

2000 Annual Report to the United States Golf Association

Calibration of Computer Model Scenarios (PRZM3/EXAMS2) For Pesticide Runoff and Leaching in Turfgrass Environments

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Executive Summary

To address the overarching objectives of this investigation, this year's research focused on collecting current and historical data on specific pesticide degradation products in golf course leachate from lysimeters constructed into golf course greens as well as characterizing the fate of one of the degradation products in laboratory investigations. This data is needed to conduct further exposure modeling in years two and three. Chlorothalonil and chlorpyrifos are commonly used to control disease and insect pests on golf course greens in the southeastern U.S. While they are relatively immobile in the soil profile, their respective soil degradation products, 4-hydroxy-2,5,6-trichloroisophthalonitrile and 3,5,6-trichloropyridin-2-ol are more polar may be present in green leachate. To investigate this possibility, six stainless steel lysimeters were constructed into two practice greens at a country club in a northern Atlanta, Georgia suburb. Over a period of 1 year after rainfall events, lysimeter leachate samples were collected into glass bottles, filtered, and directly analyzed by HPLC. Chlorpyrifos was not detected in any sample and chlorothalonil was detected only in one sample at a concentration of 0.12 mg/L. Hydroxychlorothalonil and trichloropyridinol were respectively measured in 87% and 63% of the samples at maximum and median concentrations of 2.21 mg/L and 0.55 mg/L for hydroxychlorothalonil and 1.77 mg/L and 0.15 mg/L for trichloropyridinol. Data generated by the pesticide registrant for chlorpyrifos has shown that trichloropyridinol is rapidly degraded by water by sunlight. Irradiation with simulated sunlight degraded hydroxychlorothalonil in DI water, phosphate buffer, and pond water with half-lives of approximately 30 minutes. Simulated degradation of hydroxychlorothalonil in a pond setting using the US EPA's EXAMS MSPond scenario suggested that this laboratory generated 30 minute half-life would equate to approximately a 2.6 day half-life in a 2 m deep pond. Although hydroxychlorothalonil is moderately stable and mobile in soil, these data suggest that in surface water it should be rapidly degraded by sunlight to small aliphatic acids upon transport into aquatic systems.

RESEARCH INITIATED PAST 12 MONTHS

Objectives:

The overall objectives of this investigation are to:

- 1) Conduct field investigations for pesticide offsite movement such that the data can be used to calibrate regulatory computer model scenarios for turf.
- 2) To calibrate PRZM/EXAMS scenario(s) for turf based upon the data collected in objective 1 such that the scenarios can be used in tier 2 exposure assessments for turf pesticides.
- 3) To modify the code of PRZM as necessary based upon the collected data to best represent the turf environment.

To address objective 1, this year's research focused on collecting current and historical data on specific pesticide degradation products in golf course leachate from lysimeters constructed into golf course greens as well as characterizing the fate of one of the degradation products in laboratory investigations. Such information will be needed to conduct modeling investigations in years two and three. Specific investigation on greens and fairways could not be conducted this year due to watering restrictions placed upon golf courses. The north Georgia area is in its second year of drought and is approximately 16 inches below normal in rainfall.

Thus the specific objectives this past year were to

1. Establish a multidisciplinary team representing the turf pesticide industry and turfgrass regulators that has stake in developing regulatory models
2. Characterize the occurrence of trichloropyridinol (degradation product of chlorpyrifos) and hydroxychlorothalonil (degradation product of chlorothalonil) in lysimeters constructed into golf course greens.
3. Investigate the potential of hydroxychlorothalonil to be degraded by sunlight in water. This information has not been collected by the pesticide registrant and will be crucial to modeling its fate in aquatic ecosystems.

Objective 1. Establish a multidisciplinary team representing the turf pesticide industry and turfgrass regulators that has stake in developing regulatory models

In order for any of the model scenarios to be developed in a manner to impact the regulatory industry, each of the various groups must develop "ownership" of the project. Therefore a team was created involving members of pesticide registrants who have products used by the golf course industry and have experience with the pesticide regulatory process. Some members are also team members of the FIFRA Exposure Modeling Validation task Force (FEMVAT). Additionally members of the US EPA's Environmental Fate and Effects Division (EFED) of the Office of Pesticide Programs (OPP) were also included on the team as well as Mark Cheplick (Waterborne Inc). who is the author of PRZM and Dr. Larry Burns (EPA/ORD) who is the author of EXAMS. The team has met twice this past year and a protocol is being established for the team to review.

Objective 2. Occurrence of trichloropyridinol and hydroxychlorothalonil in lysimeters constructed into golf course greens

Lysimeter Construction

Six lysimeters were built into two practice putting greens at the Cherokee Town and Country Club in 1994 at the time of their construction. In 1999 the golf course was renovated and one of the original, smaller putting greens was removed leaving the larger putting green. At this time, additional lysimeters were constructed into two of the course greens, #12 and #15. Each lysimeter consisted of a stainless steel sink (38 cm x 53 cm) with 0.635 cm diameter stainless steel tubing attached to the drain. The construction of each of the lysimeters in the 1999 greens was similar to that of the 1994 greens except that Teflon tubing was used in place of the stainless steel tubing. Each sink was situated such that the drain-line sloped to a water-valve box placed just off the collar of the green. With this arrangement leachate flowed via gravity to a stainless steel container in the valve box. Lysimeters were placed into the greens after the gravel had been laid, but before the addition of greens-mix. After the placement of the lysimeters, the greens were filled with greens-mix to USGA specifications and planted in Krenshaw bentgrass.

