Evaluation of the Potential Movement of Pesticides Following Application to Golf Courses

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POTENTIAL MOVEMENT OF CERTAIN PESTICIDES FOLLOWING APPLICATION TO GOLF COURSES

1997 Annual Report and Project Summary Report Submitted to United States Golf Association

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Executive Summary.

The objectives of our research program over the past 6 years has been to evaluate the potential movement of pesticides and fertilizer components following application to golf courses and to develop Best Management Practices to reduce the potential for pesticide transport to potable water systems. The initial steps for evaluating the potential movement of pesticides has been accomplished using pesticides registered for use on golf course greens and fairways on simulated greens and fairways at the Georgia Experiment Station. The facilities were constructed at the Georgia Station and analytical procedures were developed in our laboratories for this research program. Our simulation facilities were developed for the control of the environmental parameters in order to determine the potential transport of pesticides through the soil and in surface water runoff. Experimental control was necessary for defining and controlling the variable parameters that influence pesticide transport into the environment

Although, some of the recommended Best Management Practices resulting from our research program may already be in practice, there are no real data to support those practices. Additionally, there may be a concern for the choice of pesticides included in our research. Initially, we realized that the actual molecule used was not as important as to establish the characteristics of an expanse of molecular structures in the simulated greens and fairways (i.e. 2,4-D, dicamba, and mecoprop are not used on a lot of golf course greens but there is more research information available on these molecules than any other analytes). Therefore, we included 2,4-D, dicamba, and mecoprop in many of our simulated greens treatments. From these data we are developing models for predicting the potential movement of many molecules through golf course greens and from golf course fairways. In 1995 high school student conducted research to determine the potential risk from kneeling on a green that had been treated 2,4-D, mecoprop, and dicamba (included in 1995 annual report). Additionally, in 1997 a senior from Mercer University conducted research to determine the potential risk from licking a golf ball that had been rolled across a treated green and from chewing a tee that had been placed in a treated tee-box.

The construction of golf course greens according to USGA specifications results in the rapid infiltration and percolation of water through the rooting media and out the drain system onto surface drainage areas. At first inspection these characteristics could allow for the movement of large quantities of pesticides onto the surface drainage areas. Our data indicate that the quantities of pesticides transported through the simulated greens are very low. The more water soluble pesticides (i.e. 2,4-D; dicamba; and mecoprop) were found to have short residence time under the sod due to the rapid microbial degradation of the molecules. The pesticides with lower water solubilities (i.e. benefin, pendimethalin, dithiopyr, chrolothalonil, and chlorpyrifos) had higher soil sorption capacities increasing their residence time in the rooting medium (because of the sphagnum peat moss component) allowing for degradation even if the half-lives were much longer. This concept is best demonstrated by dithiopyr and the specific results are included in published reports and in previous annual reports. Assuming that the simulated greens mixture is a worst case scenario, it can be concluded that pesticide transport in soil water probably is not a major problem if the pesticides are applied according to the label and massive amounts of water are not applied after application. Certainly, the desired management practice would be to restrict incoming water to an amount slightly above the quantity lost by evaporation/transportation.

Loss of surface water from fairways is not uncommon and in some areas of the United States as much as 70% of the incoming water can be lost as surface runoff. Our simulated fairways were developed with a 5% slope which is considered average for the southeastern U.S. Also, the simulated rainfall intensities of 2.3 cm hr⁻¹ are not uncommon for summer rain events in the Piedmont Region. Results of our research indicate that the water solubility of the pesticide and sequence of rain events influenced the quantity of pesticides transported from the fairways. The more water soluble pesticides (i.e. 2,4-D; mecoprop, and dicamba) readily dissolve in the water during runoff and are transported from the treated fairway. The less water soluble pesticides (i.e. benefin, pendimethalin, chlorpyrifos, chlorothalonil, and dithiopyr) are resistant to transport in surface runoff (see 1995 and 1996 annual reports). We also present data to support the hypothesis that the soil moisture content at the time of applying pesticides influences the quantity of water and ultimately pesticide to be transported from the application site. A soil moisture content near the field capacity at the time of applying the pesticide results in as much as 5 times more pesticide to be transported from the fairway than a soil moisture content near the wilting point. The data indicate that sequencing irrigation prior to and following pesticide application could help reduce the quantity of water soluble analyte to be transported in surface water runoff. Additionally, more pesticide was transported from dormant sod than green sod.

Some pesticides (the insecticide trichlorphon) can be pressure injected into the thatch and rooting medium reducing the potential for transport of the pesticide in surface water. We found that pressure injection significantly reduced the quantity of the water soluble pesticides transported in surface water runoff from the fairway. Additionally, our

data indicate that a buffer zone between the point of application and the exit point does not reduce the fraction of the applied water soluble pesticide transported from the site. The buffer zone only dilutes the solution concentration due to a reduced area of treatment. Certainly, this does not imply that pesticide applications should be made up to the water's edge. It only substantiates that the transported water soluble analytes are in solution and buffer zones will not screen out the molecules. Buffer zones do screen out soil and foliage particles that have pesticides adsorbed to them and for this reason should be a part of the Best Management Practices.

Our data indicate that pesticides having a low water solubility generally have a high soil sorption capacity (K_{oc}) and will have a higher residence time on the foliage of the grass. These pesticides will have a higher probability of being removed with the clippings and could result in a nonpoint source of pollution as compared to water soluble pesticides that will be washed from the foliage surface. We found that as much as 20% of the dithiopyr was removed over a 10 week period on leaf clippings (See manuscripts in 1996 annual report specific data). The water solubility of dithiopyr would not allow for the analyte to be readily washed from the waxy surface of the leaf during simulated rain and irrigation events. These data indicate the importance of the management of the clippings following mowing the treated greens. Distribution of these clippings over the fairway or rough areas would be much better than accumulating the leaves for disposal.

The data on potential risk from kneeling on the treated green, licking a ball rolled across a treated green, and chewing on a tee placed in a treated tee-box indicate that the exposure is minimal especially at 24 HAT. However, 2,4-D, mecoprop, and dicamba were recovered from the simulated skin, ball, and tee indicating that although the potential risk may be low, it isn't wise to lick the golf ball or chew on the tee following use.

Data collected from lysimeters in the practice putting greens located at the Cherokee Town and Country Club indicate that very little of the chlorothalonil and chlorpyrifos were transported through the greens. However, nitrates and phosphates were found in the leachate from the greens and pointing out the need for additional research to determine the mode of phosphate transport.

In summary, our data indicate that golf course management should include environmental impact as a quality measure for a pest management strategy and the academy must recognize the importance for developing Best Management Practices based on reliable data. We commonly restrict the quality measure of a pest management strategy to its degree of control of the pest and the safety to the sod.

INTRODUCTION

Assuming that 2% of a golf course is managed as putting greens, there are 13,900 ha of greens in the U.S. which are constructed for maximum infiltration and percolation of water through the rooting media (RM). The RM composition, generally, includes at least 80% by volume (97% by weight) coarse sand allowing for rapid water percolation and having an extremely low cation exchange capacity. Additionally, soil sterilization is recommended during construction for weed and disease management. The sterilization ultimately influences soil microbial decomposition of applied pesticides. These characteristics of the RM could result in rapid movement of pesticides through the RM allowing for a potential source of contamination of the effluent water from the greens.

Fairways compose approximately 98% of the golf courses and are typically intensively managed. The fairways are developed on soils typical for the region and in the Piedmont these soils have a high clay content allowing for a low water infiltration rate especially when crusted. As much as 70% of the rainfall can occur as runoff water from the sloped areas. This surface water can eventually terminate in potable water containments.

The major concern for the impact of pesticides on the environment is their potential entrance into drinking water sources which is facilitated by movement in surface water and groundwater from the treated site. Although the predominance of the drinking water for rural areas comes from groundwater, much of the drinking water in urban areas is derived from surface water containments such as reservoirs. It is estimated that as much as 95% of the drinking water for some major metropolitan areas comes from reservoirs.

We developed a research program in 1992 to determine the potential movement of pesticides following application to golf courses. Funds for this research program were furnished by the United States Golf Association and the University of Georgia Agricultural Experiment Stations. The methods used in this research and the results have been reported in five previous annual reports and six semiannual reports submitted to the Greens Committee. Since the research has been a continuum, the same research facilities, with minor changes, have been used throughout the project for the various treatments. Analytical methods have been changed as new analytes are used in treatments to the existing facilities. Realizing that there are new members on the Greens Committee, we have included a brief description of the facilities and methods and more detailed descriptions can be found in previous semiannual and annual reports.

MATERIALS AND METHODS

Measurement of Pesticide Movement Through Simulated Greens

Greenhouse Lysimeters: Thirty-six lysimeters were constructed during 1991 by placing turfgrass growth boxes (40 X 40 X 15 cm deep) on top of the bases. The bottom of the wooden growth boxes was perforated steel and at the inside-center of the growth boxes a 13-cm length of polyvinyl chloride (PVC) tubing (15 cm diam.) was fastened to the bottom with acrylic caulk. The base of the lysimeter consisted of a 52.5 cm length of PVC tubing (15 cm diam.) with a cap over the bottom of the tube. The cap had a drain tube placed in the bottom for the collection of aqueous effluent in 1-L black glass bottles. The PVC bases contained 3 equally spaced (1.5-cm thick) rings of acrylic caulk on the interior to restrict edge flow. The growth boxes were designed for removal from the bases to allow for pesticide application to the turfgrass sod using a spray chamber at a location separate from the greenhouse in order to minimize contamination to the greenhouse.

Prescribed rooting medium (RM) (sand and sphagnum peat moss) was based on the percolation rate as determined for the sand used in the mixture. The distribution of the sand-particle size used in the RM was: (>2) 0, (1-2) 5, (0.5-1) 29, (0.25-0.5) 45, (0.1-0.25) 19, (0.05-0.1 mm) 1, and (silt) 1%. The RM component proportions were selected to give percolation rates of 39 and 33 cm hr⁻¹ as recommended for Penncross bentgrass and Tifdwarf bermudagrass, respectively. The RM mixture of sand and sphagnum peat moss at v:v ratios of 85:15 and 80:20 (87.7:2.3 and 86.8:3.2 by mass, respectively) resulted in the respective percolation rates as tested (Tifton Physical Soil Test Laboratory, Tifton, GA). The RM was steam sterilized prior to use. The lysimeter bases were filled with sized gravel (10 cm), coarse sand (7.5 cm), and RM (35 cm) in ascending sequence from the bottom simulating USGA specifications for greens construction. The layers were carefully packed into the tubes using a vibrating table. Prior to placement into the lysimeters, the 85:15 medium had a field capacity of 0.13 cm³ cm⁻³, a wilting point of 0.03 cm³ cm⁻³, and an effective saturated conductivity of 39.6 cm hr⁻¹. The 80:20 medium had a field capacity of 0.15 cm⁻³ and an effective saturated conductivity of 33.5 cm hr⁻¹.

