpyrifos on test soil at 26°C. Each plot represents the mean of two replicates.

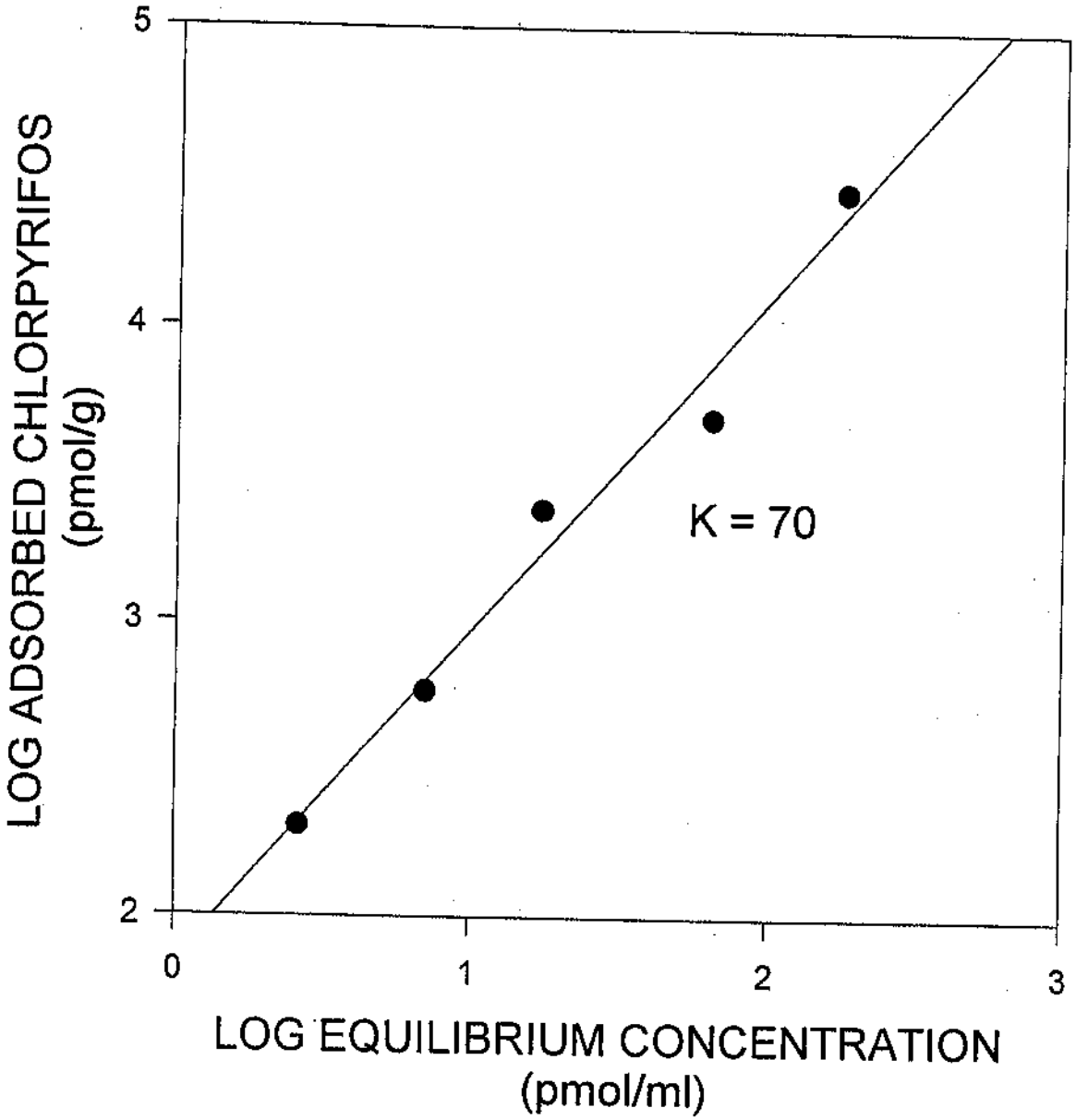



**Fig. 2:** Freundlich adsorption isotherm for chlorpyrifos on test soil at 26°C. Each plot represents the mean of three replicates.

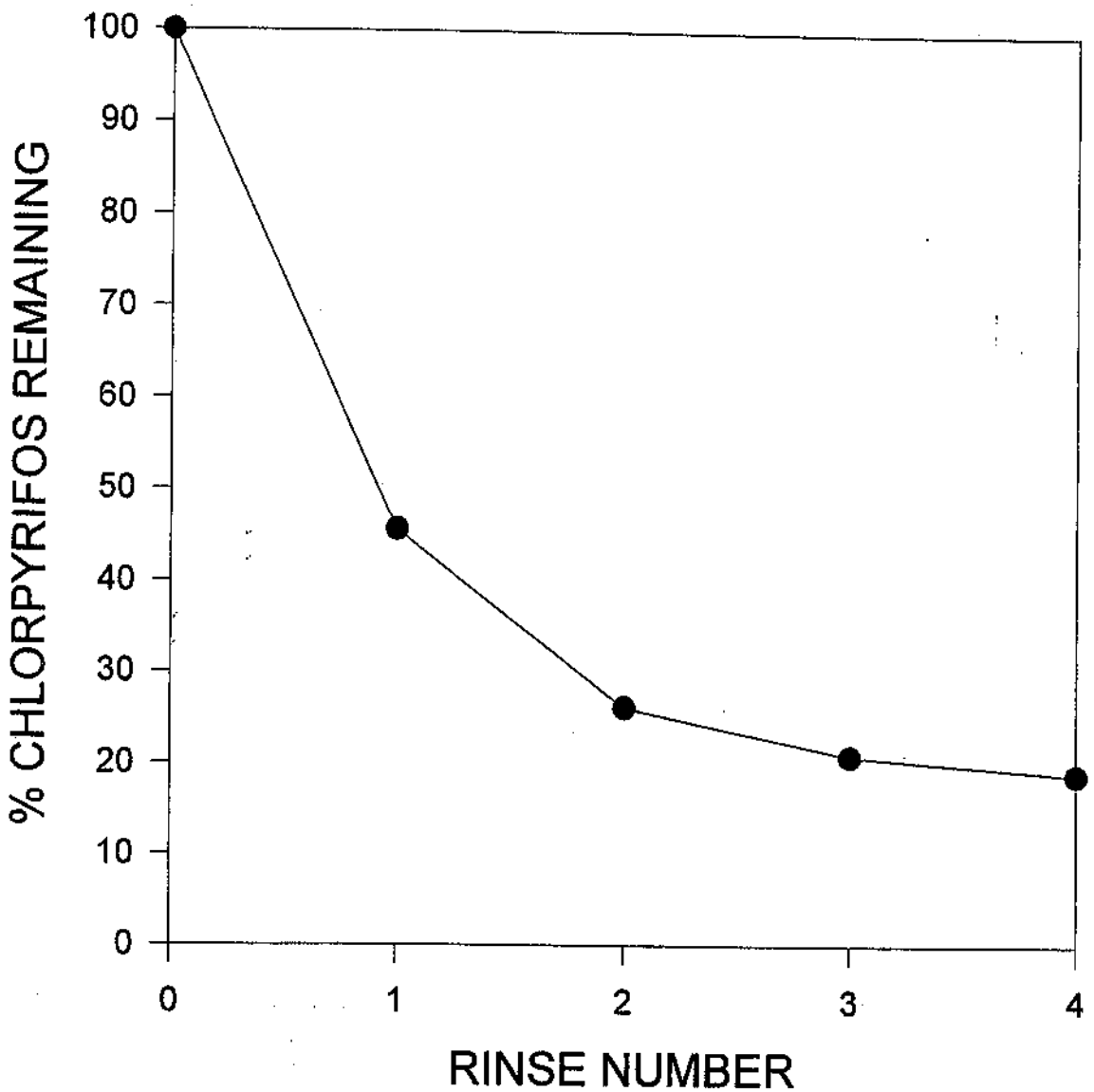



**Fig. 3:** Desorption of chlorpyrifos from test soil with four rinses of MilliQ water at 26°C. Each plot represents the mean of two replicates.

the same method as that described here. The implication, therefore, is that chlorpyrifos could move relatively easily into the deeper layers of our test soil compared with soils examined by others.