Green Leachate Monitoring

Leachate from the putting greens was monitored from November 1997 – December 1998 in the small putting greens. In January of 1999 the small putting green was removed and monitoring continued for the large green. Leachate was monitored from the 1999 course greens from the time of their construction in 1999. During this time daily rainfall was monitored with a weather station constructed at the site. The weather station at Cherokee was removed in January of 1999 and was not restored until June of 2000. Thus weather data from January of 1999 to June of 2000 was based upon data collected from a weather station approximately 15 miles away at the Atlanta Athletic Club.

Lysimeter drains were checked at least on a weekly basis for drain water or immediately after rainfall events as recorded by the weather station. At the time of collection the volume of water in the container was measured and water was poured into an amber glass jar with a teflon-lined lid. The stainless steel containers were rinsed with fresh water and replaced into the valve boxes. The water samples were then transported on ice to the lab and stored refrigerated at 2 degrees or frozen until analysis.

Chlorpyrifos and chlorothalonil were applied respectively as Dursban Pro[®] and Daconil[®] to the greens by golf course staff who recorded date and amount of pesticide applied to the green. These products are typically two of the most heavily applied pesticides to golf course greens in the south.

Leachate Analysis.

Chlorpyrifos, chlorothalonil, and each of their degradation products, HC and TCP, were analyzed by direct injection of 1.0 mL of filtered leachate water onto a Waters HPLC outfitted with a variable wavelength UV absorbance detector set at 220 nm. Analytes were eluted from a 25 cm long C-8 column with 5 μ m packing (Alltech Associates) with an acetonitrile:aqueous phosphoric acid gradient ramped from 10 % to 90 % acetonitrile over 30 minutes. The analytes were detected by UV absorbance at 220 nm. To confirm the presence of HC and TCP, approximately 15 % of the leachate samples were analyzed

by GC/MS. For these samples, a 50 ml aliquot was acidified to pH 2 with 1 M HCl and extracted into 25 mL of ethyl acetate by liquid-liquid extraction. The extract was dried over anhydrous sodium sulfate, reduced in volume under nitrogen and derivatized with diazomethane. Analytes in the extract were analyzed on a Hewlett Packard 5890 gas chromatograph with a HP 5971 mass selective detector using a 30 m DB-5 capillary column with 1.2 μ m film thickness. After an initial hold time of 1 minute at 60° C, the column was raised to 160° C at 15° C/minute and then to 270° C degrees at 8° C/minute over 20 minutes.

Objective 3. Investigate the potential of hydroxychlorothalonil to be degraded by sunlight in water.

To determine the potential for direct photolysis to be important for HC the UV absorption spectra of a 5 ppm (M) HC was obtained in solutions of water buffered at a concentration of 0.01 M at pH values of 5, 7, and 9 in acetate, phosphate and borate buffers respectively. Absorption spectra were acquired between wavelengths of 190 and 500 nm using a Beckman DU640B spectrophotometer.

To determine the photolysis rate, solutions of HC were prepared at a concentration of 5 ppm in distilled-deionized (DI) water, water buffered (phosphate) at pH 7.0, filter-sterilized pond water. As no differences were observed in UV absorption between pH values(Figure 1), kinetic experiments were not conducted at pH values of 5 and 9. For kinetic experiments, solutions were placed into 2 mL capped clear borosilicate glass vials and irradiated at 25° C in a temperature-controlled growth chamber outfitted with florescent lamps simulating the UV output of sunlight (figure 1). This system has been used in prior experiments to investigate the photodegradation of chemicals in water. Solutions used as dark controls were placed into amber vials. All experiments were run in duplicate and dark controls were run simultaneously with solution set. Samples were withdrawn at 0, 20, 40, 60 and 120 minutes. Water samples were analyzed by direct injection of the water sample onto a Waters 2690 High Performance Liquid Chromatograph (HPLC) with UV detection at 220 nm using a photodiode array detector.

PROGRESS AND RESULTS

Occurrence of Hydroxychlorothalonil and trichloropyridinol in leachate.

Water samples collected prior to 1997 were analyzed only for nitrate and phosphate fertilizers and were not analyzed for pesticides. Spray records indicated that 51.147 kg of chlorothalonil and 1.73 kg of chlorpyrifos were applied to the greens between 1995 and 1997, thus the soil was likely to contain HC and TCP from these prior applications. During the monitoring period of 1997-1998, 23.44 kg and 0.576 kg of each was applied. The amounts for chlorothalonil used up to 1997, and chlorpyrifos throughout the monitoring period, are typical of the amounts of each chemical used on golf course greens in the southeastern US to curb insect and disease pressure in turf and are summarized in figure 2. During the late summer and fall of 1998, these particular greens came under heavy disease pressure and the golf course superintendent increased the amount and frequency of chlorothalonil applications.

