# 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

**A. E. Smith and D. C. Bridges**

**Executive Summary.**
Funding provided by USGA for the previous project (1991-1994) resulted in the development of facilities at the Georgia Experiment Station and the initiation of a research program to determine the potential movement of pesticides following application to golf courses. The research focus during the first three years was to use lysimeters developed in the greenhouse and outside for the determination of the potential for pesticides to move through golf course greens. Data indicated that only small quantities (<1%) of the applied 2,4-D DMA, dicamba DMA, mecoprop DMA, dithiopyr, chlorpyrifos, and chlorothalonil are transported through the sod and the lysimeters. In summary, it appeared that the dynamics of a well maintained sod contribute to a high adsorption and decomposition rate for these pesticides and the GLEAMS model, developed for agricultural row-crops, underestimates the dynamics of the ecosystem around the sod. Research has been continued to document movement of additional pesticides through the lysimeters and to resolve the differences between the GLEAMS model prediction of analyte transport and data obtained from the lysimeters.

Results of recent studies inticated that only small quantities of methyl bromide and bromide ion were transported through the outside lysimeters following treatment with methyl bromide. It can be concluded that the small quantities transported would be of minor importance compared to the quantities released as a gas following fumigation.

Plots to determine the potential transport of pesticides in runoff water from treated plots during storm events were developed on soils typical of the Piedmont region. As much as 40-70% of the rainfall left the plots as runoff during simulated storm events. The collected surface water contained moderately high concentrations of treatment pesticides having a high water solubility. Data for 9 analytes resulted in a high correlation ($r^2$=0.91) between the fraction of analyte transported and the water solubility for the analyte when fit to a quadratic equation. Less than 1% of the applied chlorothalonil, chlorpyrifos, benefin, and pendimethalin was transported from the plots in the runoff water. Whereas, as much as the 9-16% of the 2,4-D, dicamba, mecoprop, and nitrate were transported in the surface water from the first 2 simulated storm events. Compared to broadcast application, pressure injection decreased the fraction of 2,4-D (7.4X) and trichlorphon (5.2X) transported and the inclusion of a buffer strip between the points of treatment and water collection did not significantly reduce the fraction of analyte transported. Research on reducing the potential movement of pesticides in surface water will be continued.

Leachate collected from lysimeters under practice greens at a Town and Country Club golf course contained only trace quantities of chlorothalonil, chlorpyrifos, and OH-chlorpyrifos. Slightly more OH-chlorothalonil and nitrate were determined in the leachate in response to treatments with chlorothalonil and fertilizer.

Results of a project designed to determine the potential herbicide exposure from kneeling on a treated golf course green indicate that an average sized golfer can kneel as much as 20,000 times on greens, at 6 hours after treatment with 2,4-D, mecoprop, and dicamba, before receiving an exposure equal to the NOEL.

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## INTRODUCTION

Assuming that 2% of a golf course is managed as putting greens, there are 13.6 thousand ha of greens in the U.S. which are constructed for maximum infiltration and percolation of water through the rooting media. Root zone mixture composition generally includes at least 85% 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 the soil microbial decomposition of applied pesticides. These characteristics of the root zone mixture could result in rapid movement of pesticides through the rooting mixture allowing for a potential source of contamination of the effluent water from the greens. The Ground Water Contamination Potential rating for use of certain herbicides ie. benzoic and phenoxyalkanoic acid herbicides on golf course greens, constructed according to U.S. Golf Association (USGA) specifications, would be RISKY.

Results of greenhouse and outdoor lysimeter research conducted, over the last three years, at Griffin, GA; indicated that only small quantities (<1%) of the applied 2,4-D, dicamba, and mecoprop (dimethylamine salt formulations) are transported through the sod and the lysimeters. The highest concentrations of the analytes in the leachate were 3.2, 3.6, and 3.8 ppb; respectively (See 1994 final report). This is 10 fold less than the predicted values obtained by the GLEAMS model using the inputs from this research. Greens constructed according to USGA specifications are designed for the rapid infiltration and percolation of water through the system. This system would present a worst-case scenario for the movement of pesticides through a sod and soil for entry into groundwater or from a drain system into surface water. The data, from our research, indicated that the dynamics of a well maintained sod contribute to a high adsorption and decomposition rate for these herbicides and the GLEAMS model, developed for agricultural row-crops underestimates the dynamics of the ecosystem around the sod. However, it is important to continue to document the potential movement of pesticides through golf course greens.

The use of methyl bromide (MeBr) for soil sterilization and stored food preservation has increased dramatically over the last decade. It controls all living plant, stem, or root tissue, most seeds, nearly all insects, and most disease organisms which makes it an important soil treatment for seed beds of tobacco, flowers, vegetables, turf, and tree seedlings. It is an effective treatment for propagating beds and as a preplanting treatment for trees, shrubs, fruits, and gardens and is commonly used as a soil sterilant by the glasshouse industries due to its toxicity to insects, nematodes, fungi, and weed seeds. About 70% of the MeBr produced in the United States goes into pesticidal formulations. The majority of the research with MeBr and its degradation products was conducted prior to 1985 on contaminants in produce following treatment with MeBr as a soil sterilant before planting the crop or as a precautionary control of disease and insect organisms during shipment. Much of the research conducted during this period was due to the attention given to fumigants just prior to the 1984 ban of 1,2-dibromomethane (EDB).

MeBr is used as a fumigant on golf course greens during renovation and initial construction. Currently, there are over 14,000 golf courses in the United States. Assuming an average size of 48.6 ha per course and 2% of these hectares are managed for putting greens, there are 13.6 thousand ha of golf course greens in the United States. Greens are renovated on periodic bases (ie. every 10 years) indicating that on the average 1,360 ha of greens are renovated each year. The National Golf Foundation estimates that a golf course will need to be opened every day over the next decade to keep pace with the projected increase in number of golfers. This would equate to 364 additional hectares of greens to be fumigated each year. Over the next ten years there is a potential for 1,700 ha of greens to be fumigated, annually in the United States, with MeBr at a rate of 385 kg/ha.