The base of the lysimeter was located against the bottom of the growth box aligned with the PVC tube on the inside of the box for direction of the aqueous percolation from the center of the growth box into the base of the lysimeter. Although the total growth box was seeded with Penncross bentgrass or sodded Tifdwarf bermudagrass and treated to minimize edge effects, the only area of concern for effluent movement was the central area directly above the lysimeter base (176.6 cm²). The grass cultivars were sodded or seeded in all lysimeters allowing for the determination of the influence of the two organic matter contents in the rooting media on pesticide movement. The bases of the lysimeters were enclosed and cooled by an air conditioner in order to maintain the soil temperature between 18-21°C. The lysimeters were housed in a greenhouse covered

with Lexan^R thermoclear sheet glazing. The glazing had approximately 90% of the light transmission of monolithic glass and a transmission of 80% for the wavelengths between 400 and 1200 ηm. The ambient temperature was monitored and controlled with a steam heating system and water cooled pads.

The research was designed to simulate golf course greens following seeding of bentgrass and sodding bermudagrass onto RM. Treatments were made to established stands of Penncross bentgrass or Tifdwarf bermudagrass on predetermined periods. All treatments were replicated three times and all experiments were repeated at least once over time.

An automatic track-irrigation system was developed for controlling the rates and times for irrigation. The watering nozzles traversed a horizontal track located above the growth boxes at a speed of 2.9 m min⁻¹. The flow rate of the water was adjusted to 1.82 mL sec⁻¹ at 138 kPa. The daily irrigation of 0.625 cm of water and a weekly rain event of 2.5 cm were controlled with an automatic timer. These conditions were chosen to simulate management practices and average rainfall events for golf course greens in central Georgia. During watering the coefficients of variation were less than 0.08 across the boxes laterally and on the length of the track. The turf was mowed and clippings removed thrice weekly with a greens (reel-type) mower leaving 0.4 cm of verdure. Broadcast pesticide applications were made in 204 L ha⁻¹ water diluents at 160 kPa under compressed air. After the spray on the foliage had dried, the growth boxes were returned to the top of the tubes. The leachate in the sample bottles, at the base of the lysimeters, was collected on alternate days. The samples were stored in a refrigerator maintained at 4°C. The collections were combined for weekly intervals and quantified for pesticides in the leachate.

Field Lysimeters: The Field-lysimeter facility consisted of small greens subtended with lysimeters for directing the flow of water and pesticides into a collection area. The small areens were developed with similar RM as used in the greenhouse experiments. The RM of 85:15 and 80:20 (v:v) sand:sphagnum peat moss subtended Penncross bentgrass and Tifdwarf bermudagrass, respectively, according to specifications developed by USGA. The design of the lysimeters allowed for replacement of the RM at the end of the experiment if necessary. Stainless steel inserts placed into fiberglass jackets resulted in easy removal of each lysimeter. The interior diameter of each lysimeter was 55 cm and the depth was 52.5 cm allowing for layers of gravel, sand, and rooting media as developed in the bases of the greenhouse lysimeters. The tops of the lysimeters were located 5 cm below the surface for seeding the bentgrass and at the base of the sod for the bermudagrass and were plumbed in the bottom for the collection of the aqueous effluent from the rooting profile in closed stainless steel containers housed in a covered walkway located between the two greens. Controlled applications of irrigation water and fertilizer were according to cultural practices for maximum maintenance. Penncross bentgrass was seeded on 15 October 1991 and Tifdwarf bermudagrass was sodded during March, 1992. All broadcast pesticide treatments were applied with a CO₂ backpack sprayer in 252 L ha⁻¹ water diluent at 260 kPa. A horizontal moving irrigation system, similar to the one developed in the greenhouse,

was used to simulate irrigation and rainfall events and an automatic moving rain shelter was constructed for movement over the greens area during natural rain events. The event intensities and frequencies were similar to the ones described for the greenhouse. A complete fertilizer (N:20 P:20 K:20) was applied biweekly in water to an N rate of 2.44 g m⁻². The sod was mowed and the clippings removed using a greens (reel-type) mower leaving 0.4 cm of verdure. The treatments were applied in three replications randomized over the lysimeters for each cultivar.

Measurement of Pesticide Transport from Simulated Fairways

Twelve individual plots (3.7 x 7.4 m) were developed in a grid with a 5% slope from the back to the front. A ditch at the front of the plots was used for installation of a herbicide-collection trough to direct the runoff water into a tipping-bucket sample collection apparatus. The soil was a Cecil sandy clay loam (thermic Typic Hapludult) with a mixed surface horizon (49.8, 18.0, and 32.2% sand, silt, and clay; respectively). The slope was developed by removing the mixed top soil, forming the subsoil into the 5% slope, and returning the top soil over the entire area. The individual plots are separated by landscape timbers with the top edge located 2 cm above the soil surface to direct the runoff water within each plot. The plots were sprigged with 'Tifway 419' bermudagrass on 17 May 1993 and the surface soil was firmed over the sprigs using a rotary-drum packer. The plots were completely covered by 1 August 1993. The WobblerTM offcenter rotary action sprinkler heads (Senninger Irrigation Inc., Orlando, FL) were mounted 7.4 m apart and 3.1 m above the sod surface. The system operated at 138 kPa resulting in a very even distribution of the simulated rainfall over the total area at a rainfall intensity of 3.3 cm hr⁻¹.

The treatments were initiated on June 1 1994, and have continued through 1996. All treatments were applied during the months of June through October to actively growing bermudagrass sod except the dormant treatment which was made during January, 1994 and 1995 to a dormant sod. Treatments were applied to the center 3.1 m of the plot width and for the total length resulting in a treatment area of 22.9 m². Spray treatments were applied using a backpack sprayer calibrated to deliver 206 L ha¹¹ at 166 kPa except for treatments applied through the pressure injection system. Selection of the specific treatment dates was based on meteorological forecasts that allowed for at least a 72-hr period with a low probability of rainfall. All treatments were replicated between 3-12 times and the experiments were repeated.

Rain events were simulated at 24 (2.5) hr prior to treatment and 24 (5.0), 48 (5.0), 96 (2.5), and 192 (2.5 cm) hr after treatment (HAT). Normal rainfall events were monitored during the sampling period and the subsamples were collected following the storm event and stored at 4°C. Following the simulated rainfall period normal rainfall events were monitored until herbicides in the runoff water were not detected. The runoff water was quantified and subsamples were collected by the tipping-bucket apparatus. Soil moisture was determined at the time of the first simulated rain event following treatment.

Influence of Management on Pesticide Transport in Surface Water

Dicamba, 2,4-D, and mecoprop were applied to plots not receiving the rain event for at least 120 hr prior to treatment to determine the influence of soil moisture on water runoff and pesticide transport. Additionally, 2,4-D was applied to the back 75% of the runoff plots to determine the influence of a 2-m band between application and point of collection to simulate a 2-m buffer strip between source point and off-site point receiving water. The rate of application to the remaining 75% of the plot was 2.24 kg ha⁻¹. 2,4-D and trichlorfon were applied through a high-pressure injection system under 21.3 MPa pressure and in 4,702 L ha⁻¹ to determine the influence of chemical injection into the sod/soil on analyte movement in surface water. The pesticides were applied at the same rates as the broadcast application methods for comparison. Storm simulation, sample collection, and analyte analyses were conducted the same as for samples from the normal broadcast application.

Pesticide Removal from Simulated Greens on Grass Clippings

The growth boxes used on the greenhouse lysimeters (described in previous annual reports) were used for this experiment. The sod on the growth boxes were maintained at a close clipping height. Five boxes were treated with mecoprop (1.68), dicamba (0.56) and 2,4-D (2.24 kg ha⁻¹). The treated boxes were mowed every 3 days, using a small hand held rotary mower, and the clippings were analyzed for the herbicides. The treated boxes were irrigated daily with 0.64 cm of water applied through a horzontal-movement track irrigation system. On days 3, 10, and 17 after treatment the growth boxes received a simulated rain event of 2.5 cm through the track irrigation system. The watering regimen would be similar to a sequence of events for golf course greens in the Piedmont Region. The herbicides remaining the clippings were extracted in 50% aqueous water and analyzed by gas chromatography.

Potential Pesticide Dose from Licking a Golf Ball and Placing a Tee in the Mouth

Since we were concerned with the tongue and lips as the body contact areas, these had to be simulated. The closest representation of these body parts was determined to be chamois leather. Artificial saliva was developed according to a method published in the Journal of Dental Research.

The field lysimeter area was used for this research. The mini greens were "Tifdwarf' bermudagrass. The greens were mowed every three days to height of 4 mm. The greens were treated with 2,4-D, mecoprop, and dicamba at 0.56, 1.40, and 0.28 kg/ha, respectively. After treatment, the greens were managed daily using practices commonly used on golf courses which included watering daily with 0.63 cm of water. Seventy-two hours after treatment they were mowed and the grass clippings were removed. The rainout shelter automatically closed during natural rainfall events.

A method for the release of the golf ball was developed to allow for a consistent simulation of a ball chipped onto the green. The apparatus was a 1.23 m PVC pipe

with a 2.5 cm diameter hole placed 15 cm above the mini green at a 45° angle. A gol ball was dropped down the tube and allowed to roll onto the green. Samples were taken at 0, 6, 30, 54, 78, and 102 hr after treatment (HAT) of the greens. To simulate the act of licking each golf ball, small pieces of chamois leather (2.5 X 2.5 cm) were cut to represent a human tongue. These small pieces of chamois leather were soaked in the artificial saliva for about 12 hr in order to wet the leather. These pieces would also be used to simulate the lips for the tee chew experiment.

In order to simulate the tee chew, clothes pins were used to apply pressure to the chamois surrounding the tee to simulate human lips. The tees were placed in the ground to a depth of 2.5 cm for 60 sec. The used tee was placed in a clothes pin which contained a piece of the wet chamois leather. The tee was pulled slowly through the leather in the clothes pin. Following the treatment period, the herbicides were extracted from the chamois leather pieces, ball lick, and tee chew, and were analyzed by GC.

The experiment was conducted twice by treating the east and west greens with the three herbicides. The ball-licking and the tee-chew activities were replicated four times and each sample was injected into the GC twice. All data were subjected to statistical analyses and means were separated by the standard error of the mean.

Nitrate, Phosphate and Pesticide Transport Through Golf Course Putting Greens

During the summer of 1994, three stainless steel lysimeters were placed in each of two practice putting greens during the renovation at a Town and Country Club in north Atlanta. The lysimeters were stainless steel sinks placed 5.0 cm below the surface of the green that was seeded to creeping bentgrass in August of 1994. The lysimeters were plumbed to the exterior of the greens for collection of leachate transported through the sand/sphagnum peat moss (85/15 v:v) greens mixture. The infiltration rate for the greens mixture was 37 cm hr⁻¹. The greens are maintained by the superintendent and records of fertilizer and pesticide applications are maintained.

Water samples are collected from the stainless steel sample-collection canisters and stored in a freezer (-9°C) until transported to the laboratory at Griffin, GA. All water samples are stored at 4°C until analyzed for NO₃-N and pesticides. Methods for analyses have been described in previous reports.

Extraction and Analysis of Pesticides

Dicamba, 2,4-D, and mecoprop were analyzed by procedures developed in our laboratory. Subsamples of 100 mL were transferred from the storage bottle into a 250 mL beaker. An internal standard (2,4,5-T) was added to the beaker and the mixed solution is acidified to a pH of 2 with 0.2M HCl. The pesticides were extracted from the acidified solution by liquid-liquid partitioning into 200 mL diethyl ether. The diethyl ether was evaporated and the analytes were esterified with triflouroethanol and the esters were quantified by gas chromatography using an electron capture detector (GC-ECD)

(citations for manuscripts are included in Published Reports listed in previous annual reports).