Large volume injections onto the HPLC allowed each of the analytes to be measured with a quantitation limit of 0.05 ppm. Recovery checks in both distilled-deionized water and spiked leachate samples showed that less than 5% of any analyte was

lost to the Teflon filter. Between November 1997 and October 1998, 105 leachate samples were collected and analyzed for the presence of each analyte. During this period, 48.29 inches of rain were recorded at the golf course, which is very typical of rainfall in the Atlanta, Georgia area. During this same period approximately 255 liters of water were collected from the lysimeters. These same greens are also regularly irrigated by the superintendents, however experience with these lysimeters has shown that only rainfall events result in water moving into the lysimeters.

Chlorpyrifos was not detected in any sample and chlorothalonil was detected in one sample at 0.12 ppm. These results are not surprising given the relatively high soil adsorption coefficients of each compound. Additionally the thatch of golf course greens tends to have a higher organic carbon content than the underlying rooting media, which would further retard the downward movement of non-polar pesticides. The degradation products TCP and HC were respectively detected in 63% and 87% of the samples. The highest concentrations were typically associated with periods of greater rainfall (Figure 3 and 4). The respective maximum concentrations of HC and TCP in green leachate were 2.21 ppm and 0.55 ppm whereas the median concentrations were 1.77 ppm and 0.15 ppm. HC was consistently present at higher concentrations and more frequently detected in leachate than TCP undoubtedly due to its higher and more frequent use for control of disease on greens. Based upon an area of 1.2 square meters and the volume of leachate collected from the lysimeters, 0.134 grams and 0.064 grams respectively of HC and TCP were leached from the lysimeter rooting media over a period of 1 year. Extrapolated to the area of the entire green and assuming the concentrations of chemicals in leachate are representative of the mass exported from green tile drainage, 335 grams of HC and 160 grams of TCP would be expected to be transported from the green in leachate. On-going monitoring is continuing on the large putting green as well as on greens #12 and #15. These data are shown in figures 5-8 which also includes data on the small putting green separated from the large putting green.

These data are consistent with the available literature in that chlorothalonil has been reported to be converted to HC in soil with half-lives ranging from 5 to 36 days and HC has been reported to dissipate slowly in soil after it is formed following use in cereal crops in Europe and use in peanut fields in the southeastern US. The fate of chlorothalonil in turf and soil has been reviewed, however all of the investigations appear to focus on the parent chemical and suggest that it is quickly degraded in the soil environment or bound to the soil or thatch. This data supports the hypothesis that degradation is occurring, however it does not appear that chlorothalonil is extensively degraded and the degradation products appear to be rather persistent.

Limited acute toxicity data has been collected on HC and TCP. Reported acute LC₅₀ values for HC are 15 - 45 ppm for bluegill sunfish, *Lepomis macrochirus* and 24 ppm for the water flea, *Daphnia magna*. Acute toxicity values for TCP range from 1-3 ppm for rainbow trout, *Oncorhynchus mykiss* and 12 ppm for *Daphnia magna*. However levels of HC and TCP at the high ppb and low ppm level were chronically present in this investigation and LC₅₀ values for chronic exposure are typically lower than for acute exposures. As the concentrations detected in lysimeters may be indicative of chemical levels present in tile drainage there is the potential for HC and TCP to accumulate in ponds or lakes and harm aquatic life should they be persistent in surface water. Thus

studies are needed to determine the persistence of these chemicals in the aquatic environment.

Photolysis of hydroxychlorothalonil

HC was shown to strongly absorb radiation within the sunlight spectrum (Figure 1) indicating direct photolysis would likely occur in aquatic systems. There was no significant change in the spectrum within the sunlight actinic range between pH values of 5 and 9 suggesting that degradation would not likely be affected by changes within the normal pH ranges of natural waters.

In all cases, no degradation was observed in any dark control solution. Experiments were highly reproducible with less than a 5 % difference between any replicate sample, thus the average values of samples at each time point were used to calculate half-lives. When exposed to simulated sunlight, HC dissipated rapidly from solutions of phosphate buffer ($t_{1/2} = 26$ min), DI water ($t_{1/2} = 32$ min), or pond ($t_{1/2} = 37$ min) water as shown in figure 9.

It is often difficult to estimate the importance of photolytic processes to chemical fate in natural water systems based solely upon laboratory data. In natural waters a pesticide can partition to sediment or suspended particulate matter and sunlight can be attenuated by natural components of water as a function of depth. The Exposure Analysis Modeling System (EXAMS) can be a useful tool for this purpose as it accounts for these complicating factors. To assess the significance of photolysis to HC fate in a pond setting, the dissipation of HC in a pond receiving green leachate was predicted using the US EPA's MS Pond scenario in EXAMS2.97.5 (need a reference for MS Pond). The values selected for the Koc (448) and soil half-life (6 months) were based upon literature data [2]. A 65 gram pulse of HC was simulated into a 1 ha pond that was 2 meters deep. This pulse is the maximum amount of HC observed in leachate from a single storm event from a golf course green that had received applications of chlorothalonil during the 1997-98 monitoring period. HC was predicted to occur at a maximum concentration of 3.25 ppb and to degrade with a half-life of 2.6 days in the pond (figure 10). Photodegradation was predicted to be responsible for 81 % of the degradation. HC was predicted to be virtually stable in water over a 30 day period if photodegradation were neglected. These data appear to be consistent with data showing little to no detections in surface water.