There are many problems when using MeBr for soil fumigation. MeBr is an odorless gas placed in the acute oral toxicity category II and acute inhalation toxicity category I. The high mammalian toxicity and phytotoxicity of this compound, necessitates the thorough removal of any unchanged residues from the soil prior to reentry and planting. After application MeBr is slowly converted to inorganic bromide ion (Br) and methane in the soil. Br has been found to accumulate in the soil and on foliage of crops following fumigation, causing concerns for human health and phytotoxic effects to the crop plants. The rate of degradation in fumigated soil is estimated at 6-14% per day at 20°C with highest rates in soils having high organic matter contents. More leaching occurs in sandy soil than in loamy soil.

Probably as important as the residual MeBr and degradation products on foodstuffs and human exposure is the potential for contamination of the environment resulting from the treatment. The comparatively high water solubility of MeBr and the persistence and low soil retention of Br allows for their potential movement into surface and groundwater. Escape of the gases (MeBr and methane) to the atmosphere has resulted in concerns for their influence on ozone depletion and, ultimately, the long-term global environment changes. Since MeBr has been identified as a significant ozone depleting chemical, EPA has entered an intensive study that will affect the future (2001) use of this compound that is of great importance to the golf course industry. Therefore, we designed a study to determine the potential movement of MeBr and Br through golf course greens using simulated greens.

Fairways compose approximately 98% of the golf courses and are typically intensively managed. 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 from a storm event will result in runoff water from the sloped areas. This surface water could eventually terminate in potable water containments. It is estimated that 95% of the drinking water consumed by residents of the Piedmont comes from surface water containments resulting in a concern for surface water quality. Preliminary research indicated that as much as 10-15% of the applied 2,4-D, dicamba, and mecoprop (DMA formulations) are transported from runoff plots having a 5% slope. Concentrations of the analytes in the collected runoff water from the first simulated storm event ranged from 289 ppb for dicamba to 762 ppb for 2,4-D (See 1994 final report). We are continuing research to determine the potential movement of pesticides surface water using the small plots developed during 1993. Additionally, we are investigating the influence of management practices on reducing pesticide movement in surface runoff following a storm event.

Research has been continued on testing additional pesticides for movement through the greenhouse and outdoor lysimeters and from the runoff plots. Additionally, preliminary data have been obtained on the use of management systems for the decreased movement of pesticides from the runoff plots. Finally, this report includes data on reentry exposure of golfers to herbicides developed in our laboratory by Ms. Michelle Morton, a mentor student from Griffin High School[1].

## MATERIALS AND METHODS

### Pesticide Movement Through Simulated Greens (See 1994 annual report for detailed description).

Thirty six lysimeters were constructed, in the greenhouse, by placing turfgrass growth boxes (40 x 40 x 15 cm deep) on top of 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) tube (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.) capped at the bottom. The cap had a drain tube for the collection of aqueous effluent.

Prescribed rooting mixtures (sand:sphagnum peat moss) were based on the percolation rate for the sand. The proportions 85:15 and 80:20 v:v were selected to give final percolation rates of 39 and 33 cm $hr^{-1}$, respectively. The rooting media were steam sterilized prior to use. The lysimeter bases were filled with sized gravel (10 cm), coarse sand (7.5 cm), and rooting mix (35 cm) in ascending sequence from the bottom simulating USGA specifications for greens construction. 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® thermoclear sheet glazing. Established (>1 yr old) of 'Penncross' creeping bentgrass (Agrostis stolonifera L.) and 'Tifdwarf' bermudagrass [Cynondon dactylon (L.) Pers. x C. transvaalensis Burtt-Davy] were established in the rooting mixes in the boxes by seeding and soding. An automatic track-irrigation system was developed for controlling the rates and times for irrigation. The daily irrigation of 0.63 cm of water and a weekly rain event of 2.5 cm were controlled with an automatic timer. The

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[1]Michelle Morton is a Junior at Griffin High School working as a mentor student with Al Smith. The project won first-place honors at the Regional Science Fair, 2-first and 2-second place honors at the Georgia State Science Fair; and by invitation was presented at the International Science Fair in Hamilton, Ontario, Canada.

conditions were chosen to simulate management practices and average rainfall events for golf course greens in central Georgia and the weekly water input was approximately 2X the loss by open-pan evaporation. The pesticide treatments to the sod were applied to the growth boxes in 204 L $ha^{-1}$ water diluent. A complete fertilizer was applied in water to an N rate of 2.44 g $m^{-2}$. The leachate in the sample bottles, at the base of the lysimeters, was collected and stored in a refrigerator maintained at 4°C. Collections were combined for weekly intervals and quantified for pesticide in the leachate.

The outside facility consisted of small greens subtended with lysimeters for directing the flow of water and pesticides into a collection area. The small greens were developed with similar rooting media as used in the greenhouse experiments. We used the 85:15 mix for the bentgrass green and 80:20 mix subtending the 'Tifdwarf' bermudagrass green. The interior diameter of each lysimeter is 55 cm and the depth is 52.5 cm allowing for layers of gravel, sand, and rooting media as developed in the bases of the greenhouse lysimeters. Bentgrass was seeded on October 15, 1991 and bermudagrass was sodded March 1992. A horizontal moving irrigation system was installed to simulate irrigation and rainfall events and an automatic moving rain shelter was constructed to protect the greens during rain events. The simulated event intensities and frequencies were similar to the greenhouse.

Influence of Pressure Injection on Trichlorphon Movement Through Simulated Greens.
Pressure injection of pesticides has potential for decreasing their movement from the application site in surface water and as vaporization. However, pressure injection could result in increased movement of the pesticide through rooting media of golf course greens and into soil increasing the potential for increased movement to groundwater. Therefore, we conducted research to determine the influence of pressure injection of, the insecticide, trichlorphon movement through simulated greens using the outside lysimeter facility.