### *1.2 Soil Abiotic and Biotic Degradation Rates:*

The results of the degradation study are graphically presented in Fig 4. Assuming a first-order decay process for both treatments of the form:

$$C = C_0 e^{-kt}$$

where C is the pesticide concentration at time t, $C_0$ is the initial pesticide concentration, k is the decay rate ($day^{-1}$) and t is time (days), decay rates for chlorpyrifos in sterilized and unsterilized soil samples were computed by linear regression techniques.

Half-lives of chlorpyrifos in each treatment were determined from the decay rates as:

$$t_{1/2} = -\ln(0.5)/k$$

From the data, it is clear that both abiotic and microbial transformation mechanisms appear to be operating in our test soil. The relative importance of each is approximately equal, with the half-life of chlorpyrifos in sterilized soil being double that determined in unsterilized soil. This finding compares well with data reported by Getzin (1981), where half-lives for chlorpyrifos were 1.7-2.7 time greater in sterilized compared with unsterilized clay loam. However, other workers have reported greater differences between the two treatments. For example, Miles *et al.* (1984) found half-lives of >18 weeks in sterilized sandy loam compared with 1.5-6 weeks in unsterilized soil. Such differences, presumably, reflect differences in soil composition, especially the organic matter content, in addition to dominant environmental parameters like temperature.

### *1.3 Degradation Rates in Groundwater:*

Data from this study implies that the level of microbiological activity in the water itself profoundly influences the loss of chlorpyrifos from Guam's groundwater. For example, a half-life of a little less than 1 week was determined in water samples activated by the test soil (Fig. 5), whereas losses in water receiving no such treatment were negligible over a 30-day incubation period. It would seem, therefore, that the persistence of chlorpyrifos in Guam's groundwater will be determined largely by the extent and nature of resident microbial populations in the underlying aquifer. This in turn will be dependent, at least in part, upon the availability of utilizable carbon and energy sources. Such information is currently unavailable and one can only speculate that microbial activity in this region is relatively low, in view of physical removal processes operating (e.g. filtration, adsorption) in the overlying vadose zone, and the nutritionally impoverished environment that the aquifer likely represents.

Finally it is noteworthy that the degradation of chlorpyrifos in soil and water is known to proceed at a faster rate in alkaline conditions compared with neutral or acid conditions (Meikle

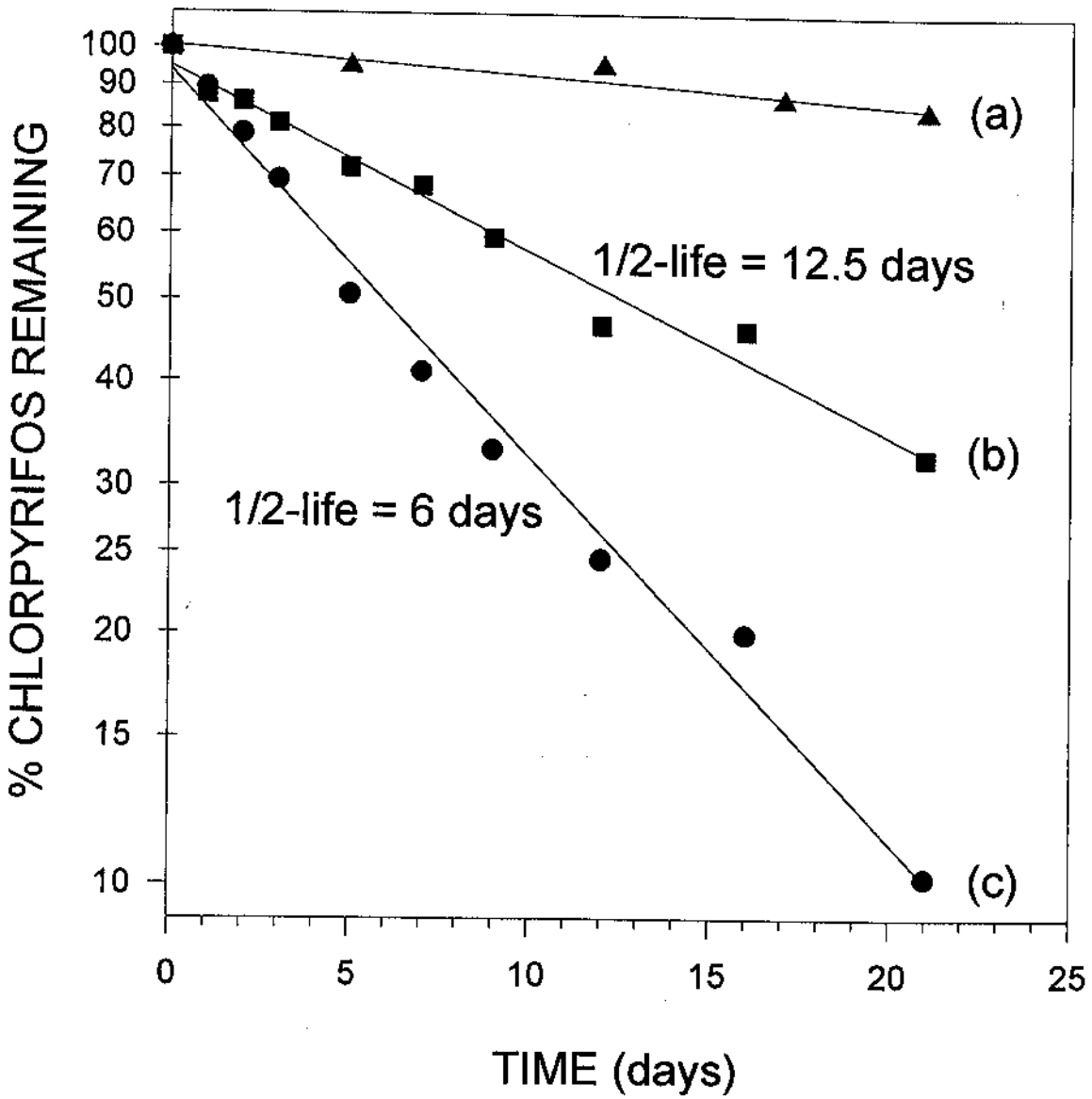



**Fig. 4:** Degradation of chlorpyrifos in test soil in the dark at 26°C. Treatments: (a) glass fiber filter (control); (b) sterilized test soil; (c) unsterilized test soil. Each plot represents the mean of two replicates.