These data suggest that although formed in significant quantities in soil, HC should be rapidly and extensively degraded by sunlight in aquatic systems.

PROPOSED RESEARCH SCHEDULE FOR THE NEXT YEAR

Research the next year will encompass the following objectives:

- Finalize protocol for field leaching and runoff.
- Install autosamplers and flowmeters at field locations at the Golf Club of Georgia to monitor leaching and runoff.
- Monitor specific events (both natural and or irrigated) to generate leaching and runoff) following specific compounds.

- Initiate laboratory investigations on pesticide fate using field site soil as necessary for individual probe molecules.
- Based upon the data, prepare for preliminary modeling investigations.

Publications and Presentations

Armbrust, K.L. Occurrence of Chlorpyrifos and Chlorothalonil Degradation Products in Lysimeter Leachate from a Golf Course Green. Pest Management Science (In Review).

Armbrust, K.L. (2000). *Photodegradation of Hydroxychlorothalonil in Aqueous Solution*. American Chemical Society Annual Meeting, Division of Agrochemicals. San Francisco, CA. March 26th – 30th, 2000.

Armbrust, K.L. (1999). *The Occurrence of Chlorothalonil and Chlorpyrifos Degradation Products in Leachate from Golf Course Greens*. Society of Environmental Toxicology and Chemistry. Philadelphia, PA. November 14-18, 1999.

Figure 1. UV absorption spectrum of hydroxychlorothalonil in pH 5, 7 and 9 buffered solutions overlayed and the output of the florescent bulbs (Light Sources F40 BL) and sunlight as measured in June in Griffin, Georgia.

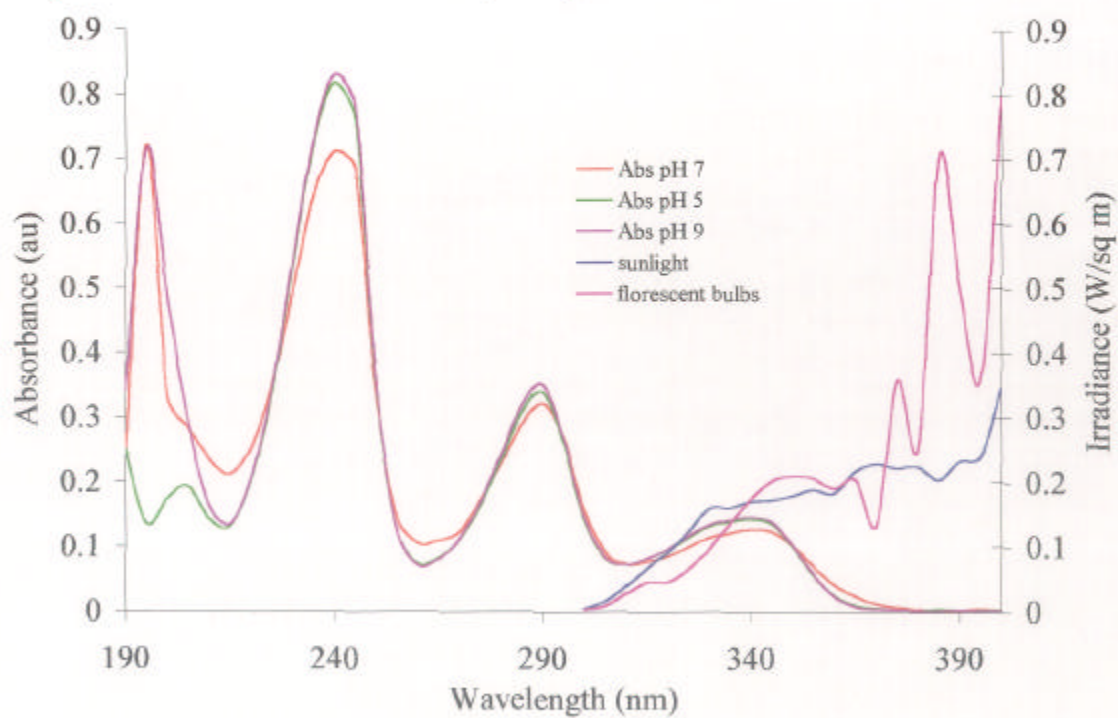


Figure 2. Cumulative Mass of Chlorothalonil (diamond) and Chlorpyrifos (square) Applied to Putting Greens (1995 - 1998)