The bermudagrass green, having lysimeters, were utilized for these treatments. The sod above four lysimeters was treated by using a broadcast application (BDCST) from backpack sprayer and four lysimeters were used for the pressure injection treatment (PI). Trichlorphon was applied at 10.25 kg $ha^{-1}$, in both application methods. The BDCST application was made in 206 L $ha^{-1}$ at a pressure of 166 kPa and the boom was 0.45 m above the sod during application. Pressure injection was accomplished using the Toro Experimental Pressure Injection System. The trichlorphon was injected in a diluent volume of 4,702 L $ha^{-1}$ at a pressure of 21.3 MPa. The sprayer exit port was located 10 cm above the sod and the injection tips sprayed in streams located 7.5 cm apart.

The simulated irrigation and rainfall was controlled as previously described and leachate was collected from the bottom of the lysimeters. The leachate was collected on alternate days and stored in a cooler at 4 °C for weekly accumulation. The weekly accumulation volume was measured and subsampled for laboratory analyses.

Movement of Methyl Bromide Through Golf Course Greens.
During September, 1994 the bermudagrass sod was removed from over 3 of the lysimeters in the outside facility to simulate removal for resodding of a golf course green. Fiberglass caps (55 cm i.d.X 32.5 cm deep) were manufactured to fit over the top of the stainless steel insert of the lysimeter and to be sealed at the interface with a sealant. On October 3, 1994, 123 g

MeBr were released into each of the three sealed lysimeters to give a treatment rate of 533 g $m^{-2}$ and on March 6, 1995 15 g MeBr were released into the three sealed lysimeters to give a treatment rate of 65 g $m^{-2}$. Prior to treatments, the lysimeter exit tubes were placed into 15 L stainless steel canisters below the surface of 12 L of deionized water for collection of the gaseous MeBr. On daily intervals following treatment, 100 mL aliquats were removed from each canister for analyses of MeBr and Br. At 2 DAT the fiberglass caps were removed from the tops of the lysimeters and at 4 DAT the lysimeters were irrigated with 2.5 cm of water to simulate a rainfall event. Following this irrigation the lysimeters were irrigated with 0.63 cm water daily for six day periods and every seventh day with 2.5 cm of water until the experiment was terminated at 22 DAT. At 4 DAT, when irrigation was initiated, the 12 L of sample water were replaced with 4 L of deionized water and each succeeding day the volume of water in the canister was measured, 100 mL samples were collected for quantifying the MeBr and Br, and the water in the canister was replaced with 4 L of deionized water. The exit tube for the lysimeter always remained below the water level in the canister. Following the sampling period for the October treatments the greens received at least 7.5 cm of water from rainfall or irrigation each week until the March treatment.

**Laboratory Analyses of MeBr.** The aqueous samples, obtained from the canisters, were stored in sealed containers at -18 °C until analyzed. Subsamples (5 mL) of the aqueous samples were transferred to the sample holder of a Tekmar 2016 Purge and Trap (P&T) Autosampler (Tekmar, Cincinnati, OH). A quantity of 1-chloro-2-flurobenzene was added to the subsample to a concentration of 100 µg $L^{-1}$, as an internal standard (IS) for quantifying the MeBr. The subsamples were purged for 11 min with helium and the MeBr and IS were sorbed on a Vocarb 3000 (Supelco, Inc., Bellefonte, PA) trap. The trap was desorbed at 250 °C for 6 min. The desorbed sample was introduced through a closed-couple into a HP 5890 (Hewlett Packard, Atlanta, GA) gas chromatograph equipped with an electron capture detector (GC-ECD). The Rtx-1 column (30 m in length and 0.53 mm id) was coated with a 1 micron film of 100% crossbond dimethyl polysiloxane (Restek Corp., Bellefonte, PA). The detector and injection port temperatures were 280 and 50 °C, respectively and the oven temperature was programmed to include an initial temperature of 30 °C for 5 min; a ramped temperature of 40 °C $min^{-1}$ to a final temperature of 280 °C; and a final temperature hold for 3 min. The purged 5 mL aqueous subsample was analyzed for Br in a Lachete Instrument (Lachat Instruments, Milwaukee, WI).

The two treatment dates included different treatment rates and were analyzed as experiment 1 (October treatment) and experiment 2 (March treatment). Each treatment was replicated thrice (three lysimeters), analyses of variance was performed on all data within each experiment, and Fisher's LSD values (P=0.05) were calculated for mean comparisons.

<u>Nitrate and Pesticide Movement Through Putting Greens at Town and Country Club.</u>
Two practice greens that were renovated at a Town and Country Club located north of Atlanta, Georgia were each instrumented with 3 lysimeters during the renovation phase. The rooting media consisted of a graded sand and sphagnum peat moss similar to the 85:15 rooting medium used in the greenhouse. The lysimeters were constructed by placing stainless steel sinks (37.5 X 52.5 X 17.5 cm deep) on the drainage gravel and plumbing the sinks to a location outside the green area. The lysimeters were filled with rooting media as the greens were developed. Leachate from the lysimeters is collected in stainless steel containers

protected by an exclosure. Leachate in the containers was collected on alternate days and combined in a larger container for weekly collections. The weekly collections are subsampled and analyzed for pesticides and nitrate.

**Pesticide Movement from Simulated Fairways (See 1994 report for detailed description).**

Twelve individual plots (3.7 x 7.4 m), separated by landscape timbers, were developed in a grid with a 5% slope from the back to the front. The subsoil was a clay loam and the top soil was a sandy loam. A ditch was dug at the front of the plots to install a trough for collecting the runoff water in a tipping-bucket sample collection apparatus. The plots were sprigged with 'Tifway 419' bermudagrass on May 17, 1993 and the plots were completely covered with grass by August 1, 1993. The Wobbler$_{TM}$ off-center rotary action sprinkler heads were mounted 7.4 m apart and 3.1 m above the sod surface. When operated at 138 kPa, the system produced an even distribution of simulated rainfall at an intensity of 3.3 cm $hr^{-1}$.