Dithiopyr was extracted by solid phase extraction and analyzed by GC-ECD according to a method developed in our laboratory (see published reports by Song Hong in Appendix). Benefin and pendimethalin were extracted from the 50 mL aqueous subsamples by liquid-liquid partitioning into 150 mL dichloromethane. The dichloromethane was concentrated under a vacuum to 1 mL and diluted with 1 mL toluene containing metribuzin as an internal standard. Analytes were quantified by GC-ECD. The trichlorphon was extracted from the water with ethyl acetate and the ethyl acetate was injected directly into the GC.

Chlorothalonil and chlorpyrifos were extracted by liquid-liquid partitioning into ethyl acetate. The ethyl acetate volume was reduced under vacuum to 1 mL and the hydroxy metabolites of chlorpyrifos and chlorothalonil were methylated using 1 mL diazomethane and 0.034 g silica gel. Following a 30 min reaction period and ether dry down, the solution containing the analytes and methylated metabolites was brought to volume with ethyl acetate containing dicamba-methyl ester as an internal standard.

The 2,4-D extraction from the soil samples, was adapted from published procedures and procedures developed in our laboratory. The soil samples were extracted twice with 250 mL acidified acetone. The acetone was filtered from the mixture and evaporated under a hood. The 2,4-D was dissolved in diethyl ether and transferred to esterification vials. The internal standard (2,4,5-T) was added to the vial, the diethyl ether was evaporated, the herbicides were esterified with diazomethane, and the methyl esters were quantified by GC-ECD. The diazomethane was prepared fresh each day. The extraction and quantification systems were established to give a minimum detectable concentration (MDC) of 1 μ g L⁻¹ in the aqueous effluent. Column and conditions for the GC-ECD are listed in TABLE 1.

TABLE 1. GC-ECD operating conditions for the analytes analyzed.

		Temperatures (°C)					
Analyte	Column	Gas ¹ flow	Inlet	Detector	<u>Col</u>	umn	Program rate
		(ml min ⁻¹)			initial/(min)	final/(min)	(°C min ⁻¹).
benefin	RTX-1	12	270	300	160/3	192/5	30
pendimethlin	RTX-1	12	270	300	160/3	270/3	40
2,4-D	RTX-1	14	250	300	136/8	250/3	30
dicamba	RTX-1	14	250	300	136/8	250/3	30
mecoprop	RTX-1	14	250	300	136/8	250/3	30
chlorpyrifos	RTX-35	14	250	300	150/3	178/5	30
chlorothalonil	RTX-35	14	250	300	150/3	250/3	30
trichlorphon	RTX-35	10	250	335	120	156/.5(25	60/1) 4(15)

¹ Carrier gas=helium; Make-up gas=Ar/methane (5/95%)

RESULTS AND DISCUSSION Pesticide Transport Through Simulated Greens, Summary

The data for the second year repeat of the study on chlorpyrifos, chlorothalonil, and dithiopyr were added to the data base presented in previous annual reports (TABLES 2&3). These data indicate that only a small fraction of the applied pesticides are transported through the greenhouse and field lysimeters. Less than 0.5% of the treatment pesticides could be accounted for in the leachate from the lysimeters except the 2,4-D LV treatment in which 0.9% of the 2,4-D was found in the leachate. The high Standard Error (SE) of the mean is probably a response to the analyte concentrations being near the minimum detectible concentration (MDC) of 1 µg L-1. When the concentration of the analyte in the sample is less that 1 µg L-1 that sample concentration reverts to 0 (i.e. an analyte concentration in the effluent of 0.9 µg L-1 would be registered as 0 and a concentration of 1.1 µg L-1 would be regestered as actual concentration). The experiments on chlorothalonil and chlorpyrifos for both lysimeter locations were repeated during the summer of 1996 and the data have not been compiled at this time. The highest concentration for chlorpyrifos in the effluent from the greenhouse lysimeters (42.4 µg L⁻¹) occurred from one weekly sampling. The data for chlorpyrifos transport from the field lysimeters indicate that the highest weekly concentration for chlorpyrifos was only 7.2 µg L⁻¹. We have presented data that indicate that projections by the GLEAMS model on 2,4-D transport would be much greater received in this study. We have also presented data that show that the half-life for 2.4-D in the turfgrass sod is much lower than used in the GLEAMS simulation (1996 annual report).

TABLE 2. Pesticide transported from greenhouse lysimeters containing Penncross bentgrass or Tifdwarf bermudagrass on two rooting medium (RM) mixtures (vol. coarse sand:vol. sphagnum peat moss).

		Application	Highest	Total pesticide transported
RM	Pesticide	rate	concentration	over 70 days
		kg ha ⁻¹	μg L ⁻¹	% applied±SE
85:15	2,4-D DMA ¹	0.28	3.5	0.43±0.31
	2,4-D LV ²	0.28	5.8	0.92±0.81
	dicmba DMA	0.07	0	0
	mecoprop DMA	0.56	3.3	0.44±0.42
	dithiopyr EC ³	0.56	2.4	0.17±0.10
	dithiopyr G⁴	0.56	2.4	0.15±0.32
	chlorpyrifos	1.14 (monthly)	42.4	0.2 <u>+</u> 0.1
	chlorothalonil	9.5 (twice month	ly) 9.5	0.01
80:20	2,4-D DMA	1.12	3.2	0.05±0.04
	dicamba DMA	0.28	3.6	0.20±0.16
	mecoprop DMA	1.40	3.8	0.16±0.14
	dithiopyr EC	0.56	1.9	0.23±0.18
	dithiopyr G	0.56	1.5	0.24±0.18

¹ DMA=dimethylamine salt analyte ² LV=butoxyethyl ester analyte

³ EC=emulsifiable concentrate formulation ⁴ G=granule formulation

TABLE 3. Pesticide transported from field lysimeters containing Penncross bentgrass or Tifdwarf bermudagrass on two rooting medium (RM) mixtures (vol. coarse sand:vol. sphagnum peat moss).

RM	Pesticide	Application rate kg ha ⁻¹	Highest concentration µg L ⁻¹	Total pesticide transported over 70 days % applied±SE
85:15	2,4-D DMA ¹ dicamba DMA mecoprop DMA dithiopyr EC ² dithiopyr G ³	0.28 0.07 0.56 0.56 0.56	0 1.22 0 2.41 1.67	0 0.5±0.4 0 0.49±0.26 0.44±0.32
	chlorpyrifos chlorothalonil	1.14 (monthly) 9.5 (twice month	7.2 ly) 2.6	0.01±0.01 0.01±0.01
80:20	2,4-D DMA dicamba DMA mecoprop DMA dithiopyr EC dithiopyr G chlorpyrifos chlorothalonil	1.12 0.28 1.40 0.56 0.56 1.14 (monthly) 9.5 (twice month	0 2.58 0 2.42 1.79 0	0 0.2±0.1 0 0.48±0.28 0.48±0.34 0 0.03±0.02

¹ DMA=dimethylamine salt analyte

Pesticide Transport in Surface Water from Simulated Fairways, Summary

Total summary data are included in this annual report and includes the second years data which was obtained during 1997. Twenty four hours prior to treating the plots at least 2.5 cm of irrigation or rainfed water, were placed on the plot area. At 24, 48, 96 and 192 HAT the plots received only simulated rainfall events at averages of 5.0, 5.0, 2.5, and 2.5 cm, respectively. Only samples collected over the first 192 HAT contained concentrations of the pesticides above the MDC of 1 µg L⁻¹. The average fraction of water leaving the plots as runoff following the respective simulated rain events were 44.8, 72.1, 40.0, and 35.5%. These high fractions of water leaving the plots are due to the relatively low infiltration rate of the soil and the high soil moisture content at the time of each simulated rain event. The highest concentrations of pesticides in the runoff water occurred during the first simulated rain event applied at 24 HAT and approximately 84% of the recovered analytes were transported during the first two simulated rain events.

The analytes having the highest water solubilities were found in highest concentrations in the water collected from the first rainfall event at 24 HAT (TABLE 4). The concentration of nitrate-N, mecoprop, 2,4-D, and dicamba in the runoff water from the first simulated rain event was 12,500, 810, 800, and 360 µg L⁻¹, respectively. The

² EC=emulsifiable concentrate formulation

³ G=granule formulation

magnitude of the concentration of these analytes in the runoff water was a response to the application rate and water solubility. The less water soluble analytes (benefin, pendimethalin, dithiopyr, chlorothalonil, and chlorpyrifos) were present in very low concentrations of less that $50~\mu g~L^{-1}$.

TABLE 4. Fraction of applied analyte transported from runoff plots and analyte concentration in runoff water from 24 HAT storm event.

Analyte	Application rate	Fraction transported	Concentration at 24 HAT
	(kg ae:ai/ha ⁻¹)	(%±SE)	(µg L ⁻¹)
Nitrate-N	24.4	16.4±3.1	12,500
Dicamba-DMA	0.56	14.6±2.2	360
Mecoprop-DMA	1.68	14.4±2.0	810
2,4-D-DMA	2.24	9.6±2.3	800
Dithiopyr	0.56	2.3±0.4	39
Chlorothalonil ¹	9.50	0.8±0.3	290
Chlorpyrifos ²	1.12	0.1±0.1	19
Benefin	1.70	0.01	3
Pendimethalin	1.70	0.01	9

¹ Total for chlorothalonil and OH-chlorothalonil.

The average of 16.4, 14.6, 14.4, and 9.6% of the applied nitrate-N, dicamba, mecoprop, and 2,4-D, respectively, were transported in the runoff water over the treatment period. Lower fractions of the less water soluble analytes were transported over the same period. Less than 1% of the applied chlorothalonil, chlorpyrifos, benefin, and pendimethalin were transported from the treated plots (TABLE 4).

The relationship of analyte fraction transported to the log of the analyte solubility in water (pSw) was better fit by a quadratic (y=a-bx+c) (R^2 =0.96) than a linear (y=a-bx) function (R^2 =0.86) (FIGURE 5). The data indicate the close relationship between the water solubility and the potential for transport of the analyte in surface water runoff from the treated site.

² Total for chlorpyrifos and OH-chlorpyrifos.

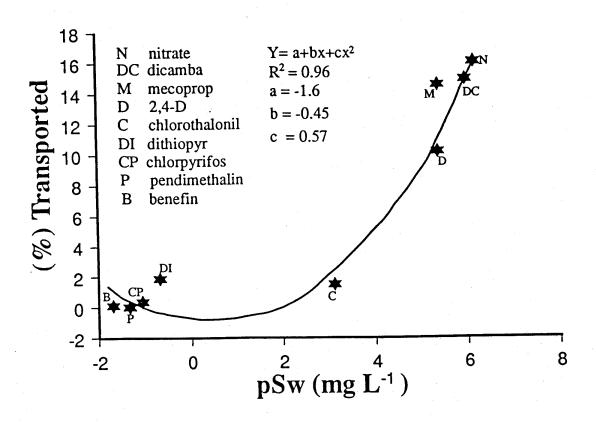


FIGURE 1. Fraction of the applied pesticides transported from simulated fairway plotted for the log of the water solubility (pSw) of the analyte.