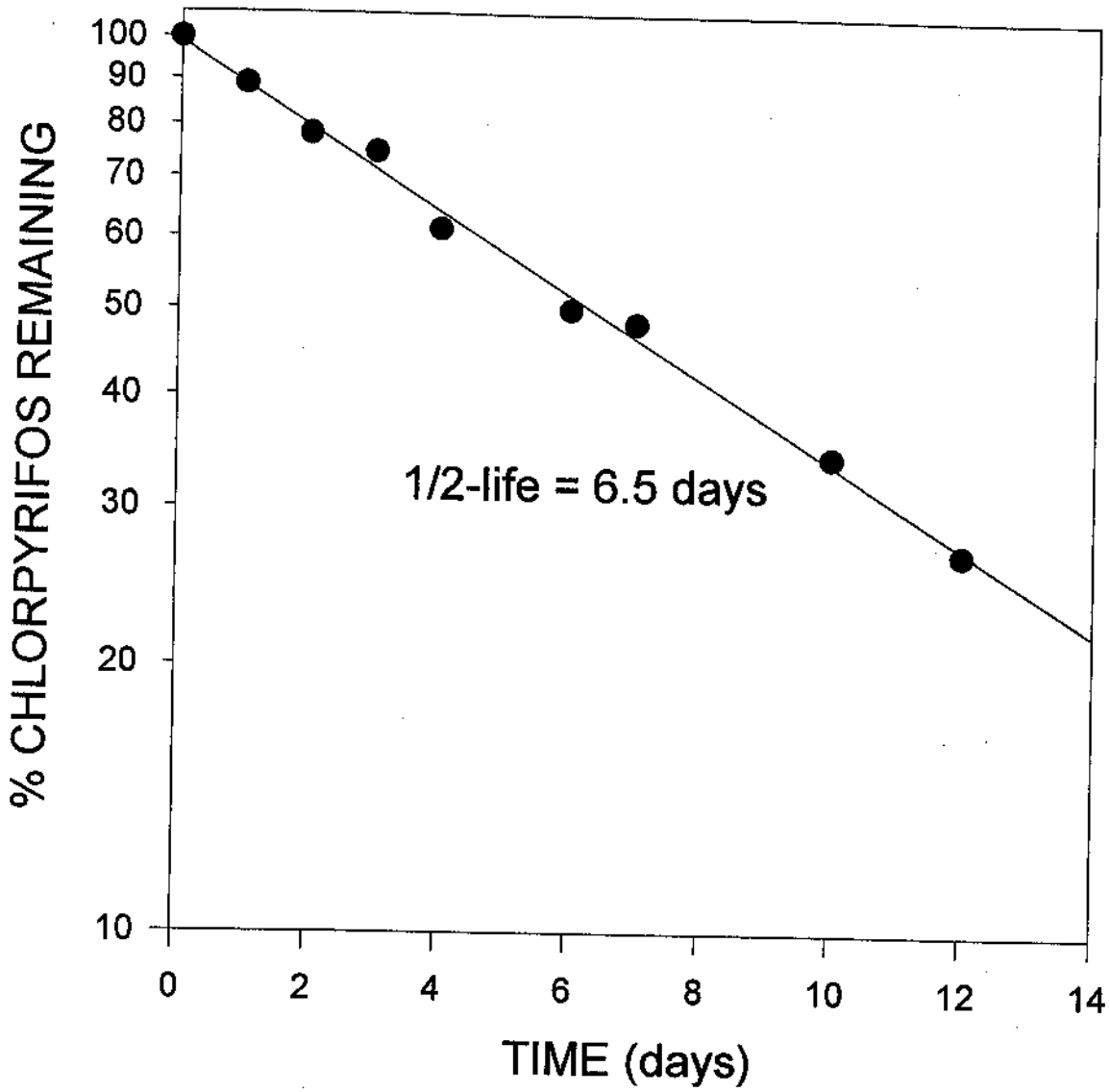



**Fig. 5:** Degradation of chlorpyrifos in Guam's groundwater (dechlorinated tap water) at 26°C after microbiological activation with test soil. Each plot represents the mean of four replicates.

and Youngson 1978). However, our experiments indicate that this pesticide is reasonably stable over the alkaline pH range normally encountered in groundwater on the island.

## 2. FIELD-BASED INVESTIGATIONS

### *2.1 Simulated Dry Season Moisture Regime (high irrigation):*

During this experiment, the lysimeters were maintained at, or close to, field capacity. Each collectively received 1750-ml of irrigation water (dechlorinated tap water) per week. Weekly contributions from rainfall over the study period (Fig 6) ranged from 46 ml to 2,854 ml. Mean volumes of effluent water discharged each week varied from 1,150 ml to 3980 ml. Losses due to evaporation and/or transpiration were not accounted for.

Crude estimates of field capacity turnover times were made, based on observed volumes discharged from the lysimeters each week. The purpose of this was to obtain a first order approximation of the times required for water to pass through the lysimeters. Turnover times were dependent upon rainfall and ranged from 1-2 weeks in the early part of the experiment and 4.5 weeks at the end.

Ambient air temperatures recorded throughout the 16 week period ranged from a night-time low of 21°C to a day-time high of 39°C in full sun. Soil pH values, at the beginning and end of the experiment, ranged from 6.7-6.81 and 7.67-7.89 respectively.

Levels of chlorpyrifos in the lysimeter drainage water were, for the most part, below the analytical detection limit, indicating that this pesticide was not readily mobilized through the soil columns of either treatment. The only exception was encountered on days 4 to 7, in drainage water from four of the twenty-four lysimeters. These findings were coincident with the passing of tropical storm Cecil that dumped in excess of 4 inches of rain into the lysimeters. However, amounts detected were extremely small (1.5-9.6 ng/l) and accounted for less than $1x10^{-5}$ % of the initial application dose.

Analysis of the sectioned soil cores in this experiment revealed several important findings. First, chlorpyrifos was predominantly confined to the top 2 cm of soil in both treatments and was rarely detected below 10 cm. This is illustrated by the data presented in Table 1 for cores sectioned at 2-cm intervals. Second, by the end of the first week, proportionately greater amounts of the pesticide had moved into the deeper layers of the bare soil treatment compared with the turfed treatment (Table 1), although differences between the two were not particularly great and were insignificant in later sections. Third, the pesticide disappeared very rapidly from the soil, with losses of around 95% in both treatments within 2 weeks of application (Table 1). The half-life was estimated to be in the order of 3 days in both treatments. Finally, the degradation curve (Fig. 7) did not follow simple first-order kinetics over the 16-week period, i.e., the first-order rate constant decreased with time. As a result, residual amounts, equivalent to 0.2% of the initial application dose, still remained in the upper 2 cm of soil section by the end of the experiment.