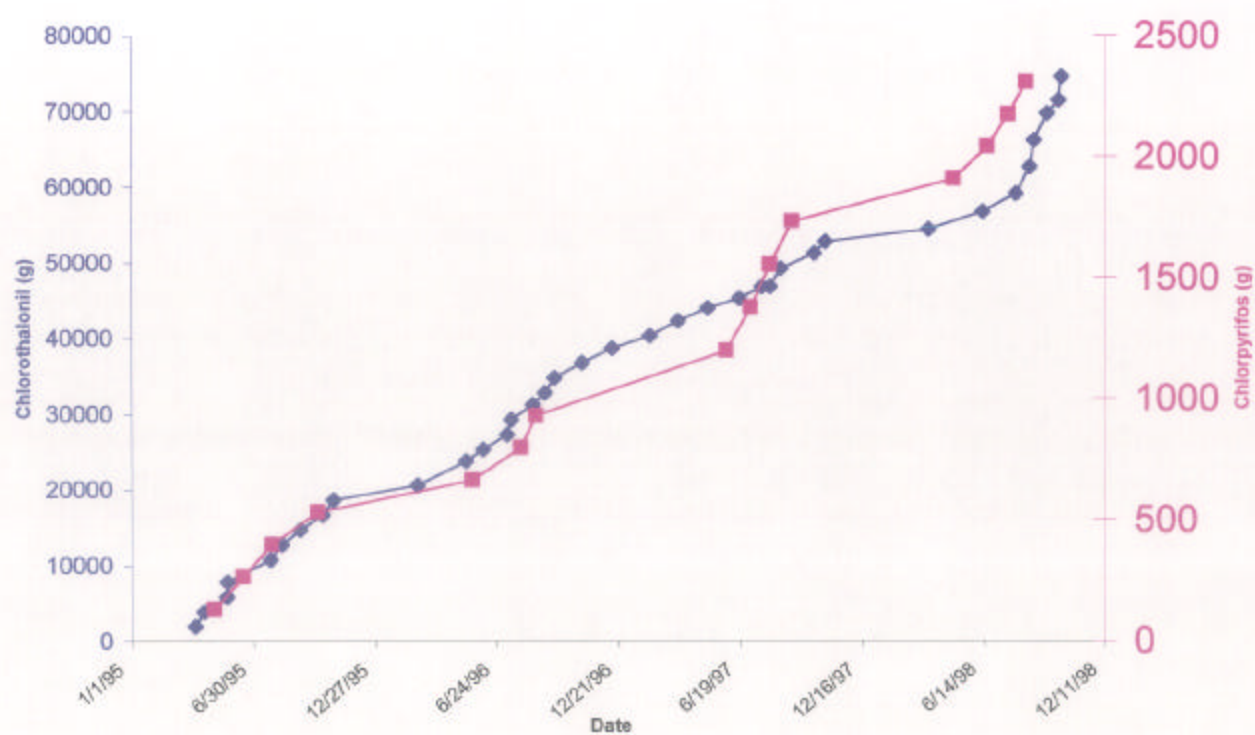


Figure 3. Concentration of HC in green leachate.