The simulated fairway system was developed in the Piedmont Region on a kaolinite-clay loam soil which resulted in at least 40% of the rainfall to leave the plots as surface runoff under the conditions of this research. Additionally, this runoff water transported moderately high concentrations of the treatment nitrate-N and the pesticides; 2,4-D, mecoprop, and dicamba; at 24 and 48 HAT. Concentrations of nitrate-N in the runoff water were slightly above the recommended (EPA guidelines) maximum contaminate levels in potable water (MCL) of 10,000 µg L⁻¹, and 2,4-D, in the runoff water, was a factor above the recommended MCL of 70 µg L⁻¹. Although, the concentration of chlorothalonil transported in the first simulated rainfall event was moderately high, it must be realized that much higher rates were applied compared to other pesticides and these data included the additive of the analyte and the highly water-soluble first-order metabolite (OH-chlorothalonil). Only 0.7% of the applied chlorothalonil was transported from the plots as analyte and metabolite during the experimental periods.

The soil in the treatment plots was near the saturated moisture level due to the rain simulation to the area at 24 hr prior to the treatment. This was accomplished to assure a similarity of soil moisture content on the treatment dates. Additionally, it must be realized that the runoff water will probably be diluted many fold prior to reaching potable water systems. The sequence of rainfall simulations, used in these experiments, would represent extreme conditions compared to normal rainfall occurrences in the southeastern U.S. However, it would not be uncommon for a lawn or golf course fairway to be watered 24 hr prior to treating with a pesticide and to receive additional water from a summer rainstorm 24 hr after treatment at an intensity used in this research. Additionally, the simulated rainfall is instantly turned on at maximum intensity as compared to a natural rainfall event which probably would not be at maximum intensity at the onset. A light shower prior to maximum intensity could allow the pesticides, having higher water solubilities, to be transported into the soil. Regardless of the conditions, these data would indicate that precautions must be exercised when applying pesticides, with high water solubilities, to lawns and golf course fairways, in the Piedmont Region.

These data are probably the first data of this type to be obtained from the Piedmont Region including turfgrass as a cover. Watschke described a series of plots established at Pennsylvania State University with slopes of 9 to 14% containing a turfgrass cover. Rainfall intensities as high as 15 cm hr⁻¹ were needed to obtain runoff.

Although conclusive evidence of health effects from long-term exposure to pesticides has yet to be established, there is intense public perception of risk concerning pesticides in drinking water. The EPA is currently establishing drinking water standards of reference doses for surface and groundwater. Standards will be based on the same toxicological research used to establish reference doses (formerly called Acceptable Daily Intake, or ADI) for food. These standards will be the MCLs allowed for pesticide concentrations in potable water. The MCLs for only a few pesticides used on turfgrass have been recommended. In addition to federal efforts to alleviate environmental quality concerns, state governments are also in the process of developing water quality regulations. State governments recognize the need to protect valuable surface and groundwater resources through both education and enforcement. Some states, such as California, New York, Nebraska, and Wisconsin, have selected a regulatory approach to water quality issues. Others, including lowa, are legislating a combined approach of education, research, and demonstration. Because of this increasing interest it is imperative that we develop Best Management Practices to reduce the potential for pesticides to move from the site of application. We don't think that any quantity of pesticide in water should be considered too small to improve upon. However, our research has been directed toward the most apparent concern of reducing the potential for pesticide transport in the surface water in the Piedmont Region.

Influence of Management on Pesticide Transport from Golf Courses Successful pesticide application is dependent on a combination of a large number of parameters that involve the type of molecule, application method, and environmental conditions prior to, following, and at the time of application. Generally, pesticide application success is measured by the degree of pest control and the extent of turfgrass damage. Data in this report indicate that the degree of success should include the ability to restrict the potential for the pesticide movement from the application site. As was pointed out in a previous section, the application of certain pesticides, namely the analytes and metabolites that have a relatively high water solubility, could result in the transport of fairly high quantities of these molecules in the surface water runoff during intense rainstorm events. It is important to determine the conditions that result in the least potential for pesticides to be transported in runoff water following application to turfgrass.

Pesticides were applied to the runoff plots (TABLE 4) under fairly uniform environmental conditions in order to compare the relative transport of each pesticide. At 24 hr prior to treatment application, the plot area received at least 2.5 cm of irrigation or rainfed water. At treatment time the top 15 cm of the soil had a moisture content that was near field capacity (19.0% m.c. at 9 cm Hg). It would be considered to be a worst-case scenario to treat at field capacity and 24 hr before a rainstrom event delivering 5.0 cm water at 3.3 cm hr⁻¹. However, this probably is common on golf course fairways that receive irrigation during the summer just prior to a thunder storm.

Pesticide formulation: Research was conducted to determine the influence of pesticide analyte on transport from the treated plots. We found no significant difference in the fraction of 2,4-D applied or 2,4-D concentration in the transport water at the first storm event between the use of the ester (LVE) analyte of 2,4-D compared to the salt analyte (DMA) (TABLE 5). The lower water solubility for the ester analyte should result in lower potential for transport in the water. The lack of difference may be a response to the rapid hydrolysis of the ester analyte in the thatch during the 24 HAT period between treatment and first rain event and the resulting salt analyte would transport similarly to the DMA formulation.

Applications of granule formulations should reduce the potential for pesticide transport compared to broadcast application of a liquid formulation. Very low quantities of pendimethalin and benefin were transported regardless of the formulation and application and difference due to formulation could not be determined. However, a significantly higher fraction of dithiopyr was transported following liquid application compared to the granule application (TABLE 5). The difference, due to formulation, in fraction transported would probably be greater for the more water soluble pesticides. However, attendant to the assumption that the granules will not be transported in the runoff water is the assumption that the analyte will elute from the granule over time resulting in similar quantities of pesticide to be transported but this transport will be distributed over time resulting in lower peak concentrations of the analyte in the initial rain events. It is the concentration that is of major concern by the EPA as evidenced by their Maximum Contaminate Level in potable water system classification.

TABLE 5. Influence of formulation on pesticide transport from treated plots and analyte concentration in transport water from 24 HAT storm events.

Pesticide	Application rate	Analyte formulation	Fraction transported	Concentration at 24 HAT
	(kg ha ⁻¹)		(%)	(µg L ⁻¹)
2,4-D	2.24	DMA	9.6	800
2,4-D	2.24	LVE	9.1	812
benefin	1.70	liquid	0.01	3
benefin	1.70	granule	0.01	6
pendimethalin	1.70	liquid	0.01	9
pendimethalin	1.70	granule	0.01	2
dithiopyr	0.56	liquid	2.3*	39
dithiopyr	0.56	granule	1.0	26

Soil Moisture Content: Management practices that would reduce water transport from the site during the storm event should reduce the total fraction of pesticide to be transported from the treated area. A management strategy could include delaying treatment until the soil moisture is below the field capacity. We applied the more water soluble pesticides to the simulated fairway plots at soil moisture contents near the wilting point and field capacity (10.9 and 18.5%, respectively) (soil moisture content at 9 cm Hg=19.0% and at 15 bar=8.4%). The soil moisture content at the time of the routine applications 24 hr after a 5.0 cm rainfall event ranged between 18 and 19%. The quantity of the three pesticides transported from the treated sites was reduced by 3-fold when applications were made at the lower soil water content (10.9%) compared to the higher soil water content (18.5%) (TABLE 6). The 3-fold reduction in the fraction transported occurred at both rain events following treatment (24 and 48 HAT). Additionally, the quantity of water transported from the site was reduced by 3-fold when the storm event at 24 HAT occurred on the drier soil compared to the soil with the higher water content. Only 16% of the water left the plots, following the 24 HAT rain event, with the lower soil moisture content compared to 44% leaving the plots having a higher soil moisture content (TABLE 6).

The important lesson to be learned, from this information, is the importance of the role of soil moisture, at the time of pesticide application, on the potential transport of pesticides in surface runoff water. A second management practice involving the use of irrigation, to be researched next summer, will be to determine the influence of applying the pesticides to plots with soil moisture well below the field capacity and following the application with a small amount of irrigation (without runoff potential) to transport the pesticide into the soil. For post emergence herbicides, 4 hr of residence time on the leaf is generally adequate and a light irrigation following that time interval may be adequate to move the pesticide into the soil prior to receiving a rain event. Other management practices to increase the infiltration rate of the soil will be researched next year.

TABLE 6. Influence of soil moisture content at first simulated rain event following treatment (24 HAT) on the applied pesticide transported in runoff water at 24 and 48 HAT. Fraction transported is the % of applied pesticide and water transported.

	Application	Soil Moisture	Fra	action transp HAT	oorted
Pesticide	rate	24 HAT	24	48	Total : AVE
	(kg ae ha ⁻¹)	(%)	(% pesticide : % water)		
2,4-D - DMA	2.24	10.9	2.6 : 16	0.9 : 42	3.5 : 29
dicamba - DMA	0.56	10.9	3.1 : 16	1.6 : 42	4.7 : 29
mecoprop - DMA	1.68	10.9	1.3 : 16	0.6 : 42	1.9 : 29
2,4-D - DMA	2.24	18.5	7.3 : 44	2.3:70	9.6 : 57
dicamba - DMA	0.56	18.5	9.7 : 44	4.9 : 70	14.6 : 57
mecoprop - DMA	1.68	18.5	9.5 : 44	4.9 : 70	14.4 : 57

Winter Dormancy: Certain herbicides are commonly used during the winter months for the management of broadleaf weeds in fairways. The common herbicides recommended for this use include dicamba, mecoprop, and 2,4-D. The DMA salts of these acid herbicides have very high water solubilities and have been shown to be transported in runoff water from the simulated fairway plots. We treated the simulated fairway plots during December 1995 when the 'Tifway' bermudagrass was dormant. The soil moisture content was near field capacity at the time of treatment. Considerably more of the analytes were transported in the runoff water when applied during the dormant stage compared to applications during the nondormant stage (TABLE 7). Total fraction transported and the concentration of the analyte in the transport water at the 24 HAT rain simulation were greater for the treatments applied during the dormant stage compared to treatments applied during the nondormant stage.

Buffer Zone: The inclusion of a 2-m buffer zone at the terminus point for the runoff water from the simulated fairways did not significantly decrease the fraction of applied 2,4-D from the simulated fairway plots (TABLE 8). Even though 2% less of the applied 2,4-D was transported from the treatment containing the buffer zone compared to the treatment not having a buffer zone, the difference was not significant. The concentration in the 24 HAT rainfall event was considerably less in the transport water from the plots having a buffer zone compared to plots without the buffer zone. This difference was probably due to less treated area in the plots with the buffer zone and ultimately less herbicide available for transport. It isn't surprising that there was no significant influence of the buffer zone on herbicide transport since the analytes transported from a turfgrass site is primarily in solution, in the transport water, and not adsorbed to soil particles. Additionally, the buffer zone is also receiving the rain event and this water serves to only dilute the transport solution.

TABLE 7. Influence of winter applications to dormant sod on pesticide transport from simulated fairway plots and analyze concentration in the transport water from 24 HAT storm event.

Pesticide	Application rate Dormant		Fraction transported	Concentration at 24 HAT	
	(kg ae/ai ha ⁻¹)		(%±SE)	(µg L ⁻¹)	
dicamba DMA	0.56	no	14.6±3.1	360	
dicamba DMA	0.56	yes	37.3±5.4	752	
mecoprop DMA	1.68	no	14.4±	810	
mecoprop DMA	1.68	yes	23.5±4.9	1,369	
2,4-D DMA	2.24	no	9.6±2.4	800	
2,4-D DMA	2.24	yes	26.0±6.2	1,959	

TABLE 8. Influence of 2-m buffer zone between application and terminus for runoff on pesticide transport from simulated fairway plots.