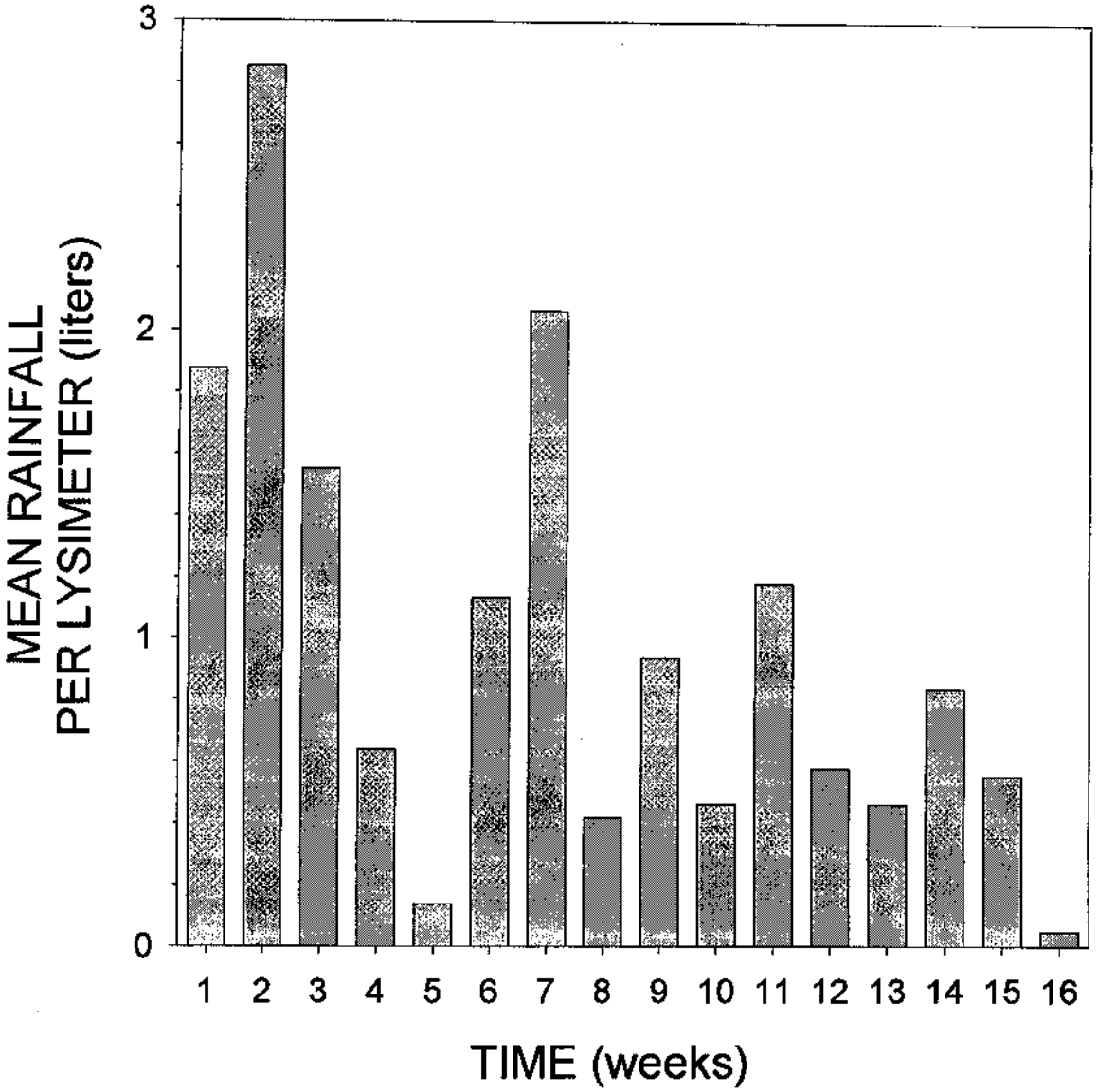



**Fig. 6:** Weekly volumes of rainfall passing through the lysimeters during experiment 1 (dry season - high groundwater irrigation scenario). In this experiment, Bermudagrass was the turf-grass of choice.

# Table 1.

## Mobility and Persistence of Chlorpyrifos in Packed Lysimeters (Bermudagrass Turf vs. Bare Soil) Irrigated with Groundwater Under Simulated Dry Season Conditions

**(data expressed as % of initial application dose* remaining)**

| Post Application Time (weeks) | | Depth (cm) | Treatment | | | |
|---|---|---|---|---|---|---|
| | | | Turfed | | Bare Soil | |
| | | | mean | range | mean | range |
| 1 | | 2 | 15.0 | 13.0-17.1 | 12.0 | 8.40-15.6 |
| | | 4 | 0.81 | 0.80-0.83 | 1.63 | 1.40-1.85 |
| | | 6 | 0.60 | 0.11-0.15 | 0.44 | 0.34-0.54 |
| | | 8 | 0.02 | 0.02-0.02 | 0.15 | 0.11-0.19 |
| | | 10 | <0.01 | <0.01-<0.01 | 0.04 | 0.03-0.04 |
| | **Total:** | **0-10** | **16.0** | **14.0-18.0** | **14.2** | **11.0-17.5** |
| | | **10-20** | **<0.01** | **<0.01-<0.01** | **<0.01** | **<0.01-<0.01** |
| 2[a] | **Total:** | **0-10** | **6.53** | **4.44-8.62** | **2.47** | **1.88-3.07** |
| | | **10-20** | **<0.01** | **<0.01-<0.01** | **<0.01** | **<0.01-<0.01** |
| 4[b] | | 2 | 1.16 | - | 1.13 | 0.18-2.08 |
| | | 4 | 0.13 | - | 0.07 | 0.02-0.11 |
| | | 6 | 0.04 | - | 0.02 | 0.01-0.03 |
| | | 8 | 0.01 | - | 0.01 | <0.01-0.01 |
| | | 10 | <0.01 | - | <0.01 | <0.01-<0.01 |
| | **Total:** | **0-10** | **2.01** | **1.34-2.85** | **1.22** | **0.21-2.22** |
| | | **10-20** | **<0.01** | **<0.01-<0.01** | **<0.01** | **<0.01-<0.01** |
| 8[a] | **Total** | **0-10** | **0.27** | **0.19-0.34** | **0.25** | **0.22-0.27** |
| | | **10-20** | **<0.01** | **<0.01-<0.01** | **<0.01** | **<0.01-<0.01** |
| 16 | | 2 | 0.16 | 0.13-0.18 | 0.12 | 0.01-0.22 |
| | | 4 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | | 6 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | | 8 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | | 10 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | **Total** | **0-10** | **0.16** | **0.13-0.18** | **0.12** | **0.01-0.22** |
| | | **10-20** | **<0.01** | **<0.01-<0.01** | **<0.01** | **<0.01-<0.01** |

* Initial application dose was 8132 µg chlorpyrifos per lysimeter

[a] soil columns from both lysimeters were sectioned at 10 cm intervals on these occasions

[b] on this occasion one soil column was sectioned at 2 cm intervals and the other was sectioned at 10 cm intervals