The plots were treated, in 12 replications, with the pesticides listed in Table 1 between June 1 and November 1 of 1994 and 1995 (for nondormant treatments). 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 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 $m^2$. Spray treatments were applied using a backpack sprayer calibrated to deliver 206 L $ha^{-1}$ 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.

Storm events were simulated at 24, 48, 96, and 192 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.

<u>Influence of Management Strategies on Pesticide Movement in Surface Runoff Water.</u>
2,4-D was applied during December to dormant bermudagrass sod to determine the influence of dormant grass on pesticide movement in surface water runoff. Additionally, 2,4-D DMA 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 DMA 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. 2,4-D DMA and trichlorfon 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.

TABLE 1. Pesticide applications made to simulated fairways.

| Pesticide | | Rate |
|---|---|---|
| common name | chemical nomenclature | kg ha$^{-1}$ |
| benefin | N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine | 1.70 |
| 2,4-D DMA[1] & LVE | (2,4-dichlorophenoxy)acetic acid | 2.24 |
| dicamba DMA | 3,6-dichloro-2-methoxybenzoic acid | 0.56 |
| dithiopyr | S,S-dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarbothioate | 0.56 |
| chlorothalonil | (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) | 9.50 |
| chlorpyrifos | O,O-diethyl O-(e,5,6-trichloro-2-pyridyl)phosphorothioate | 1.12 |
| mecoprop DMA | (±)-2-(4-chloro-2-methylphenoxy)propanoic acid | 1.68 |
| pendimethalin | N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine | 1.70 |
| trichlorfon | dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate | 9.15 |
| nitrate-N | | 24.60-N |

[1]DMA = dimethylamine salt formulation.
LVE = low volatile ester; butoxyethyl ester

**Potential Reentry Exposure.**

The purpose of this research was to determine if herbicides commonly used on golf course greens are potentially harmful to golfers who kneel on the treated sod to align a putt. The hypothesis was that golfers who kneel to align a putt are at risk of being exposed to herbicides such as 2,4-D, dicamba, and mecoprop used to control weeds on golf course greens.

To determine the pressure applied to the fabric during knee-contact with the turf while aligning to putt the golf ball, James, was weighed as he assumed the kneeling position. After measuring the diameter of his knee, the pressure applied on the spot was calculated and the following treatment and sampling procedures were used in the experiment:

Pieces of golfer's cotton-trouser material were exposed to untreated (check) and treated bermudagrass turf maintained in 40-cm square boxes in the greenhouse. Glass-fiber filter papers, (7-cm in diam.) were placed immediately behind the fabric (FIGURE 1) to determine the potential skin exposure to herbicide passing through the trouser fabric. The fabric and filter paper were bound to a round iron weight that had a surface area the same as James' knee (7.5 $cm^2$) (FIGURE 1). The iron weight resulted in a pressure (257 $gm/cm^2$) similar to the pressure exerted on James' knee in the kneeling position.

The fabric covered weight was placed on the turf for 20 sec, the approximate time for lining up a putt. During this period the weighted fabric was gently rotated sideways twice to simulate a golfer's movements. The cloth and filter paper were then separated and transferred to labeled brown sample jars for storage until analyzed for herbicide residues. The sampling was made on different areas of the sod boxes at each sampling period.

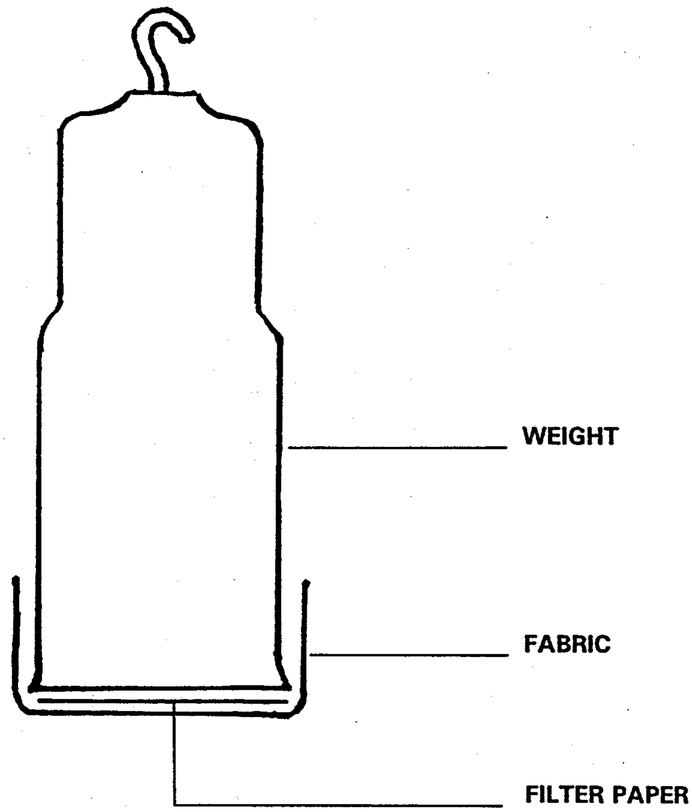


FIGURE 1. Apparatus used for determining the potential exposure of a golfer when kneeling on a golf course green treated with pesticides. The weight and area are similar to the pressure and area of a golfer's knee. The cotton fabric represented cotton trousers and the filter paper represented the golfer's skin.

Treatments were replicated three times. Three boxes of bermudagrass sod were sprayed with a formulation mixture of the herbicides, 2,4-D, dicamba, and mecoprop at concentrations to give application rates of 0.56, 0.28, and 1.40 kg acid equivalent per hectare, respectively. These herbicide rates are registered by the Environmental Protection Agency for application to golf course greens. Samples of fabric and filter paper were exposed to the treated turf at intervals of 0, 6, 30, 54, 78, and 102 hours after treatment (HAT). The boxes were irrigated with 1.25 cm of water each morning, beginning the day after treatment, to simulate irrigation of the golf course greens.