Pesticide	Application rate (kg ae/ai ha ⁻¹)	Buffer zone	Fraction transported (%±SE)	Concentration at 24 HAT (µg L ⁻¹)
2,4-D DMA	2.24	no	9.6±2.4	800
2,4-D DMA	2.24	yes	7.6±1.8	495

Pressure Injection: Pressure injecting pesticides into the sod should reduce the quantity of pesticide to be transported from the sites. We used a Toro[™] pressure injection system for comparing pressure injection to the normal broadcast application of 2,4-D and trichlorphon. It is obvious, and we realized, that a post emergence herbicide, such as 2,4-D, would not be applied by pressure injection. However, 2,4-D was used as a test analyte along with the insecticide trichlorphon. Trichlorphon is very soluble in water and can be pressure injected for soil insect control. Pressure injection reduced the transport of 2,4-D and trichlorphon by seven and 5 fold respectively compared to broadcast spray application (TABLE 9).

Even when surface transport of pesticides is reduced by pressure injection, there is possibly a greater chance for pressure injected pesticides to be transported through the soil. We conducted an experiment using the outside lysimeter facility in which 10 lysimeters were treated with trichlorphon applied as a broadcast (BDCST) application and 10 lysimeters were treated using the pressure injection system (PI). The highest

fraction of trichlorphon was found in the effluent from the lysimeters treated by the broadcast method compared to the pressure injection system (TABLE 10). Approximately twice as much was transported over a 6-week period from the lysimeters treated by the broadcast method compared to the pressure injection method. These results were not expected and the reason for the difference cannot be explained, therefore, this research was repeated this past August and the combined data will be included in next year's annual report.

TABLE 9. Fraction of applied analyte transported from runoff plots and analyte concentration in runoff water from 24 HAT (hours after treatment) storm event.

Analyte	Application M ethod	Application Rate	Fraction Transported	Conc. ac 24 HAT
		(kg ae/ai/ha)	(%)	(μ g/L)
Trichlorphon +	BDCST1	9.15	31.3±2.50 ²	6,430
Dichlorvos	INJ	9.15	4.2±0.14	180
2,4-D	BDCST	2.24	9.6±1.82	800
	INJ	2.24	2.8±0.57	379
Dicamba	BDCST	0.56	14.6±2.12	360
	INJ	0.56	6.8±1.19	124
Mecoprop	BDCST	1.68	14.4±2.10	810
114 05 /	INJ	1.68	3.0±0.65	286

¹Mean \pm SE_x (0.05).

TABLE 10. Trichlorphon concentration [μ g/L(ppb)] in leachate and fraction (%) of applied trichlorphon transported through lysimeters under 'Tifdwarf' bermudagrass treated with 9.15 kg/ha trichlorphon by broadcast (BDCST) and pressure injection (PI).

		Concent	ration	Fraction Transported	
WAT	Analyte	BDCST	INJ	BDCST	INJ
t		(μ g/L ±	:SE _x)	(%)	
,					
1	Trichlorphon	0	55.7	<.01	< .01
	Dichlorvos	0	8.0	<.01	< 01
2	Trichlorphon	0	.0	0	0
	Dichlorvos	0	0	0	0
3	Trichlorphon	0	12.5	<.01	<.01
	Dichlorvos	0	8.5	<.01	<.01
4	Trichlorphon	330.0 <u>+</u> 132	403.5 <u>+</u> 104	0.1	0.1
	Dichlorvos	62.3 <u>+</u> 23	87.4 <u>+</u> 32	<.01	0.03
5	Trichlorphon	175.0 <u>+</u> 40	153.0 <u>+</u> 73	0.1	0.02
	Dichlorvos	5.3	86.0 <u>+</u> 31	0.05	0.01
6	Trichlorphon	42.7	18.3	<.01	<.01
	Dichlorvos	24.8	1.4	<.01	<.01
7	Trichlorphon	10.4	84.0	<.01	<.01
	Dichlorvos	64.3	0	0	0
8	Trichlorphon	0	16.6	<.01	<.01
	Dichlorvos	0	0	0	0
9	Trichlorphon	0	8.7	<.01	<.01
	Dichlorvos	0	0	0	0
10	Trichlorphon	0	. 0	0	0
	Dichlorvos	0	0	0	0

 SE_x = Standard Error of the Mean.

WAT=Weeks After Treatment

Pesticide Removal from Simulated Greens on Grass Clippings

It is generally accepted that a considerable proportion of the pesticides applied to golf course greens is removed on grass clippings during frequent mowings. There is a paucity of data available on the amounts of the applied pesticides that are removed with the clippings. Our research was conducted under controlled conditions in the greenhouse using the growth boxes containing 'Tifdwarf' bermudagrass utilized in the previous lysimeter research. The watering regimen was scheduled to simulate the normal irrigation and rainfall quantities, frequencies, and intensities for the Piedmont Region during the summer months (FIG. 3).

Our data indicate that 3.1, 5.3, and 5.7% of the applied dicamba, 2,4-D, and mecoprop, respectively, was removed with the treated grass clippings at the first harvest (FIG. 3). The cumulative fractions removed on the grass clippings increased, for each herbicide, over the 23-day experimental period. The data indicate that as much as 4.1, 5.8, and 6.8% of the applied dicamba, 2,4-D, and mecoprop, respectively, were removed on the grass clippings over the 23-day harvest period (FIG 3).

• Mecoprop 1.68 kg ai/ha Dicamba 0.56 kg ai/ha 2,4-D DMA 2.24 kg ai/ha

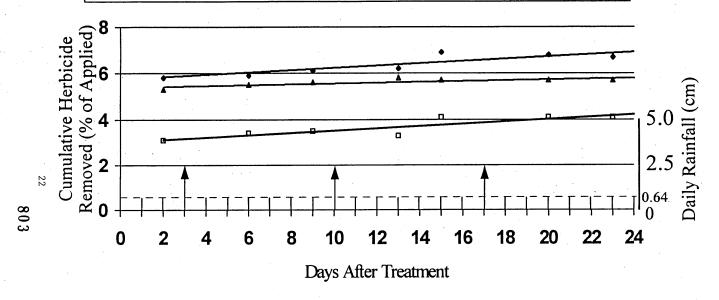


FIG. 3. Cumulative fraction of applied herbicide removed with grass clippings from simulated greens in the greenhouse under simulations irrigation adm rainfall events.

Potential Pesticide Dose from Licking a Golf Ball and Placing a Tee in the Mouth

Jennifer Starr and Al Smith

INTRODUCTION

If golf courses in the world were joined end-to-end, the total length would equal 132,000 km, 82,000 miles, or 4 times around the equator (Internet). With 800 million rounds of golf played annually around the world, 500 million of those are played here in the United States (Internet). A 1995 nationwide survey by the National Golf Foundation reported Georgia to rank 13th in the country in the total number of golf courses. Estimates suggest that the turfgrass industry size in Georgia is around 1.3 million acres making it one of the largest agricultural commodities in the state (Landry,1995). The cost to maintain just one acre of turfgrass is about \$660.00 per year. High quality turfgrass has become the expected necessity for golf courses and this condition requires the use of intensive management to control pests (Harris and Solomon, 1992). With such high standards, golf course superintendents are under a great amount of pressure to keep and maintain well-kept greens. Therefore, pesticides potentially harmful to humans and the environment are used in order to protect turfgrass from being invaded by weeds, insects, and diseases. The general public considers that golfers who enter areas that have been treated with pesticides may be at risk. The increasing interest and awareness by the general public for the environmental impact of pesticide use on turfgrass at recreational facilities is due to: (1) the increased use of pesticides since the 1960's and (2) the advancements in technology allowing scientists to detect pesticide presence at very low concentrations (Smith, 1994). There is a continuing debate on the potential risk that golfers take when entering a treated course, however, recent studies have shown that a maximum of only 6% of the originally applied herbicide 2,4-D can be dislodged from the turf immediately after spraying (Thompson et al., 1984). Additionally, they found that when the application is followed by rainfall or irrigation, this percentage drops to essentially zero. A possible reason for this is that turfgrass acts like a sponge and soaks up and binds the chemicals (Grossman, 1993). Common greens management requires the turf to be irrigated every morning. Since most courses do not allow golfers on to the course until 24 hours after treatment with pesticides, they are at virtually low risk to being exposed to large amounts of herbicide. However, because of the continuing debate, the United States Golf Association (USGA) is currently funding a \$3 million study on the use of pesticides on golf courses (Internet). A recent article released in Ireland in Gut Magazine suggests that golfers who lick the golf ball that is in play have a higher incidence of liver diseases (Howe, 1997).

The purpose of this research was to determine if herbicides commonly used on golf course greens are potentially harmful to golfers who repeatedly lick a golf ball and place a golf tee in their mouth. The hypothesis is: Golfers who repeatedly lick a golf ball or place a golf tee in their mouth are at risk of being exposed to herbicides such as 2,4-D, dicamba, and mecoprop which are used to control broad-leaf weeds on golf course greens.

MATERIALS AND METHODS

Materials: In order to determine whether the oral dose received by a person was significant, the LD₅₀ (oral dose) for rats was used. To create a realistic scenario, a material to best represent a human tongue had to be found. The closest representation to a human tongue was found to be the chamois leather because it has characteristics similar to a human tongue. Before the leather could be used, it had to soaked in a water bath for 48 hr in order to remove any chemicals that were used by the manufacturer to tan the product. Also, a small piece was removed to be tested by the gas chromatograph (GC) in order to establish the type of chemicals that were still in the cloth, whereas not to disrupt the readings taken from the later samples that could possibly contain the herbicides 2,4-D, dicamba, or mecoprop. Another important aspect of the project that had to be taken into account was the simulation of human saliva. The method to create saliva included mixing together several different chemicals to create a composition similar to that of human saliva. The artificial saliva was made by mixing the following: 0.1 L each of 25 mM K₂HPO₄, 24 mM Na₂HPO₄, 150 mM KHCO₃, 100 mM NaCl, and 1.5 mM MgCl₂. To this were added 0.006 L of 25 mM citric acid and 0.1 L of 15 mM CaCl₂. The pH was then adjusted to 6.7 with NaOH or HCl and the volume was made up to 1 L (Soderholm et al., 1996).

Herbicide Treatment: The mini greens used were 'Tifdwarf' bermudagrass. They were three years old and mowed every three days to a height of 4 mm. The greens (40 feet long x 3 feet wide) were treated with herbicides 2,4-D, mecoprop, and dicamba at treatment rates of 0.56, 1.40, and 0.28 kg/ha, respectively. After treatment, the greens were managed daily using practices commonly used on real golf courses which included watering daily with 0.63 cm of water. Seventy-two hours after treatment they were mowed and the grass clippings were removed.

Simulation of Putt: In order to create a consistent simulated putt in every trial, a method for the release of the golf ball was developed. The apparatus was a 1.23 m PVC pipe with a 2.5 cm diameter placed 15 cm above the mini green at a 45° angle. A golf ball was dropped down the tube and allowed to roll onto the green. Samples were taken for four trials every 0, 6, 30, 54, 78, and 102 hr after treatment (HAT) of the greens.