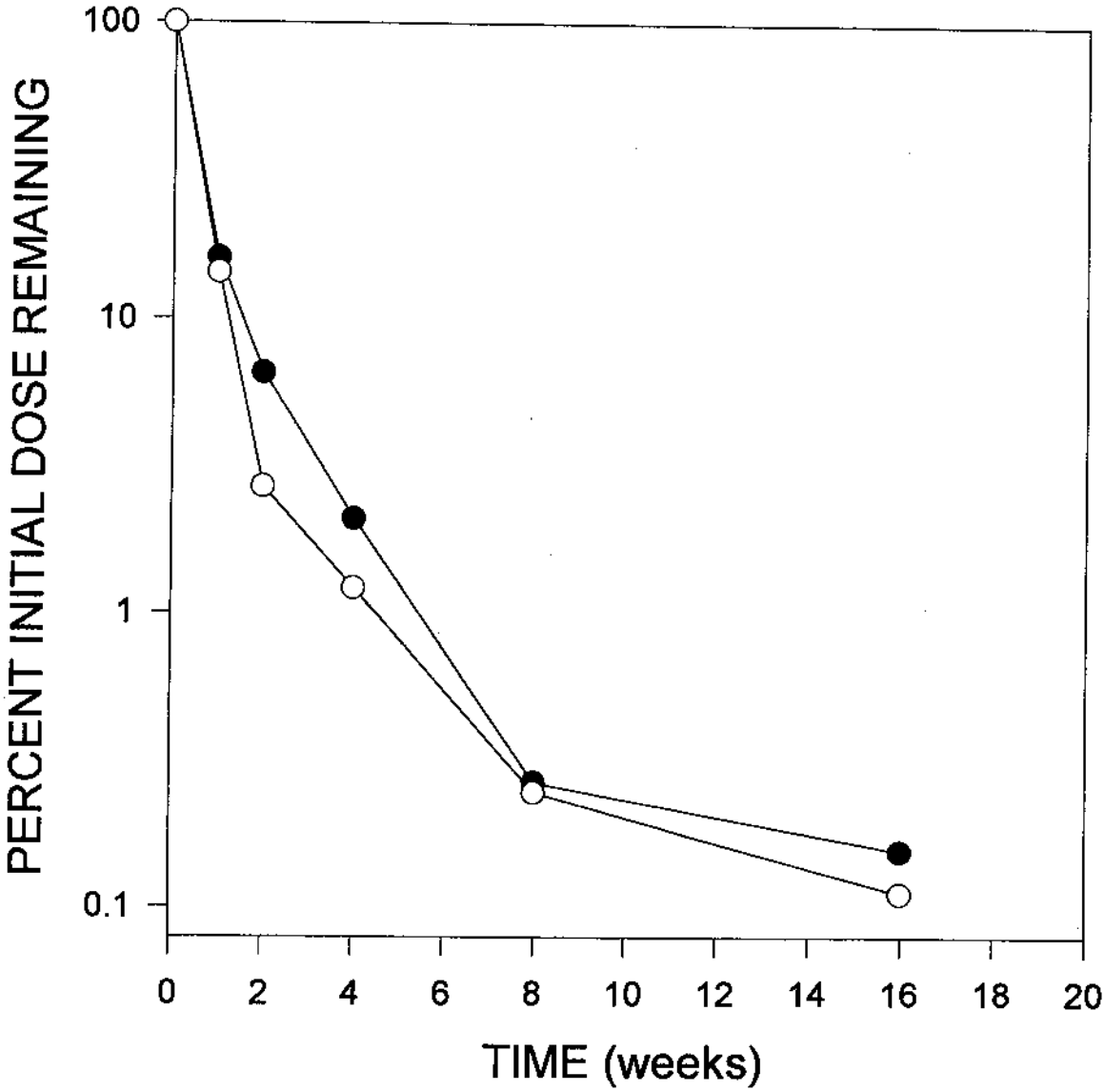



**Fig. 7:** Loss of chlorpyrifos from the upper 10 cm of test soil columns during experiment 1 (dry season – high groundwater irrigation scenario). Open and closed circles represent data points (mean of two lysimeters) from bare soil and turfed (Bermudagrass) treatments respectively.

*2.2 Simulated Wet Season Moisture Regime (high rainfall):*
During this experiment, the lysimeters were maintained at field capacity. Each lysimeter received 7,000 ml of irrigation water (MilliQ) each week. Weekly contributions from rainfall over the study period (Fig. 8) ranged from 46 ml to 2,803 ml. Mean volumes of effluent water discharged each week varied from 4,648 ml to 9,812 ml. Once again, losses due to evaporation and/or transpiration were not accounted for.

Crude estimates of field capacity turnover times, based on observed volumes discharged from the lysimeters each week, ranged from 3-4 days to a little over 1 week. Ambient air temperatures recorded throughout the experimental period ranged from a night-time low of 23°C to a day-time high of 38°C in full sun. Diurnal temperature fluctuations inside the insulated boxes seldom exceeded 3°C and ranged from 21°C to 31°C over the entire study period.

Lysimeter effluent waters from all active lysimeters were analyzed daily for the first 4 weeks, every other day for the next 8 weeks and weekly thereafter. Chlorpyrifos was not detected in effluent water, from either treatment, over the entire 24 weeks. However, the breakdown products 3,5,6-trichloro-2-pyridinol (TCP) and 3,5,6-trichloro-2-methoxy pyridine (TMP) were detected[1] from the second week onwards in both treatments (Fig. 9). Although accurate quantification was not possible, relative amounts of both compounds were at least an order of magnitude higher in drainage waters collected from the bare soil treatment. Levels from both treatments peaked during the fourth week and gradually declined thereafter. Levels of TMP were still detectable in effluent water samples from the bare soil treatment after 24 weeks.

The significance of these findings is that TCP is known to have a higher avian and mammalian toxicity than the parent compound (Muscarella *et al.* 1984). It is an acidic, ionizable compound and, at near neutral pH, the anionic form predominates (Racke 1993). This accounts for its high mobility in our test soil and poses the question as to whether it could become a major drinking water contaminant on the island. The other metabolite, TMP, is not usually detected under field conditions because of its high volatility (it is approximately 500 times more volatile than either chlorpyrifos or TCP). However, under tropical conditions of high rainfall, it clearly can be mobilized into the deeper soil layers and could conceivably become a groundwater contaminant. Further studies are required to determine the persistence of both compounds in Guam's groundwater and gather more information on each compound's toxicity to man and other animals.

Unlike the previous experiment, soil core analysis conducted during this study revealed marked differences in the leaching and dissipation of chlorpyrifos between treatments (Table 2). Clearly, this pesticide is not particularly mobile in the test soil alone and is even less so in the presence of a well-established turf of Zoysiagrass. Under local wet season conditions of prolonged heavy rain, it seems most unlikely, then, that this pesticide will move much beyond a depth of 10-15 cm unless it is inadvertently applied to bare soil. Even then, the fact that it

[1] We assume that TCP and TMP were present in the effluent waters collected during the previous experiment and attribute the fact that we didn't see them to the relatively inferior analytical capability that was available to us at the time.

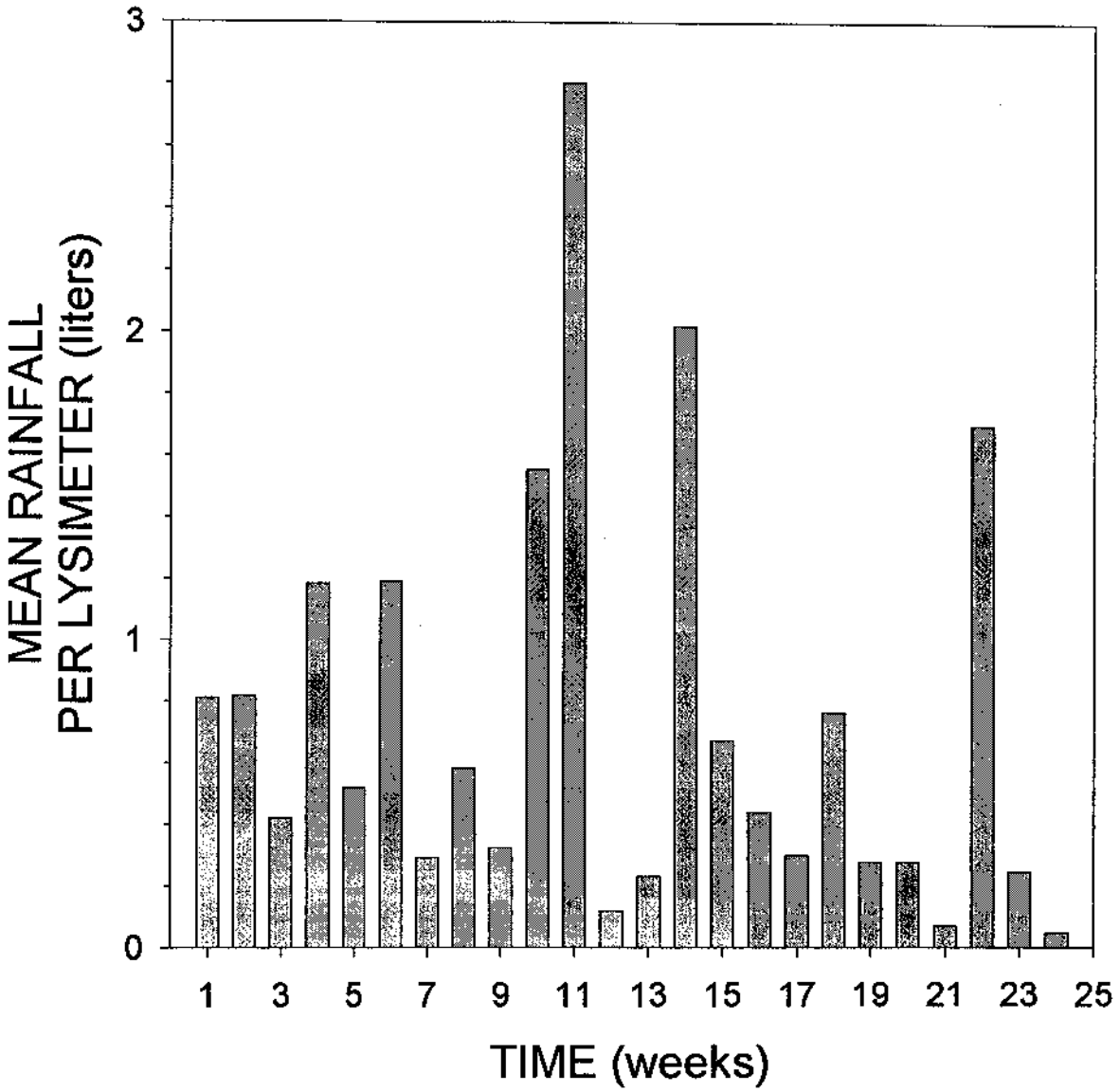
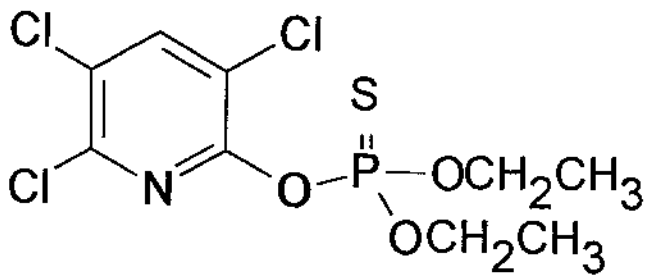