Prior to extracting the herbicides from the fabric, the pre-marked area directly exposed to the turf was cut out. The cut-out portions were replaced into the jars and the herbicide residues were extracted as follows: Fifty milliliters of acidified acetone was added to each sample jar containing the filter paper or fabric and shaken for 10 min on a mechanical shaker. The extractant was transferred to a 250-mL rotary evaporator flask. The extraction was repeated twice and the combined extracts of acetone were reduced in volume to less than 5 mL by rotary evaporation. The residue was transferred to a 25-mL vial and evaporated under nitrogen 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 capped and heated in a 60°C water bath for 2 hr. The vials were removed from the water bath and cooled before adding 10 mL of water. Five milliliters of internal standard (100 ppb dicamba methyl ester in hexane) were added, the vials were capped and shaken for 30 sec, and the two liquid layers were allowed to separate. The top layer (hexane with herbicides esters) was removed from the vial and a portion was injected into the Gas Chromatograph equipped with an Electron Capture Detector for analyses.

The research design for statistical analyses included: 3 herbicide treatments (2,4-D, dicamba, and mecoprop); 6 sampling times [0, 6, 30, 54, 78, and 102 hr after treatment (HAT)]; 3 replications; and the experiment was conducted twice. Analysis of variance was performed on the data for the combined experiments and means were separated using the least significant difference (LSD) test at the 0.05 level of significance.

**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 (TFE) and the esters were quantified by gas chromatography using an electron capture detector (ECD).

Dithiopyr was extracted by solid phase extraction and analyzed by GC-ECD according to a method developed in our laboratory. Benefin and pendimethalin were extracted from the 50 mL aqueous subsamples by liquid-liquid partitioning into 150 mL dichloromethane. The dichloromethane was concentrated under vacuum to 1 mL and diluted with 1 mL toluene containing metribuzin as an internal standard. Analytes were quantified by GC-ECD. 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 analytes and metabolites were quantified by GC-ECD and data for the analytes are presented as the additive of the metabolites and analytes. Column and conditions for GC-ECD are listed in TABLE 2. The helium carrier gas head pressure was adjusted until a 1 μL head space sampling from methylene chloride has a retention time of 2.5 min. Nitrogen gas used for make-up and purge gas was maintained at flow rates of 12-14 and 50 mL $min^{-1}$, respectively. The extraction and quantification systems were established to give a minimum detectable concentration (MDC) of 1 μg $L^{-1}$ in the aqueous effluent. The trichlorphon was extracted from the water with ethyl acetate and the ethyl acetate was injected directly into the GC.

TABLE 2. GC-ECD operating conditions for the analytes analyzed.

| Analyte | Column[1] | Gas[2] flow (ml min$^{-1}$) | Temperatures (°C) Inlet | Detector | Column initial/(min) | final/(min) | Program rate (°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(250/1) | 4(15) |

1 RTX-1= Fused silica column (crossbond 100% dimethyl polysiloxane)
0.53 mm id; 1 micron thickness and 30 m long fit with a 5 m guard column.
RTX-35=Fused silica column (crossbond 65% dimethyl-35% diphenyl polysiloxane)
0.53 mm id; 0.5 micron thickness; 30 m long fit with 5 m guard column.

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

## RESULTS AND DISCUSSION

### Measurement of Pesticide Movement Through Simulated Greens.

Influence of Pressure Injection on Movement Through Simulated Greens.
Trichlorphon is an insecticide registered for use on turfgrass. It is an important management practice for white grub control in turfgrass. It is highly water soluble (154 g L$^{-1}$ water) and rapidly degrades to dichlorvos. The leachate samples were analyzed for both trichlorphon and dichlorvos, however, for this presentation both analytes were summed and data (TABLE 3) are the sum for dichlorvos and trichlorphon for the weekly samples.

Data from only 6 WAT are presented since the research is in progress. The data indicate that less trichlorphon was present in the leachate from the lysimeters treated by PI compared to the BDCST treatments (TABLE 3). The trichlorphon concentration was consistently less in the PI treatments over the 6 week collection period. Additionally, over the 6-week period 4.0% of the trichlorphon applied as a BDCST was transported from the lysimeters whereas only 2.4% of the trichlorphon applied as a PI was transported in the leachate (TABLE 3).

TABLE 3. Trichlorphon concentration (ppb) in leachate and fraction (%) of applied trichlorphon transported through lysimeters under 'Tifdwarf' bermudagrass treated with 10.25 kg $ha^{-1}$ trichlorphon by broadcast (BDCST) and pressure injection (PI).

| | Concentration | | Fraction transported | |
|---|---|---|---|---|
| WAT | BDCST | PI | BDCST | PI |
| | ------- ppb ------- | | -------- % -------- | |
| 1 | 451.7 | 269.3 | 0.5 | 0.3 |
| 2 | 1238.9 | 888.4 | 0.8 | 0.5 |
| 3 | 1637.6 | 1133.2 | 0.7 | 0.4 |
| 4 | 1771.8 | 1375.4 | 0.9 | 0.6 |
| 5 | 1175.8 | 539.9 | 0.8 | 0.4 |
| 6 | 478.2 | 297.6 | 0.3 | 0.2 |
| Total Transported | | | 4.0 | 2.4 |

WAT = Weeks after treatment.

Movement of MeBr Through Simulated Golf Course Greens.

**Analytical Method.** A review of the literature indicated that methodology for determining MeBr in aqueous solution was not adequate for determining trace quantities (μg $L^{-1}$ range). Most of the following fumigant methods were developed to determine specific residues at levels above 1 mg $L^{-1}$: leaching, extraction and partition, sweep and codistillation, headspace, and purge-closed loop.

After preliminary trials we chose to develop a coupled P&T/GC-ECD closed system for analyses of MeBr and the Lachate system for analyses of Br in the purged aqueous subsample. Potential methane released was relative to the Br in the solution. Results of preliminary experiments indicated that a single helium purge for 11 min at 100 °C removed the MeBr and IS to a level that they could not be detected in a second purge. The relative molar response ratio of MeBr to the IS was 6.77±0.32 and the MeBr concentration curve was linear ($R^2$=0.98) over the range of 5→100 μg $L^{-1}$. The method resulted in a minimum detectible MeBr concentration of 5 μg $L^{-1}$.