Simulation of licking ball: To simulate the act of licking each golf ball, small pieces of chamois leather $(2.5 \times 2.5 \text{ cm})$ were cut to represent a human tongue. These small pieces of chamois leather were soaked in the artificial saliva for about 12 hr in order to wet the leather. These pieces would also be used to simulate the lips for the tee experiment.

For each sample period eight golf balls were needed along with 24 empty vials and eight 50 ml empty beakers in order to hold the samples while out on the greens. Fifty percent (v/v) acidified methanol water mix was used as the ball wash after swiping the golf ball with the chamois leather. The swiping of the ball with the chamois leather was done in order to simulate the act of licking the golf ball. Each ball was swiped three times and was then followed by a ball wash. The chamois leather used to swipe the

ball was placed in the vials labeled TS1-TS4 (tongue simulation) and this was repeated eight times (four times on the east green and four times on the west green). The balls were placed in the labeled beakers (B1-B4, east and west).

Simulation of Tee Chew: In order to simulate the tee chew, clothes pins were used to apply pressure to the chamois surrounding the tee to simulate human lips. The tees were first soaked in a small amount of toluene for 90 sec in order to remove the waxy coating which could possibly interfere with the GC. The tees were placed in the ground to a depth of 2.5 cm for 60 sec. Then each tee was taken and placed in a clothes pin which already contained a piece of the wet chamois leather. The tee was pulled slowly through the leather in the clothes pin. The chewed tee was then placed in the appropriate vial. These vials were labeled WT1-WT4 (wood tee), east and west. The pieces of chamois leather were placed in vials that were labeled TC1-TC4 (tee chew), east and west. The samples were taken and 50 ml of acidified methanol were added to the ball samples and 20 ml of acidified methanol were added to the remaining samples containing the wood tee, tee chew and tongue simulators.

Herbicide Extraction and Analyses: Following the treatment period, the herbicide was extracted from the chamois leather. After the sample was placed in acidified methanol, all except the wood tees samples were shaken for 10 min on a mechanical shaker. The tees contain a waxy coating which could possibly interfere with the GC. Therefore these particular tee samples were not shaken whereas to minimize the removal of the waxy cuticle. The extractants were then transferred to a 250 ml separatory flask. Seventy five ml of methylene chloride were added to the methanol extracts (from ball). The samples were shaken for 30 sec and the bottom layer was separated and saved. Fifty ml of methylene chloride were added to the remaining sample, the sample was shaken, the bottom layer was separated, and the methylene chloride from both extractions were combined and dried in a hood. This procedure was repeated for all of the ball samples. For the tee and tongue simulated samples 40 ml of methylene chloride were added to the methane/water extracts and the bottom layer was removed. The procedure was repeated with 20 ml of methylene chloride. All of the combined extracts were saved and dried. The residue was transferred from beakers to a 25 ml vial with methylene chloride and was allowed to evaporate until dry. Esterification of the acid herbicides was accomplished by adding 1 ml of trifluoroethanol and 0.5 ml of concentrated sulfuric acid to the residue. The vials were then placed in a warm water bath of (60°C) for one hour without the caps. The samples were removed and cooled. Fifteen ml of deionized water were added followed by one milliliter of internal standard (100 ppb 2,4,5-T methyl ester in hexane). The vials were then capped and shaken for 10 min on a mechanical shaker. The two liquid layers that formed were allowed to separate and the top layer (hexane with herbicide esters) was removed from the vial. The sample was injected into the GC equipped with an electron capture detector for analyses.

After the results were read and data were collected from the GC, they were compared to the LD_{50} for each herbicide. The data will indicate the potential dose received by a

golfer from licking the golf ball or placing a golf tee in his mouth following contact with a green treated with herbicides.

Experimental Design: The experiment was conducted twice by treating the east and west greens with the three herbicides. The ball-licking and the tee-chew activities were replicated four times and each sample was injected into the GC twice. All data were subjected to statistical analyses and means were separated by the standard error of the mean.

RESULTS

Figure 1 presents the data that represents the total residue remaining on the golf ball, less that removed by the lick-simulation, following simulation of the putt on the treated greens at 6 intervals following treatment with dicamba, mecoprop, and 2,4-D. The quantity of herbicides adsorbed to the golf balls during the simulated putt decreased over the 102 HAT sampling period. Although not statistically significant, generally, more 2,4-D was recovered from the golf ball compared to the other herbicides. Data on the herbicide recovered from the chamois leather used to simulate licking the golf ball indicate that the potential dose drastically decreased from the 0 to the 6 HAT sampling period (Fig. 2). Maximum amounts recovered from the leather were 0.2, 0.6, and 0.9 mg for dicamba, mecoprop, and 2,4-D, respectively. Significantly, more 2,4-D and mecoprop were recovered from the wet leather following the simulation of the lick compared to the dicamba. Nearly 5.3, 19.7, and 18.0% of the dicamba, mecoprop, and 2,4-D, respectively, recovered from the golf ball were found on the chamois leather (Figs. 1 and 2).

Only small quantities of the three herbicides were found on the tees (Fig. 3). At 0 HAT sampling period 0.08, 0.29, and 0.30 mg of dicamba, mecoprop, and 2,4-D, respectively, were recovered from the sampling tees. The quantity of herbicides on the tees decreased to nearly 0 for all three herbicides over the 102 HAT sampling period. Large fractions of the herbicides on the tees were removed with the tee-chew experiment (Fig 4). Nearly 72, 43, and 53% of the dicamba, mecoprop, and 2,4-D found on the tees was recovered from the wet leather during the first tee-chew sampling period at 0 HAT (Figs. 3 and 4). Similar fractions of the herbicides found on the tees at later dates were removed on the wet leather simulation of the tee-chew.

DISCUSSION

The toxic influence of the dose of the three herbicides on the golfer who habitually licks the ball or chews on the tee is hard to estimate. The purpose of this research was to determine the potential herbicide dose to be received when a golfer licks the golf ball or places the used tee in the mouth following exposure of the golf ball and tee to turfgrass treated with dicamba, mecoprop, and 2,4-D. The risk from the exposure to the herbicide is a combination of the factors of dose received and the toxicity of the chemical. The toxicity of the three herbicides is expressed in 2 forms (Table 1). The LD $_{50}$ is the dose (mg/kg body weight) of the herbicide that is lethal to 50% of the rats which are fed the chemical. The no observed effects levels (NOEL) for the herbicides

are the levels of human dermal exposure to the herbicides that result in no observed effects. The problem with using these toxicity ratings for the herbicides is that neither are a good indication of the influence of the oral dose of these herbicides on human beings.

Table 11. The 50% LD₅₀ for mice and the (NOEL) for 2,4-D, dicamba and mecoprop.

Herbicide NOEL		NOEL (Jennifer) ¹	LD ₅₀	Ave. LD ₅₀ (Jennifer) ¹	
-	(mg/kg)	(mg)	(mg/kg)	(mg/kg)	
dicamba	5	273	757-1707	67,145	
mecoprop	50	2725	930-1210	58,315	
2,4-D	10	545	375- 666	28,366	

¹Based on a weight of 54.5 kg.

While the LD₅₀ is a measure of the dose that results in death to 50% of the rats fed the herbicides, a golfer's concern is for the effects resulting from the exposure levels much below the levels that result in death. The NOEL is used for dermal exposure whereas we measured the oral dose. The differences between the influences of dermal exposure and oral dose to humans could be quite large. However, these are the only two measures of toxicity available for the three herbicides used in this research. Assuming that I am the golfer that licks the ball, the doses of herbicides received when licking that golf ball at 0 HAT are 1,386; 4,319; and 610 fold less than the NOEL for myself with reference to dicamba, mecoprop, and 2,4-D, respectively (Fig. 2 and Table 1). This would mean that I could lick 1,386; 4,319; and 610 golf balls that were rolled across the greens immediately after treatment with dicamba, mecoprop, or 2,4-D, respectively, before being concerned with reaching my NOEL for these compounds (Table 2). The number of golf balls that can be licked gets much larger as the period of time increases between the herbicide treatment and the rolling of the ball across the green. Probably physical abrasion to the tongue, when licking that many golf balls. would be of more concern than the effects from the herbicides. The concern for reaching a dose equal to the LD₅₀ for these herbicides is considerably less for these herbicides. The number of golf balls that I could lick before being concerned would be much larger than for the NOEL (Table 3).

Table 12. Number of golf balls that Jennifer can lick before reaching a NOEL dose.

	HAT ¹							
<u>Herbicide</u>	0	6	30	54	78	102		
dicamba	1,386	-	68,250	17,063	- -	34,125		
mecoprop	4,319	143,421	80,147	77,857	1,362,500	87,903		
2,4-D	610	21,800	17,031	7,569	109,000	6,566		

¹ Hours after treatment.

Table 13. Number of golf balls that Jennifer can lick before reaching a LD₅₀ dose.

		HAT ¹				
Herbicide	0	6	30	54	78	102
dicamba	340,838	-	16,786,250	419,656	-	8,393,125
mecoprop	92,417	3,069,211	1,715,147	1,666,143	29,157,500	1,881,129
2,4-D	31,729	1,134,640	886,438	393,972	5,673,200	341,759

¹ Hours after treatment.

Similarly, the data from my research indicates that I could chew on a lot of tees before being concerned with reaching the NOEL (Table 4) or the LD_{50} (Table 5) doses. The reason for the increase in the three herbicides on the tees after the 54 HAT sampling period and the decrease in tees that can be chewed before reaching the critical doses (Tables 4 and 5) could be due to the transport of the herbicides into the soil of the greens resulting in a greater surface area of the tee being exposed to the herbicides. This difference was consistent in both experiments.

Table 14. Number of tees that Jennifer can chew before reaching a NOEL dose.

					<u> </u>					
		HAT ¹								
Herbicide	0	6	30	54	78	102				
dicamba	6,205	4,266	91,000	5,571	273,000	-				
mecoprop	24,550	22,336	100,925	45,417	272,500	908,333				
2,4-D	2,995	3,633	11,596	5,396	28,684	34,063				

¹ Hours after treatment.

Table 15. Number of tees that Jennifer can chew before reaching a LD_{50} dose.

		HAT ¹				
Herbicide	0	6	30	54	78	102
dicamba	1,526,022	1,049,141	22,381,666	1,370,306	67,145,000	-
mecoprop	525,360	477,992	2,159,815	971,917	5,831,500	19,438,333
2,4-D	155,857	189,107	603,532	280,852	1,492,947	1,772,875

¹ Hours after treatment.

SUMMARY

While golfers who habitually lick the golf ball in play and chew on the used golf tee are not at high risk for being adversely affected, this does not mean that this is a good practice to follow. When turfgrass is treated with herbicides, golfers who lick their golf ball and chew on their golf tee will receive an oral does of the herbicides. Although the LD₅₀ and the NOEL were well below the critical rate of exposure, this does not measure the physical irritation or discomfort from coming into contact with these herbicides to golfers who may be ultra sensitive to exposure.