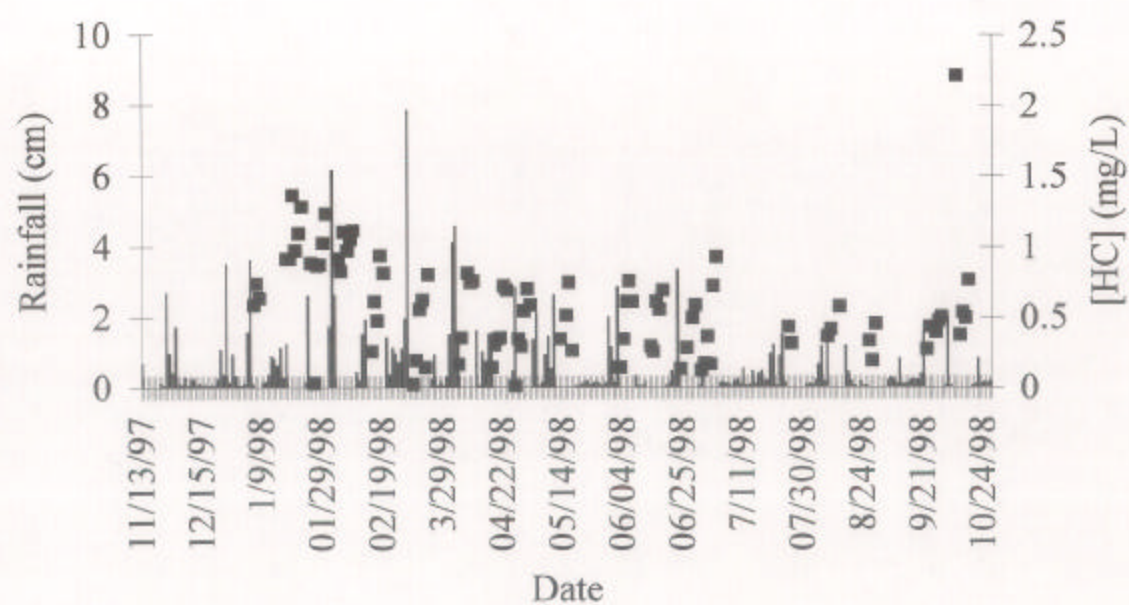


Figure 4. Concentration of TCP in Lysimeter Leachate

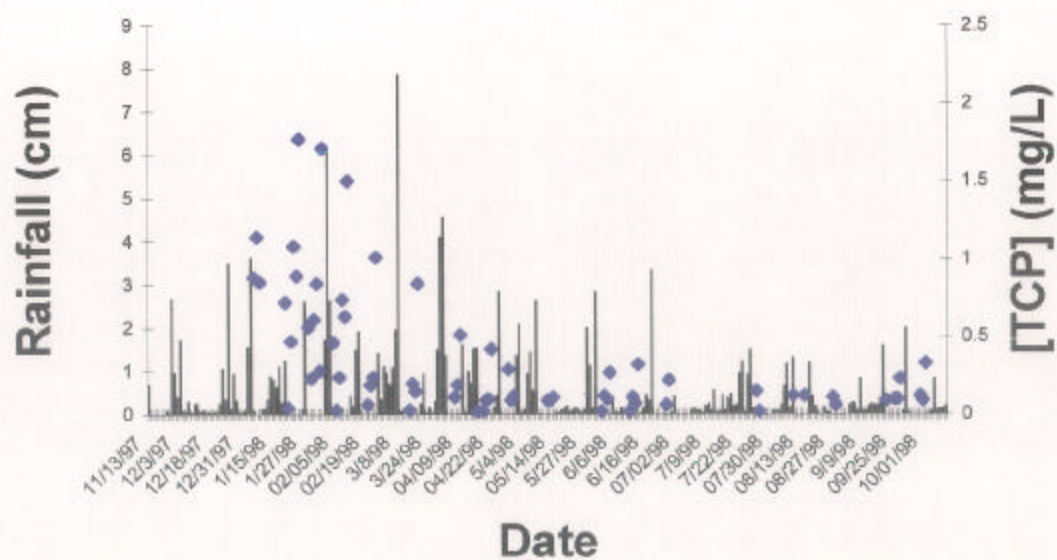


Figure 5. Concentration of hydroxychlorothalonil in lysimeter leachate collected from the #15 course green at Cherokee Town and Country Club. Rainfall (red x). Other symbols are data from individual lysimeters in the green.

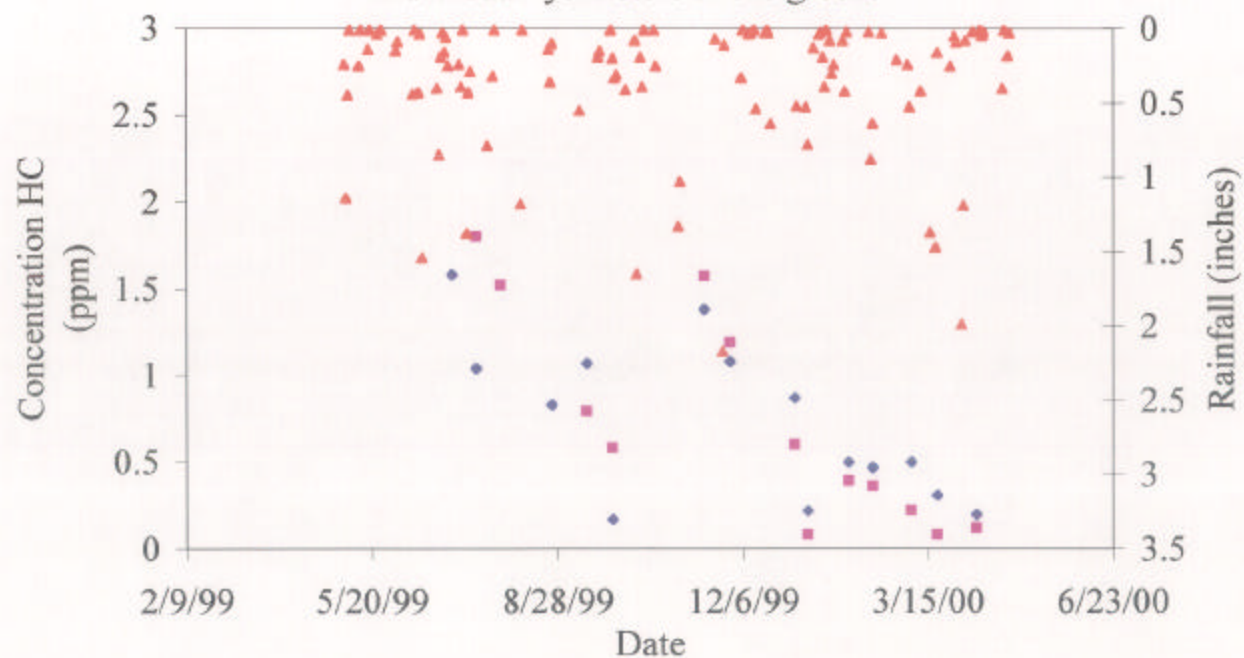


Figure 6. Concnetration of hydroxychlorothalonil in lysimeter leachate collected from the #12 course green at Cherokee Town and Country Club. Rainfall (red x). Other symbols are data from individual lysimeters in the green.