**MeBr and Br Transport.** The recommended rate of MeBr application for sterilizing soils in greens during renovation is 65 g $m^{-2}$. However, due to the complexity of gaseous application, it is estimated that application rates may range from the recommended rate to near 10X the recommended rate. Therefore, two experiments were conducted to determine the influence of rate of MeBr application on MeBr transport through the greens soil mixture. The application rate for experiment 1 was ca. 10X the recommended rate which was used in experiment 2.

MeBr accumulated in the canister over the 4 days following treatment reaching a maximum concentration at 3 DAT (TABLE 4). The quantity of MeBr transported over the 4 DAT was approximately 10 fold greater for experiment 1 (21.35 mg) compared to experiment 2 (1.79 mg) indicating that the treatment rate directly attributes to the quantity of MeBr transported. The sandy soils in the lysimeters were well drained prior to treatment which would allow for MeBr diffusion through the soil mix and into the canister. The Br concentration in the samples were below the minimum detection limit for the Lachet method.

TABLE 4. Cumulative concentration of MeBr in the collection canister and quantity of MeBr transported from the lysimeters over a 4 DAT period. MeBr was released from lysimeter covers at 2 DAT and the first irrigation occurred at 4 DAT.

| DAT | MeBr Concentration | | MeBr Transported | |
|---|---|---|---|---|
| | Experiment 1 | Experiment 2 | Experiment 1 | Experiment 2 |
| | (ppb) | | (mg) | |
| 1 | 525.79 | 81.12 | 6.30 | 0.97 |
| 2 | 1460.17 | 126.39 | 17.52 | 1.52 |
| 3 | 1906.35 | 163.16 | 22.88 | 1.96 |
| 4 | 1779.82 | 149.01 | 21.35 | 1.79 |
| LSD (0.05) | 472.16 | 54.07 | 5.66 | 0.65 |

Following the initiation of irrigation at 4 DAT, MeBr was transported through the lysimeters up to 8 to 12 DAT for both experiments (FIGURES 2 and 3). Total MeBr transported in experiment 1 was ca. 5X the quantity transported from the lysimeters in experiment 2. Br continued to be transported throughout the experiments with the rate of transport decreasing over the last 4 days. Approximately 16X more Br was transported from the lysimeters during experiment 1 compared to experiment 2. The higher than expected value for Br transport can be explained by the fact that the difference in MeBr transported was less than (only 5X) would be expected from a 10X difference in treatment rate. Assuming that the Br came from MeBr, there would be 144 and 8 mg of methane released over the duration of experiments 1 and 2, respectively.

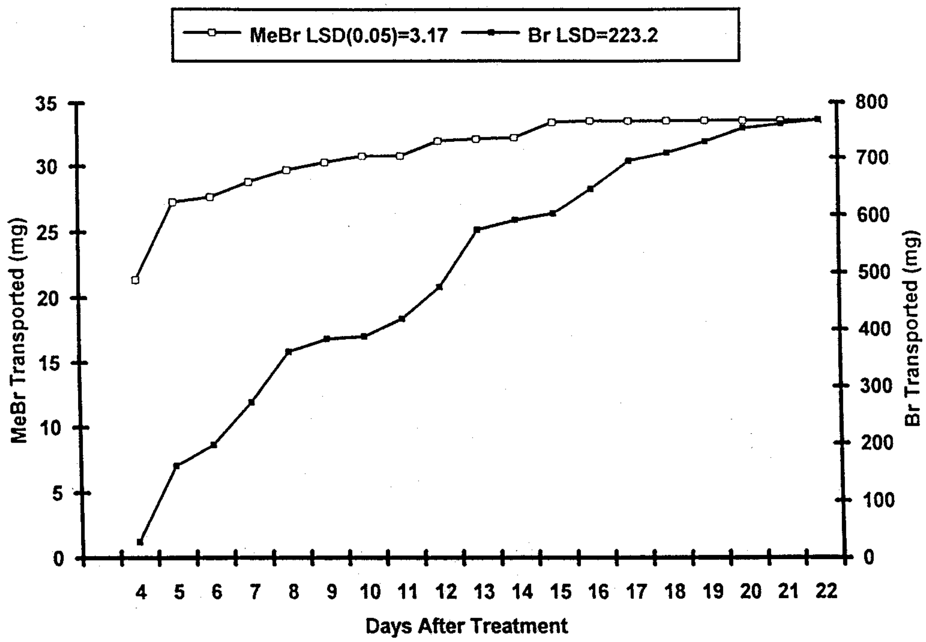


FIGURE 2. Methyl bromide (MeBr) and bromide (Br) transported through lysimeters containing golf course greens soil mixture over 22 day period following treatment with MeBr in experiment 1 (October 3, 1994).