REFERENCES

- Grossman, J. 1993. How Green are These Fairways? Audobon. Sept./Oct. pp. 90-100.
- Harris, S A. and K. Solomon. 1992. Human Exposure to 2,4-D Following Controlled Activities on Recently Sprayed Turf. J. Environ. Sci. Health 24(1):9-22.
- Howe, P. 1997. Medical Notebook: New group weighs in on mammogram issue. Boston Globe.
- Internet: http://www.intacc.com.au/Golf_Fever.
- Landry, G. 1995. Proceedings of The 1995 Turfgrass Field Day, Georgia Experimental Station, Griffin, GA.
- Smith, A. E. 1994. The Risk of Using Herbicides. GTA Today 9(6):5-10.
- Soderholm, K. J., R. Mukherjee, and J. Longmate. 1996. Filler leachability of composites stored in artificial saliva. J. Dental Research. Sep. 75(9).
- Thompson, D., G. Stephenson, and M. Sears. 1984. Persistence, Distribution and Dislodgeable Residues of 2,4-D Following its Application to Turfgrass. Pesticide Science 15:353-360.

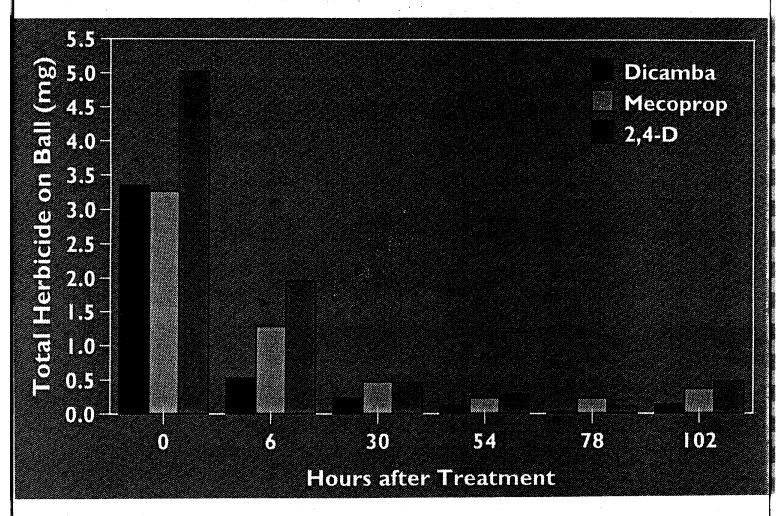


FIG. 4. Herbicide remaining on treated ball following the simulated licking.

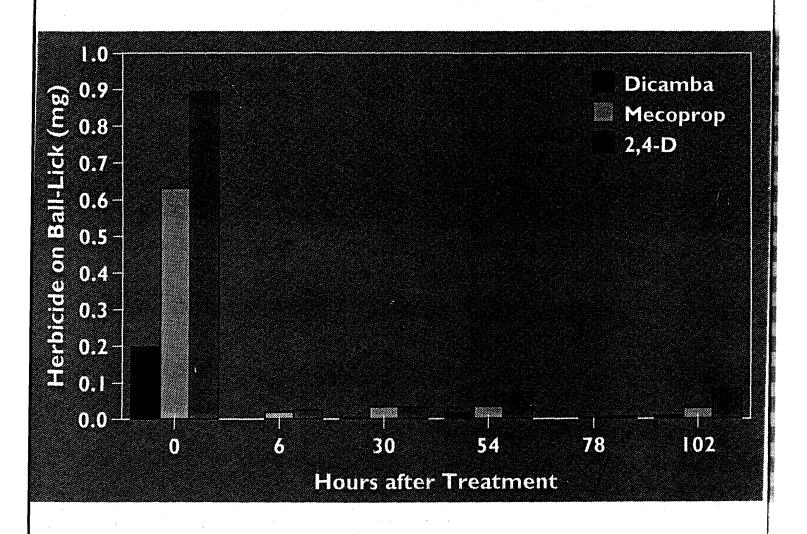


FIG. 5. Herbicide on chamois leather following simulated licking of the golf ball.

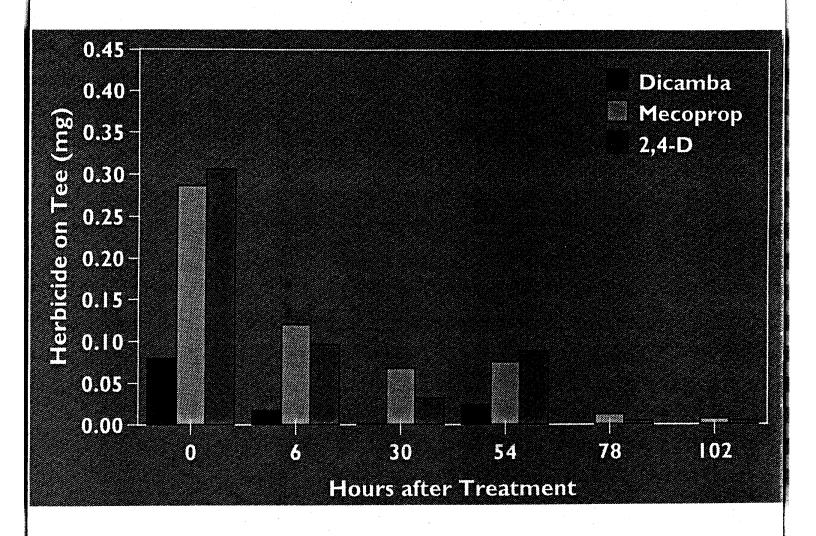


FIG. 6. Herbicide remaining on treated tee following the simulated tee-chew.

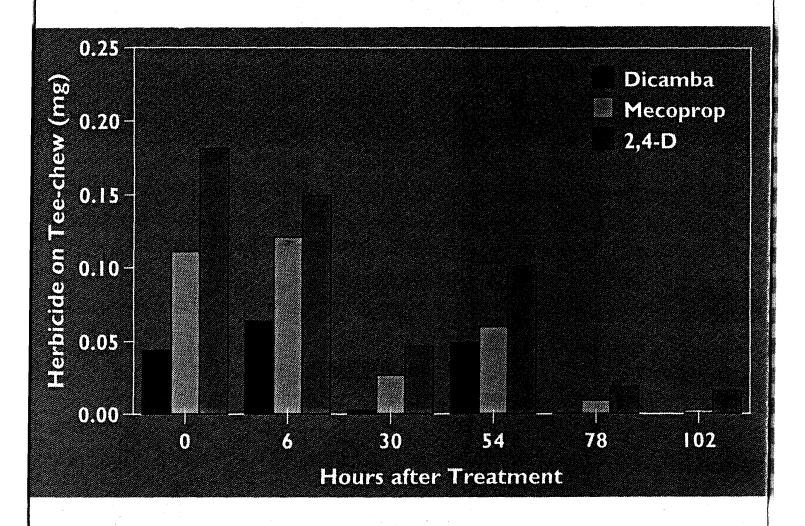


FIG. 7. Herbicide on chamois leather following the simulated tee-chew.

Nitrate, Phosphate, and Pesticide Transport Through Golf Course Putting Greens at Town and Country Club

Three lysimeters were placed in each of two putting greens at a Town and Country Club in Atlanta, GA. Data from the March to October 1995 are included in TABLE 11 and the data from analyses of leachate from November 1995 to July 1996 are included in TABLE 12. No pesticides were applied between October 12, 1995 and April 4, 1996 and only phosphate (PO₄) and nitrate (NO₃) were analyzed during this time period (TABLE 12). The phosphate concentration in the leachate tended to increase several weeks following the application of the 3-way fertilizer. From January to February the phosphate concentration increased 3-fold in the leachate collected from both greens. From February to April the phosphate concentration seemed to cycle between 700 and 1100 ug L⁻¹ with the highest concentrations occuring following the application in March. The nitrate concentration in the effluent was somewhat variable between the two greens. However, the highest average concentrations from the two greens occurred during the period of greatest rainfall and following the application of the 3-way fertilizer which included nitrate (TABLE 12). However, at no sampling period was the nitrate concentration above the MCL of 10,000 μg L⁻¹.

The data for the pesticides in the leachate have not been compiled at the time of the preparation of this report and that data will be included in the next annual report. A point of interest is the minimal quantities of water exiting the lysimeters from the greens. Each liter exiting the lysimeter represents 0.55 cm of rain/irrigation that was not used in the system. Generally, the low quantities of water exiting the lysimeters, during periods not representing a rainfall event, indicate judicious use of water.

TABLE 16. Treatments, leachate volume, and analyte concentration from 3 lysimeters in 2 practice greens at a Town and Country Club collected from March to November

1995. Data are means from 3 lysimeters.

Weekly									
<u>Weekly</u>	eam	nlo ¹	Treatment ²			Analy	<u>te concen</u>	tration	2
	reen		Analyte	Rate	NO ₃		OH-CLP		
		(L)	y	(kg ha ⁻¹)			(µg L ⁻¹)		
3-23-95	1 2	0.02 0.03	urea	50-N]	260 460	- -	-	- -	- -
3-30-95	1 2	1.19 0.04	[18-0-18 urea	34-N 12-N	3,360 440	- -	- -	- -	-
4-13-95	1 2	1.58 1.05	CTH 18-3-10	9.39 24-N	2,520 1,010	-	- -	4	- 158
4-27-95	1 2	3.51 3.97	СТН	9.39	4,210 530	- -	<u>-</u>	6 5	97 59
6-01-95	1 2	2.52 1.90	18-0-18 CLP CTH ³	24-N 1.1 18.78	3,600 760	0	0	4 4	23 70
6-15-95	1 2	0 0	urea CLP	5-N 1.1	100 0	0	0	0	6
6-29-95	1 2	1.96 2.77	urea	10- N	3,150 440	0	0 0	0 0	0 0
7-27-95	1 2		46-0-0 10-2-10 3-6-9 CTH	3-N 20-N 6-N 14.2	4,520 560	0 0	0	2. 1	177 140
8-31-95	1 2	3.09 3.76	CLP NH₄NO₃ 20-20-20 CTH³ 20-20-20 urea³	1.1 34-N 34-N 18.78 2-N 20-N	1,410 410	0	0 0	3 9	139 150
10-12-95	1 2	35 91	urea ³	29-N 9.39	250 220	0	0 0	4 9	139 126

¹ Samples were collected weekly. No data indicates no leachate for that period. ² [Treatments applied to both greens.] ³ 2 treatments.