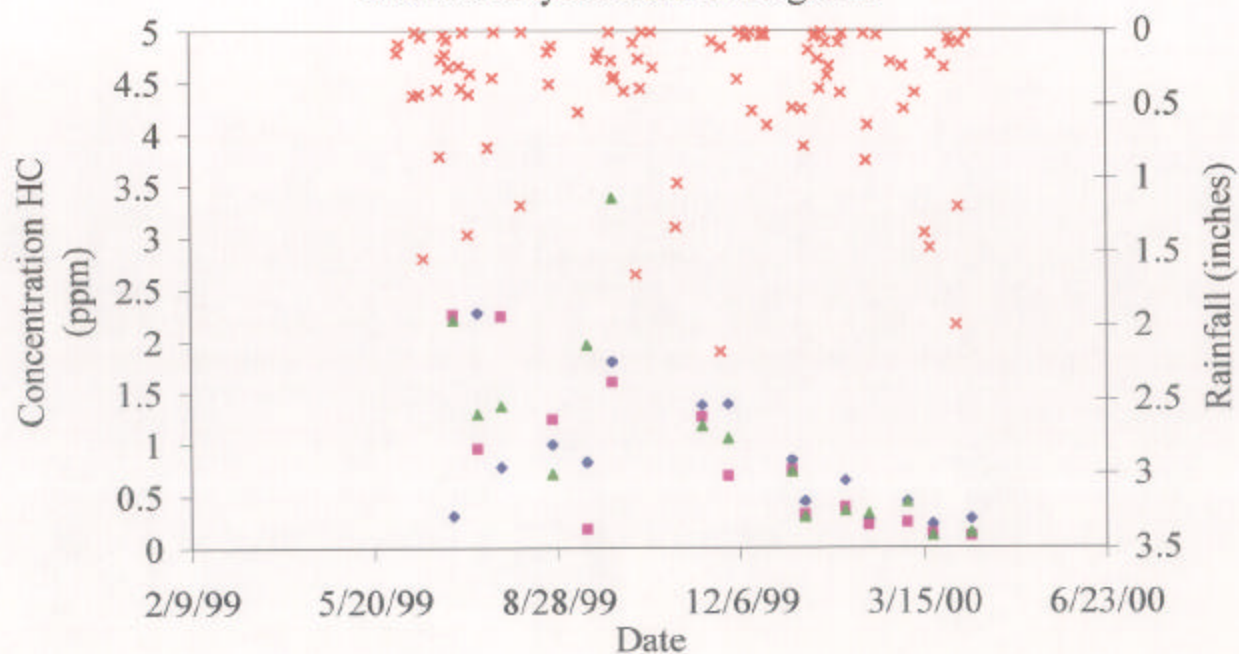


Figure 7. Concnetration of hydroxychlorothalonil in lysimeter leachate collected from the small putting green at Cherokee Town and Country Club. Rainfall (red x). Other symbols are data from individual lysimeters in the green.

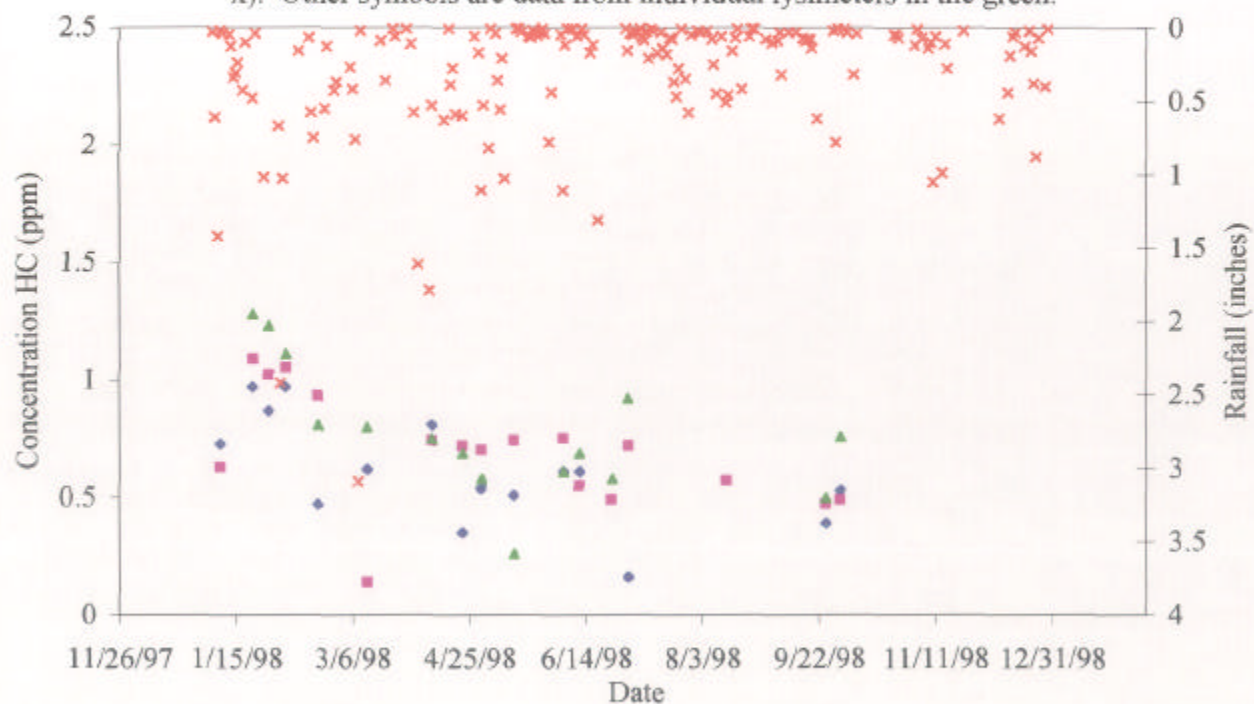


Figure 8. Concentration of hydroxychlorothalonil in lysimeter leachate collected from the large putting green at Cherokee Town and Country Club. Rainfall (red x). Other symbols are data from individual lysimeters.