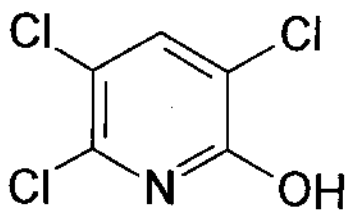

**Fig. 8:** Weekly volumes of rainfall passing through the lysimeters during experiment 2 (wet season - high rainfall scenario). In this experiment, Zoyzsiagrass was the turf-grass of choice.

CHLORPYRIFOS




O,O-diethyl 0-3,5,6-trichloro-2-pyridyl phosphorothioate

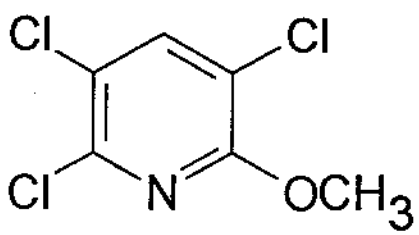
TCP




3,5,6-Trichloro-2-hydroxypyridine

3,5,6-Trichloro-2-pyridinol

TMP




3,5,6-Trichloro-2-methoxypyridine

**Fig. 9:** Chlorpyrifos and It's Major Degradation Products

# Table 2.

## Mobility and Persistence of Chlorpyrifos in Packed Lysimeters (Zoysiagrass Turf vs. Bare Soil) Irrigated with Groundwater Under Simulated Dry Season Conditions

**(data expressed as % of initial application dose* remaining)**

| Post Application Time (weeks) | Depth (cm) | Treatment | | | |
|---|---|---|---|---|---|
| | | Turfed | | Bare Soil | |
| | | mean | range | mean | range |
| 1 | 2 | 89.6 | 79.4-99.8 | 5.00 | 4.19-5.82 |
| | 4 | 10.2 | 6.88-13.5 | 10.4 | 5.67-15.1 |
| | 6 | 2.22 | 0.69-3.75 | 9.20 | 6.04-12.4 |
| | 8 | 0.61 | 0.06-1.15 | 3.08 | 2.21-3.95 |
| | 10 | 0.10 | 0.04-0.16 | 1.64 | 0.62-2.67 |
| | 12 | 0.01 | 0.01-0.01 | 1.02 | 0.89-1.15 |
| | 14 | <0.01 | <0.01-<0.01 | 0.67 | 0.67-0.68 |
| | 16 | <0.01 | <0.01-<0.01 | 0.12 | 0.05-0.20 |
| | 18 | <0.01 | <0.01-<0.01 | 0.07 | 0.04-0.10 |
| | 20 | <0.01 | <0.01-<0.01 | 0.02 | <0.01-0.04 |
| | **Total: 0-20** | **103** | **87.1-118** | **31.2** | **20.4-42.1** |
| 2 | 2 | 67.4 | 58.6-76.2 | 2.04 | 1.95-2.13 |
| | 4 | 12.9 | 12.1-13.6 | 4.37 | 0.90-7.83 |
| | 6 | 2.87 | 2.25-3.49 | 3.97 | 1.02-6.92 |
| | 8 | 0.65 | 0.08-1.22 | 1.13 | 0.37-1.90 |
| | 10 | 0.10 | 0.02-0.18 | 0.37 | 0.09-0.65 |
| | 12 | 0.03 | 0.01-0.05 | 0.39 | 0.07-0.71 |
| | 14 | 0.01 | <0.01-0.02 | 0.41 | 0.06-0.76 |
| | 16 | 0.01 | <0.01-0.01 | 0.42 | 0.07-0.77 |
| | 18 | <0.01 | <0.01-0.01 | 0.22 | 0.05-0.38 |
| | 20 | <0.01 | <0.01-<0.01 | 0.14 | 0.05-0.29 |
| | **Total: 0-20** | **83.9** | **74.6-93.3** | **13.5** | **4.57-22.3** |
| 4 | 2 | 70.5 | 50.9-90.1 | 0.46 | 0.24-0.68 |
| | 4 | 4.20 | 2.78-5.63 | 0.41 | 0.32-0.48 |
| | 6 | 0.97 | 0.47-1.46 | 0.32 | 0.16-0.48 |
| | 8 | 0.11 | 0.08-0.14 | 0.25 | 0.09-0.42 |
| | 10 | 0.02 | 0.02-0.03 | 0.29 | 0.09-0.48 |
| | 12 | 0.01 | 0.01-0.01 | 0.21 | 0.11-0.30 |
| | 14 | <0.01 | <0.01-<0.01 | 0.17 | 0.07-0.27 |
| | 16 | <0.01 | <0.01-<0.01 | 0.16 | 0.06-0.26 |
| | 18 | <0.01 | <0.01-<0.01 | 0.11 | 0.01-0.20 |
| | 20 | <0.01 | <0.01-<0.01 | 0.07 | <0.01-0.14 |
| | **Total: 0-20** | **75.8** | **54.3-97.3** | **2.42** | **1.57-3.26** |

# Table 2 (cont.)

## Mobility and Persistence of Chlorpyrifos in Packed Lysimeters (Zoysiagrass Turf vs. Bare Soil) Irrigated with Groundwater Under Simulated Dry Season Conditions

**(data expressed as % of initial application dose* remaining)**

| Post Application Time (weeks) | Depth (cm) | Treatment | | | |
|---|---|---|---|---|---|
| | | Turfed | | Bare Soil | |
| | | mean | range | mean | range |
| 8 | 2 | 38.9 | 19.9-57.8 | 0.22 | 0.12-0.32 |
| | 4 | 1.09 | 0.44-1.73 | 1.37 | 0.10-2.65 |
| | 6 | 0.11 | 0.03-0.20 | 0.04 | 0.04-0.04 |
| | 8 | 0.03 | 0.01-0.06 | 0.05 | 0.04-0.05 |
| | 10 | 0.01 | <0.01-0.02 | 0.03 | 0.03-0.03 |
| | 12 | 0.01 | <0.01-0.01 | 0.02 | 0.02-0.02 |
| | 14 | <0.01 | <0.01-<0.01 | 0.02 | 0.02-0.02 |
| | 18 | <0.01 | <0.01-<0.01 | 0.01 | 0.01-0.01 |
| | 20 | <0.01 | <0.01-<0.01 | 0.01 | <0.01-0.02 |
| | **Total: 0-20** | **40.1** | **20.4-59.9** | **1.82** | **0.44-3.19** |
| 16 | 2 | 1.93 | 1.54-2.33 | 0.08 | 0.05-0.10 |
| | 4 | 0.19 | 0.17-0.21 | 0.04 | 0.04-0.04 |
| | 6 | 0.01 | 0.01-0.02 | 0.02 | 0.02-0.02 |
| | 8 | 0.01 | <0.01-0.01 | 0.02 | 0.01-0.02 |
| | 10 | <0.01 | <0.01-0.01 | 0.02 | 0.01-0.02 |
| | 12 | <0.01 | <0.01-<0.01 | 0.01 | 0.01-0.01 |
| | 14 | <0.01 | <0.01-<0.01 | 0.01 | 0.01-0.01 |
| | 16 | <0.01 | <0.01-<0.01 | 0.01 | 0.01-0.01 |
| | 18 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | 20 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | **Total: 0-20** | **2.15** | **1.74-2.55** | **0.19** | **0.16-0.21** |
| 24 | 2 | 0.64 | 0.10-1.18 | 0.03 | 0.03-0.03 |
| | 4 | 0.02 | 0.01-0.02 | 0.01 | <0.01-0.02 |
| | 6 | <0.01 | <0.01-0.01 | 0.01 | <0.01-0.01 |
| | 8 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | 10 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | 12 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | 14 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | 16 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | 18 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | 20 | <0.01 | <0.01-<0.01 | <0.01 | <0.01-<0.01 |
| | **Total: 0-20** | **0.66** | **0.11-1.21** | **0.07** | **0.05-0.08** |