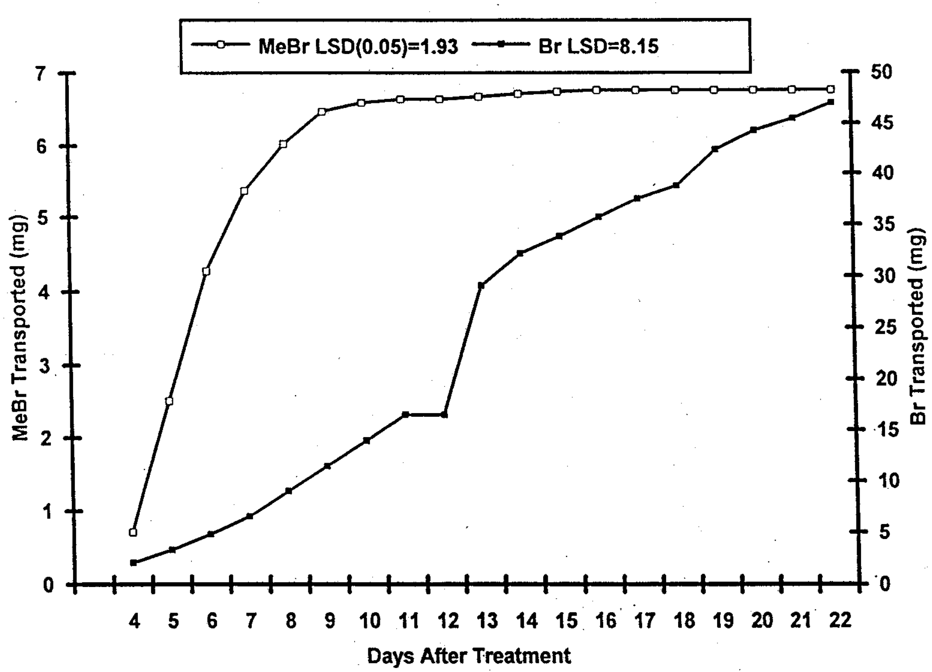


FIGURE 3. Methyl bromide (MeBr) and bromide (Br) transported through lysimeters containing golf course greens soil mixture over 22 day period following treatment with MeBr in experiment 2 (March 6, 1995)

The concentration of MeBr in the leachate exiting the lysimeters tended to decrease over the collection period in experiment 1 (FIGURE 4) except for the concentration peak on day 15 which cannot be explained. Similarly, the concentration of MeBr in the leachate from experiment 2 decreased over the treatment period (FIGURE 5). The higher concentrations of MeBr in experiment 2 are a response to the reduced water transported from the lysimeters during March compared to October. Trends of Br concentrations in the leachate were cyclical for both experiments with the major peaks in concentration occurring at 10-11 DAT after which the concentrations decreased over the remainder of the research period.

The cumulative fraction of applied MeBr and Br transported from the lysimeters is very small. Less than 1% of the total applied MeBr can be accounted for as MeBr and Br transported through the lysimeters in both experiments (TABLE 5) and apparently the majority of the fraction transported was accounted for as Br. The data indicate that only 0.75 and 0.36% of the MeBr applied in experiments 1 and 2, respectively, was metabolized in the soil mixture releasing those fractions of methane and Br.

TABLE 5. Cumulative fraction of applied MeBr and Br transported through lysimeters containing USGA soil mixture.

| | MeBr | | Br | |
|---|---|---|---|---|
| DAT | Experiment 1 | Experiment 2 | Experiment 1 | Experiment 2 |
| | (% of applied) | | | |
| 4 | 0.019 | 0.010 | 0.03 | 0.02 |
| 5 | 0.022 | 0.017 | 0.16 | 0.03 |
| 6 | 0.022 | 0.029 | 0.19 | 0.04 |
| 7 | 0.023 | 0.036 | 0.26 | 0.05 |
| 8 | 0.024 | 0.040 | 0.35 | 0.07 |
| 9 | 0.025 | 0.043 | 0.37 | 0.09 |
| 10 | 0.025 | 0.044 | 0.38 | 0.11 |
| 11 | 0.025 | 0.044 | 0.41 | 0.13 |
| 12 | 0.026 | 0.044 | 0.46 | 0.13 |
| 13 | 0.026 | 0.045 | 0.56 | 0.22 |
| 14 | 0.026 | 0.045 | 0.57 | 0.25 |
| 15 | 0.026 | 0.045 | 0.58 | 0.26 |
| 16 | 0.026 | 0.045 | 0.63 | 0.27 |
| 17 | 0.026 | 0.045 | 0.67 | 0.29 |
| 18 | 0.026 | 0.045 | 0.69 | 0.30 |
| 20 | 0.026 | 0.045 | 0.71 | 0.32 |
| 21 | 0.026 | 0.045 | 0.73 | 0.34 |
| 22 | 0.026 | 0.045 | 0.74 | 0.35 |
| 23 | 0.026 | 0.045 | 0.75 | 0.36 |
| LSD (0.05) | 0.002 | 0.013 | 0.22 | 0.06 |

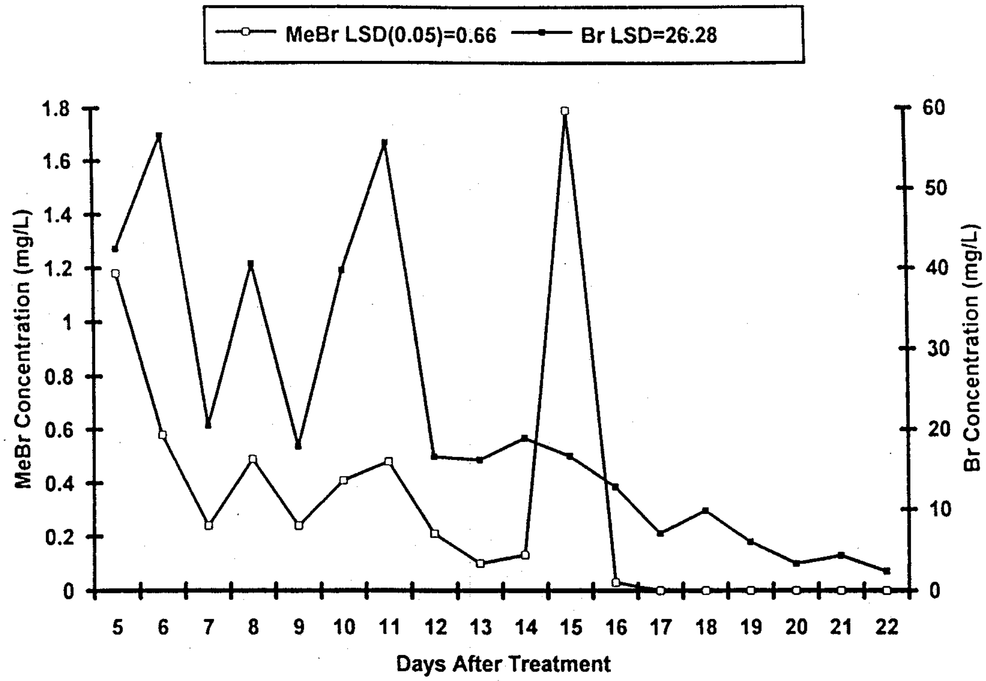


FIGURE 4. Concentration of methyl bromide (MeBr) and bromide (Br) in leachate from lysimeters containing golf course greens soil mixture during collection period following treatment with MeBr in experiment 1 (October 3, 1994).