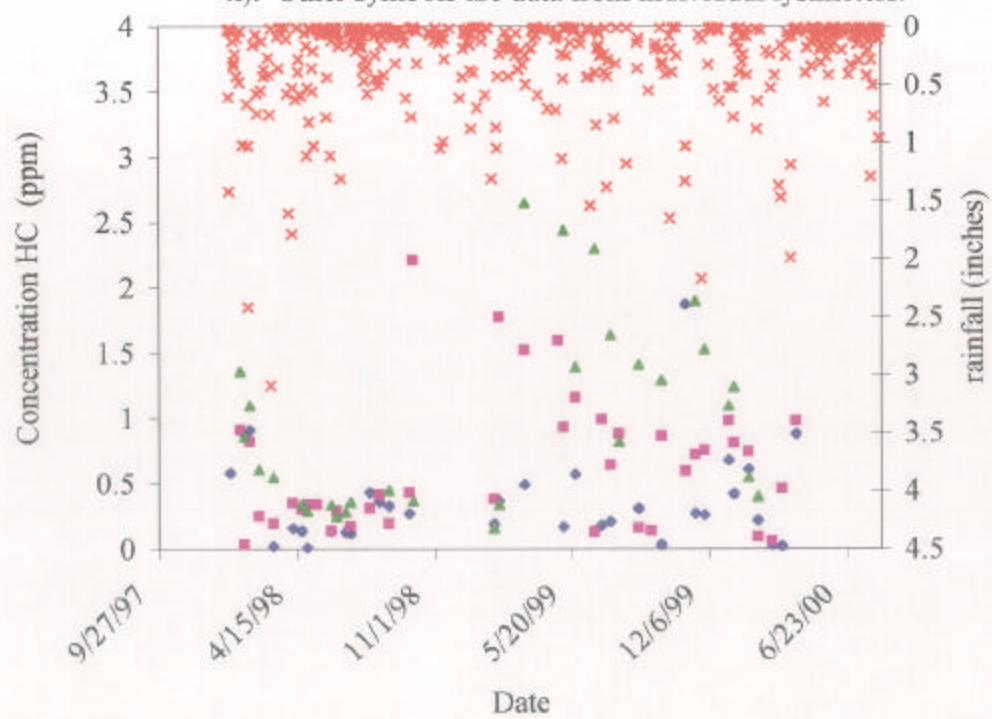


Figure 9. Photodegradation of Hydroxychlorothalonil in Aqueous Solution

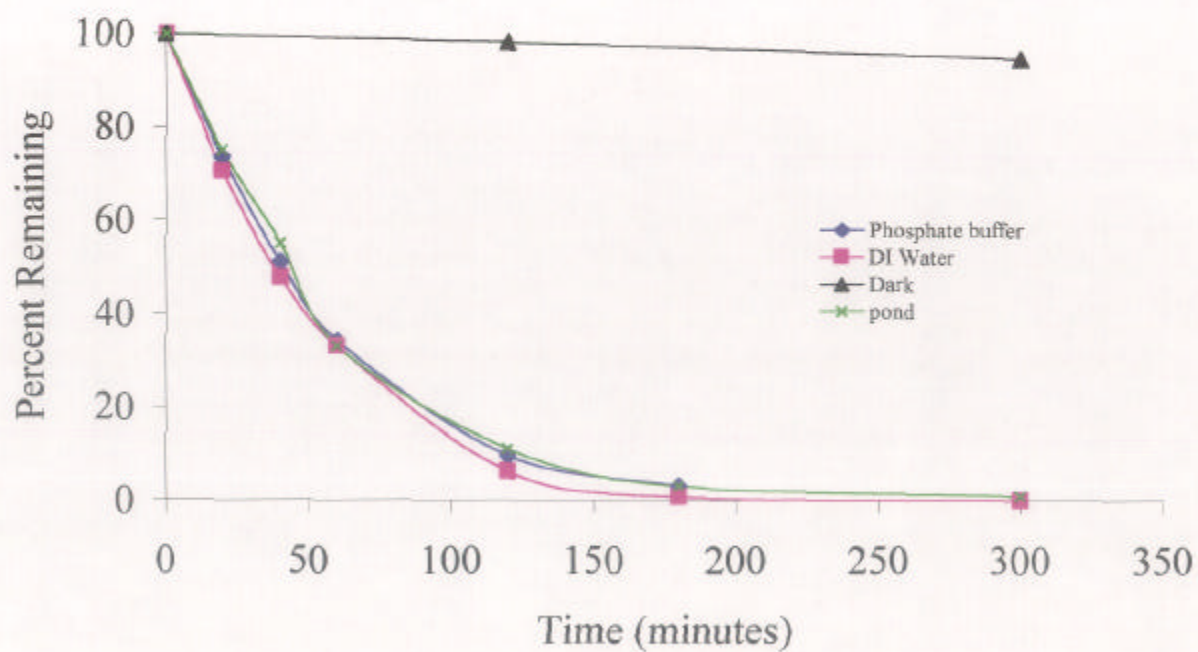


Figure 10. Predicted degradation of hydroxychlorothalonil in a pond receiving golf course green leachate. Prediction was through computer simulation using the U.S. EPA's MS Pond scenario in EXAMS 2.97.5.