* Initial application dose was 9129 µg chlorpyrifos per lysimeter

rapidly degrades in the soil greatly reduces the possibility of it ever being leached in significant quantities into deeper soil layers.

The strong affinity of chlorpyrifos for organic matter is well known (Racke 1993), and no doubt explains the restricted movement of the pesticide in the turfed experimental treatment. What is surprising, however, is the effect that this association has on the pesticide's persistence. From the data presented in Fig. 10, chlorpyrifos has a half-life in the order of 7 weeks in the turfed treatments, as opposed to 3-4 days in the bare soil treatment. And, just as before, chlorpyrifos decay rates do not follow first order kinetics in either treatment.

It will be noted from Fig. 10 that during the first 4 weeks of the experiment, chlorpyrifos is lost very slowly from the turfed treatments. Thereafter, the rate increases and parallels that observed in the bare soil treatments. The slow disappearance of chlorpyrifos from the turfed treatments was contrary to what was expected, given that the root zone is usually considered to be the most microbiologically active part of the topsoil for the breakdown of chemical residues (Deubert 1990). However, from the data, it appears that chlorpyrifos sorbed onto organic matter is somehow protected against clay surface-catalyzed hydrolysis and microbial degradation processes occurring in the soil. Why this was not observed with the Bermudagrass is currently unknown, although we suspect quantitative differences in the soil organic matter content between the two treatments is a contributing factor. Qualitative differences in living root chemistry may also contribute to Zoysiagrass being a more efficient scavenger of chlorpyrifos than Bermudagrass. The sudden increase in chlorpyrifos decay rates, from the 4$^{th}$ week onwards, certainly suggests that the 'protective effect' is intimately linked with living root material, and diminishes rapidly with the death and decay of the root hair upon which the pesticide is sorbed. In any event, further work is necessary to elucidate the mechanisms operating here, and also to determine whether or not the pesticide's biological availability and hence, its insecticidal activity is effected under these conditions

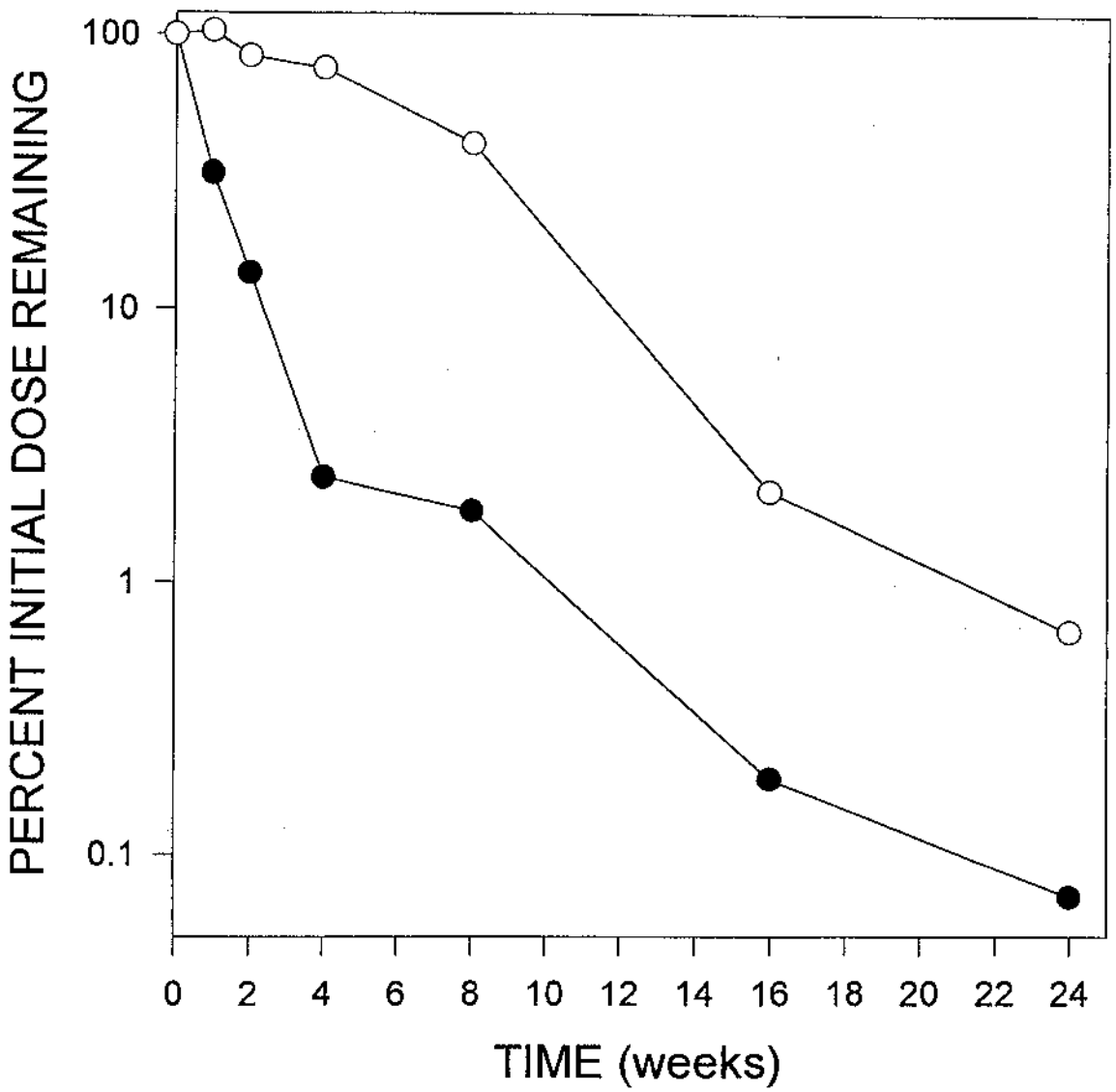



**Fig. 10:** Loss of chlorpyrifos from the upper 20 cm of test soil columns during experiment 2 (wet season – high rainfall scenario). Open and closed circles represent data points (mean of two lysimeters) from bare soil and turfed (Zoysiagrass) treatments respectively.

# GENERAL CONCLUSIONS

The following section presents some general conclusions related to the mobility and persistence of chlorpyrifos in local soils. They are based on the findings of the present study and other pertinent information gathered from the literature.

## 1. Factors Affecting Mobility

Failure to detect chlorpyrifos in almost all lysimeter drainage water implied that the pesticide was not readily leached through the test soil columns, even under conditions simulating high rainfall. The confinement of detectable residues to the upper 10-20 cm of the lysimeter soil column in both treatments of both experiments lends further support to this conclusion. Dominant factors influencing the mobility of this pesticide are briefly considered below.