TABLE 17.Treatments, leachate volume, and analyte concentration from 3 lysimeters in 2 practice greens at a Town and Country Club collected from November 1995 to October 1997. Data are means of 3 lysimeters.

	tly sample		Weekly tro		Analyte conce	
Date	Green	Qty	Analyte	Rate	Phosphate	Nitrate 1
		(L)		(kg ha ⁻¹)	(µg L	')
11-2-95	1	2.09	urea	36.60-N	-	1052
	2	0.49	Ĺ	j		2210
11-17-95	1	3.21	urea	4.88-N	-	6760
	2	2.91	l 18-3-10	34.16	-	2296
12-07-95	1	3.25			-	989
	2	3.39	· ·	·		4607
1-25-96	1	2.84		1	414	1109
	2	2.43		j	259	532
2-01-96	1	5.62	ſ	1	933	1763
	2	4.58			654	1753
2-08-96	1	2.22	urea	5.37-N]	1281	414
2 00 00	2	3.15	K-Power	2.44	1513	980
0.00.00	4	0.44	Γ	507 N 1	4007	407
2-29-96	1 2	0.44 0.04	urea	5.37-N	1067 1082	467 1176
		0.04	Ĺ		1002	1170
3-14-96	1	3.78	urea	4.88-N	798	332
	2	3.96	1		657	497
3-21-96	1	2.81		1	797	438
	2	3.68	Į.	J	744	384
3-28-96	1 .	2.13	10-18 - 18	24.40]	677	354
0 20 00	2	1.35			1166	88
4-04-96	1	0.59	Luroo	2.44-N]	1161	266
4-04-30	2	0.39	urea K-Power	4.88	1176	266 244
		0.40	[IC-I OWEI	Ţ.00]	1170	244
4-25-96	1	1.61	urea	9.27 -N]	2687	6539
	2	0.91	└ KNO ₃	7.32	739	2997
5-02-96	1	1.85	KNO ₃	4.88	930	4438
	2	1.33		0.00	828	1851
E 24 06	4	0.20	[IZNO	4.00 1	E00	4005
5-31-96	1 2	2.30	∫ KNO ₃	4.88	580 1224	1985 1680
	2	1.59	L]	1234	1680

TABLE 17 - Continued.

	dy sample		Weekly tr		Analyte conce	
Date	Green	Qty	Analyte	Rate	Phosphate	
6-06-96	1 2	(L) 1.35	[13-0-44	(kg ha ⁻¹) 29.28	(μg L ⁻ 975	1601
6-13-96	1 2	3.43 2.96			603 867	932 325
6-20-96	1 2	1.91	46-0-0 13-0-44		676	1397
7-18-96	1 2	1.53	46-0-0 13-0-44	1.37 1.02	555	3564
8-01-96	1 2	1.94 1.56			2430 4280	6550 730
8-15-96	1 2	3.06 1.63	urea CTH³ CLP	19.7-N 18.8 1.1	5600 5370	7740 5820
9-12-96	1 2	1.72 1.09	СТН	9.4	1590 3230	1570 6770
9-19-96	1 2	3.08 3.85	[10-18-18	24.4-N	1310 3900	5200 2590
9-26-96	1 2	1.89 1.86	urea	9.3-N 2.4-N	5270 2380	4150 2650
10-03-96	1 2	2.99 1.97	urea KNO₃ CTH	16.6-N 2.4-N 9.4	1760 4470	1540 4480
11-15-96	1 2	3.21 2.62	urea KNO ₃ 18-4-10	9.3-N 2.4-N 29.3-N	10,750 3960	6390 4540
12-05-96	1 2	3.09 3.47	urea KNO ₃	17.2-N 1.3-N	5010 5850	3670 2020
12-18-96	1 2	2.10 1.44			410 2950	3950 850

TABLE 17 - Continued.

	kly sample¹		Weekly tre		Analyte conc	
Date	Green	Qty	Analyte	Rate (kg ha ⁻¹)	Phosphate	Nitrate
1-9-97	1 2	(L) 3.66 3.25		(kg lia)	(µg L 828 1247	2032 1436
1/11/97	1 2	3.22 3.25	Urea KNO₃ Sprint	7.32 2.44 12.2	107 262	595 1527
1/30/97	1 2	2.93 2.53	[18-3-10	24.39	2512 1885	5251 1107
2/6/97	1 2	3.28 2.22	Daconil	13.13	563 1382	1881 1460
2/13/97	1 2	3.12 2.20			376 1237	1751 1301
2/20/97	1 2	2.14 1.54			382 1221	1719 979
2/27/97	1 2	2.34 0.00			749 0	1954 0
3/6/97	1 2	3.69 3.09	[18-3-0	29.27	420 1703	790 825
3/20/97	1 2	3.19 0.00	Daconil AquaAid Ferromec	16.19 6.11 3.05	550 0	2729 0
4/10/97	1 2	3.10 0.93			430 1392	3227 3353
4/17/97	1 2	2.03 0.00			604 0	2436 0
4/24/97	1 2	1.77 1.39			602 1446	2645 3851
5/1/97	1 2	3.37 3.62	Daconil Dylox	14.05 6.11	1544 1989	1795 1244

TABLE 17 - Continued.

Weel	kly sample¹	·	Weekly treatment ²	Analyte concentration 2
Date	Green	Qty	Analyte Rate	Phosphate Nitrate
		(L)	(kg ha ⁻¹)	(µg L ⁻¹)
5/8/97	1 2	3.39 3.07	$\begin{bmatrix} \text{KNO}_3 & 5.37 \\ \text{Ferromec} & 6.11 \\ \text{Aquaaid} & 6.11 \end{bmatrix}$	2151 1652 3263 1553
5/28/97	1 2	3.88 3.35	Dursban 4.58	1377 6213 2481 4756
6/5/97	1 2	2.70 1.65	Urea 27.81 AquaAid 6.11 Iron 6.11	1014 3015 2080 3697
6/19/97	1 2	3.45 2.66	Daconil 10.39 Subdue 3.05 Dursban Pro 3.05	1403 3695 2115 3914
7/24/97	1 2	3.53 3.86	Chipco 26019 13.13 Daconil 13.13 KNO3 1.95 AquaAid 6.11 Ferromec 6.11	961 3447 2147 4900
8/7/97	1 2	3.21 1.78	Dursban Pro 3.05	1261 2712 1963 4444
9/26/97	1 2	3.37 3.89	Urea 3.9 Aqua aid 6.11 Ferromec 6.11	1381 3766 2295 5213
10/2/97	1 2	2.16 1.58	Daconil 19.55 Subdue 3.05 Dursban Pro 3.05 Dylox 6.11	636 942 1585 1234

Samples were collected weekly. No data indicates no leachate for that period.
 [Treatments applied to both greens.]
 2 treatments.

Cumulative Annual Rainfall for Cherokee Country Club, 1995

Week ending	Cumulative rainfall
01/07/95	1.65
01/14/95	2.08
01/21/95	2.38
01/28/95	3.73
02/04/95	4.27
02/11/95	6.32
02/18/95	12.40
02/25/95	12.55
03/04/95	14.23
03/11/95	17.08
03/18/95	17.08
03/25/95	17.08
04/01/95	17.48
04/08/95	17.48
04/15/95	18.23
04/22/95	20.23
04/29/95	21.58
05/06/95	22.28
05/13/95	22.38
05/20/95	22.58
05/27/95	22.58
06/03/95	23.13
06/10/95	23.28
06/17/95	23.28
06/24/95	23.43
07/01/95	23.43

Week ending	Cumulative rainfall
07/08/95	23.43
07/15/95	23.43
07/22/95	23.43
07/29/95	23.54
08/05/95	23.91
08/12/95	24.01
08/19/95	24.21
08/26/95	25.48
09/02/95	27.40
09/09/95	27.40
09/16/95	29.80
09/23/95	30.67
09/30/95	31.10
10/07/95	37.59
10/14/95	38.20
10/21/95	38.27
10/28/95	39.12
11/04/95	40.54
11/11/95	44.93
11/18/95	44.94
11/25/95	45.03
12/02/95	45.39
12/09/95	46.62
12/16/95	46.68
12/23/95	47.95
12/30/95	47.95

Cumulative Annual Rainfall for Cherokee Country Club, 1996

Week ending Cumulative rainfall 01/06/96 1.70 01/13/96 2.32 01/20/96 3.90 01/27/96 7.66 02/03/96 11.27 02/10/96 11.31 02/17/96 11.31 02/24/96 11.91 03/02/96 12.24 03/09/96 16.39 03/16/96 18.18 03/23/96 19.48 03/30/96 20.89 04/106/96 21.45 04/13/96 21.45 04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.63	Cullidial	ive Ailiuai Railiiaii
01/13/96 2.32 01/20/96 3.90 01/27/96 7.66 02/03/96 11.27 02/10/96 11.31 02/17/96 11.31 02/24/96 11.91 03/02/96 12.24 03/09/96 16.39 03/16/96 18.18 03/23/96 19.48 03/30/96 20.89 04/106/96 21.45 04/13/96 21.45 04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25		ł
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01/27/96 7.66 02/03/96 11.27 02/10/96 11.31 02/17/96 11.31 02/24/96 11.91 03/02/96 12.24 03/09/96 16.39 03/16/96 18.18 03/23/96 19.48 03/30/96 20.89 04/106/96 21.45 04/13/96 21.45 04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	01/13/96	2.32
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02/24/96 11.91 03/02/96 12.24 03/09/96 16.39 03/16/96 18.18 03/23/96 19.48 03/30/96 20.89 04//06/96 21.45 04/13/96 21.46 04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	02/10/96	11.31
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03/23/96 19.48 03/30/96 20.89 04//06/96 21.45 04/13/96 21.46 04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	03/09/96	16.39
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04//06/96 21.45 04/13/96 21.46 04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	03/23/96	19.48
04/13/96 21.46 04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	03/30/96	20.89
04/20/96 22.77 04/27/96 23.64 05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	04//06/96	21.45
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05/04/96 24.95 05/11/96 25.24 05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	04/20/96	22.77
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05/18/96 25.48 05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	05/04/96	24.95
05/25/96 26.06 06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	05/11/96	25.24
06/01/96 27.02 06/08/96 27.80 06/15/96 30.25	05/18/96	25.48
06/08/96 27.80 06/15/96 30.25	05/25/96	26.06
06/15/96 30.25	06/01/96	27.02
	06/08/96	27.80
06/22/96 30.63	06/15/96	30.25
	06/22/96	30.63
06/29/96 31.20	06/29/96	31.20

Week ending	Cumulative rainfall
07/06/96	31.79
07/13/96	32.81
07/20/96	33.76
07/27/96	34.36
08/03/96	36.17
08/10/96	36.92
08/17/96	38.07
08/24/96	38.70
08/31/96	38.84
09/07/96	39.64
09/14/96	40.66
09/21/96	44.26
09/28/96	45.87
10/05/96	45.96
10/12/96	46.23
10/19/96	46.58
10/26/96	46.95
11/02/96	49.78
11/09/96	51.58
11/16/96	51.58
11/23/96	52.13
11/30/96	53.02
12/07/96	54.25
12/14/96	54.83
12/21/96	55.12
12/28/96	55.58

Cumulative Annual Rainfall for Cherokee Country Club

Week ending	Cumulative rainfall
01/04/97	0.15
01/11/97	2.87
01/18/97	3.96
01/25/97	5.16
02/01/97	5.88
02/08/97	7.65
02/15/97	9.19
02/22/97	10.04
03/01/97	13.67
03/08/97	14.42
03/15/97	15.83
03/22/97	15.89
03/29/97	15.92
04/05/97	16.40
04/12/97	17.07
04/19/97	17.03
04/26/97	18.61
05/03/97	21.98
05/10/97	22.01
05/17/97	22.20
05/24/97	23.10
05/31/97	25.05
06/07/97	25.51
06/14/97	27.46
06/21/97	27.85
06/28/97	28.45

Week ending	Cumulative rainfall
07/05/97	28.88
07/12/97	29.28
07/19/97	29.87
07/26/97	33.81
08/02/97	35.02
08/09/97	35.41
08/16/97	35.71
08/23/97	36.35
08/30/97	36.54
09/06/97	36.85
09/13/97	37.41
09/20/97	37.74
09/27/97	43.29
10/04/97	44.09
10/11/97	44.15
10/18/97	44.28
10/25/97	44.47
11/01/97	48.04
11/08/97	
11/15/97	
11/22/97	
11/29/97	
12/06/97	
12/13/97	
12/20/97	
12/27/97	