### *1.1 Chemical Characteristics:*

The fact that chlorpyrifos has a strong tendency to favor the sorbed rather than the dissolved state is to be expected given the nonpolar nature of the molecule and its correspondingly low water solubility (Racke 1993). These properties are generally considered to render it relatively immobile in the soil environment (McCall *et al.* 1980), and, consequently, a rare contaminant of groundwater (Parsons and Witt 1988, Williams *et al.* 1988). However, both soil and climatic conditions influence the transportation of this pesticide through the soil profile. As a consequence, reported depths of penetration from surface soil layers range from <5 cm to >30 cm (Racke 1993).

### *1.2 Soil Mineral Characteristics:*

Soil characteristics that influence the mobility of pesticides include the nature and abundance of the mineral and organic components. In terms of the mineral component, it will be recalled that the test soil is a silty, clay loam. To expand this description further, the clay fraction comprises about 80% of the soil weight and consists predominantly of hallosite (Carroll and Hathaway 1963) a polymorph of kaolinite.

Although the clay content of soil is not particularly important in determining chlorpyrifos sorption (Felsot and Dahm 1979), the ion-exchange capacity of the clay is, and operates in a positively related fashion (Felsot and Dahm 1979). Of significance here, then, is the fact that kaolinite has a particularly low ion-exchange capacity compared with other types of clay (Drever 1982).

### *1.3 Soil Organic Matter Content*

The test soil was also found to be low in terms of its organic component (<0.5%). This particular soil characteristic is known to profoundly influence chlorpyrifos adsorption in a positively related fashion (Sharom *et al.* 1980). The importance of a well established turf in limiting the downward movement of this pesticide at GICC is, therefore, indicated and clearly demonstrated by the lysimeter studies conducted here with Zoysiagrass. The reasons why we did not see such a pronounced difference between treatments in the first experiment conducted with Bermudagrass is not immediately obvious. However, of the two grasses, the local Zoysiagrass was far more vigorous and produced a much denser turf than the Bermudagrass. Root growth in the former was also considerable and completely filled the lysimeters, whereas comparatively little root growth was noted below a depth of 10 cm with the latter.

### *1.4 Climatic Factors:*

Climatic factors that influence the movement of pesticides through the soil profile, and are pertinent to this study, include temperature and rainfall. Temperature for example has been shown to affect chlorpyrifos adsorption to soil in a negatively related fashion (Ziden *et al.* 1984), and is an important consideration in view of Guam's tropical climate.

Rainfall is not generally considered to be of major importance in mobilizing chlorpyrifos because of the pesticides strong affinity for soil surfaces (Racke 1993). However, under conditions of prolonged, heavy rains and high ambient temperatures, some of the pesticide will be desorbed and moved through the soil profile. To what extent this occurs depends on the sorption capacity of the soil and the intensity and duration of the hydraulic loading. Of importance, then, is the timing of chlorpyrifos applications relative to prolonged periods of heavy rain if mobilization of this pesticide into the deeper soil layers is to be avoided.

## 2. Factors Affecting Persistence

The persistence of chlorpyrifos in soil is largely dependent on soil type and environmental variables, particularly temperature. Consequently, reported half-lives for this pesticide range from a few days to several months (Racke 1992). Predominant dissipative mechanisms identified during the present study are briefly discussed below.

### *2.1 Biotic and Abiotic Degradation:*

In the present study, chlorpyrifos was rapidly lost by dissipation processes other than leaching, in all bare soil treatments. Half-life estimates of 3-4 days compare favorably with that obtained from spiked soil samples held in sealed glass vials that were placed within the insulated lysimeter boxes. This infers that losses from the lysimeters predominantly reflect degradation processes within the soil as opposed to losses due to volatilization and photolysis. The short half-life no doubt reflects the high ambient temperatures and their accelerating effects on these processes.

In reviewing the literature, Racke (1993) concluded that microbial activity plays a significant role in chlorpyrifos degradation within soil, although this is not always the case (Jones and Hastings 1981, Yoshioka *et al.* 1991), and presumably reflects difference in soil composition and environmental parameters. In the current study, it would seem microbial activity plays a major role in the degradation of this pesticide in the test soil. This is surprising, given the very limited quantities of organic matter present in this substrate.

While little information exists on microbial degradation mechanisms for chlorpyrifos, the abiotic transformation processes primarily involve aqueous and clay surface-catalyzed hydrolysis (Racke 1993). The latter, which is related to hydration water and counter ion activity at the clay surface (Mingelgrin *et al.* 1977, Yaron 1978), is thought to be the predominant abiotic degradation process for this pesticide in soils (Racke 1993).

The inadequacy of simple first-order kinetics assumption in describing the disappearance of chlorpyrifos from the test soil may, therefore, be explained by the fact that at least two

degradation processes are operating simultaneously. In addition, different soil sorptive sites will vary in their capacity to relinquish the pesticide to these degradation processes.

### *2.2 Soil Organic Matter*

The effect of a well-established turf on the persistence of chlorpyrifos, although not obvious during the first experiment, was very clear in the second. Here, Zoysiagrass somehow protected the pesticide from degradation processes, extending its half-life by an order of magnitude. It seems odd that such a major change in persistence was not indicated between treatments during the first experiment with Bermudagrass. However, the organic thatch layers in the Zoysiagrass treatment were far more substantial than for Bermudagrass and probably accounts for this discrepancy. According to Racke (1992), chlorpyrifos residues entrained in thatch are more persistent than those present on foliage and bare soil. It is also pertinent to note here that previous work by Miles *et al.* (1979) indicates that the half-life of chlorpyrifos is significantly longer in organic soils compared with mineral soils.

### *2.3 pH and Other Water Quality Parameters*

The degradation of chlorpyrifos in soil and water is known to be profoundly influenced by pH, and proceeds at a faster rate in alkaline conditions, compared with neutral or acid conditions (Meikle and Youngson 1978). Since the pH of Guam's groundwater is mildly alkaline (pH 7.2-7.5), while that of its rainwater is mildly acidic (pH 5.5-6.5), the aqueous hydrolysis of chlorpyrifos was anticipated to proceed at a faster rate in soil irrigated with the former compared with the latter. If such was the case, then, season could well be a very important consideration when determining application rates of this pesticide at GICC. However, a comparison of the chlorpyrifos decay curves for the bare soil treatments in experiments 1 and 2 did not support this assumption. In fact, the estimated half-lives were similar in both cases (3-4 days). Also apparent, then, is the fact that other major differences in water chemistry such as hardness, alkalinity, and conductivity, exert no obvious influence on the persistence of this pesticide in the test soil.

### *2.4 Hydraulic Loading:*

Although increased hydraulic loading to some extent facilitates movement of chlorpyrifos through the soil profile, there was no obvious indication that this variable influenced the persistence of this pesticide in the test soil.

## 3. Concluding Remarks

Concerns that pesticides used on GICC fairways may contaminate the underlying groundwater are understandable given the rapid recharge rates to the underlying aquifer (Mink 1982). Likewise, the composition and shallow depths of the overlying soil, and the notable absence of information on the behavior of these chemicals in it, do little to allay fears and inspire public confidence.

For chlorpyrifos, however, such anxieties seem unnecessary for four main reasons. Firstly, this pesticide demonstrates a high propensity for sorption to GICC fairway soil, despite the soil's poor ion-exchange capacity and low organic matter content. Secondly, local climatic conditions facilitates its rapid degradation in the soil, thereby greatly reducing any possibility of

it being appreciably leached under conditions of heavy rainfall or excess watering. Thirdly, should the pesticide ever be mobilized out of the soil profile, the alkaline nature of the underlying limestone would greatly expedite the abiotic degradation process (Racke 1993). Finally, all groundwater removed for public consumption on Guam is chlorinated prior to distribution. At normal residual chlorine levels of around 0.8 mg/l, the half-lives for chlorpyrifos and its degradation products are in the order of 15 minutes. Thus, the probability of these compounds contaminating potable drinking water supplies in this part of the world is very remote.

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