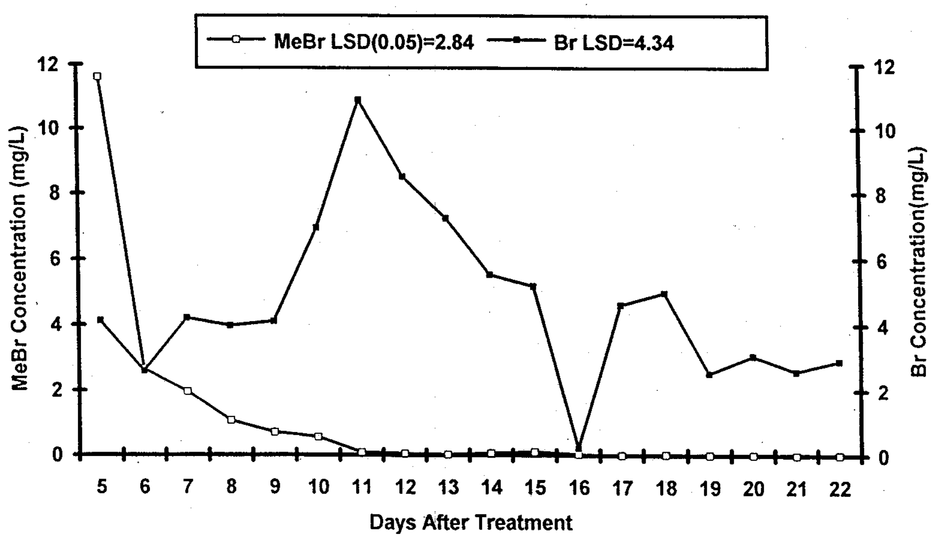


FIGURE 5. Concentration of methyl bromide (MeBr) and bromide (Br) in leachate from lysimeters containing golf course greens soil mixture during collection period following treatment with MeBr in experiment 2 (March 6, 1995).

**Nitrate and Pesticide Movement Through Putting Greens at Town and Country Club.**

Sampling was initiated on December 1, 1994. However, only fertilizer was used in the management of the putting greens until April, 1995. Beginning in April, 1995 we began to analyze the samples for chlorothalonil (CTH) and chlorpyrifos (CLP) and the hydroxy metabolites (OH-CTH and OH-CLP, respectively) in response to the treatments. Nitrate-N was analyzed throughout the sampling period.

Data (TABLE 6) indicate that only minor quantities of CTH were found in the leachate. Slightly greater quantities of OH-CTH were found in the leachate. The OH-CTH is much more water soluble than CTH and probably explains the reason for the greater concentration in the leachate from the practice greens. These data corroborate the data reported in the 1994 final report. Only very small quantities of CTH were found in the leachate and slightly higher concentrations of OH-CTH were detected. Considering the quantity of CTH applied, these concentrations would be considered as minor and only a small (<1%) fraction of the applied CTH is determined in the leachate as CTH and OH-CTH.

The $NO_3$ concentration in the leachate seemed to respond to applications of the various fertilizers containing $NO_3$. The concentration of nitrate from green 2 was always lower than in the leachate from green 1. There is no explanation for this difference since, to the superintendents knowledge, both greens were fertilized similarly.

TABLE 6. Treatments, leachate volume, and analyte concentration from 3 lysimeters in 2 practice greens at a Town and Country Club. Data are means from 3 lysimeters.

| Weekly sample[1] | | | Weekly Treatment[2] | | Analyte concentration 2 | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Date | Green | Qty | Analyte | Rate | $NO_3$ | CLP | OH-CLP | CTH | OH-CTH |
| | | (L) | | kg $ha^{-1}$ | µg $L^{-1}$ | | | | |
| 3-23-95 | 1 | 0.02 | urea | 50-N | 260 | - | - | - | - |
| | 2 | 0.03 | | | 460 | - | - | - | - |
| 3-30-95 | 1 | 1.19 | 18-0-18 | 34-N | 3,360 | - | - | - | - |
| | 2 | 0.04 | urea | 12-N | 440 | - | - | - | - |
| 4-13-95 | 1 | 1.58 | CTH | 9.39 | 2,520 | - | - | - | - |
| | 2 | 1.05 | 18-3-10 | 24-N | 1,010 | - | - | 4 | 158 |
| 4-27-95 | 1 | 3.51 | CTH | 9.39 | 4,210 | - | - | 6 | 97 |
| | 2 | 3.97 | | | 530 | - | - | 5 | 59 |
| 6-01-95 | 1 | 2.52 | 18-0-18 | 24-N | 3,600 | 0 | 0 | 4 | 23 |
| | 2 | 1.90 | CLP | 1.1 | 760 | 0 | 0 | 4 | 70 |
| | | | CTH[3] | 18.78 | | | | | |
| 6-15-95 | 1 | 0 | urea | 5-N | 100 | 0 | 0 | 0 | 6 |
| | 2 | 0 | CLP | 1.1 | 0 | 0 | 0 | 0 | 0 |
| 6-29-95 | 1 | 1.96 | urea | 10-N | 3,150 | 0 | 0 | 0 | 0 |
| | 2 | 2.77 | | | 440 | 0 | 0 | 0 | 0 |
| 7-27-95 | 1 | - | 46-0-0 | 3-N | 4,520 | 0 | 0 | 2 | 177 |
| | 2 | - | 10-2-10 | 20-N | 560 | 0 | 0 | 1 | 140 |
| | | | 3-6-9 | 6-N | | | | | |
| | | | CTH | 14.2 | | | | | |
| 8-31-95 | 1 | 3.09 | CLP | 1.1 | 1,410 | 0 | 0 | 3 | 139 |
| | 2 | 3.76 | $NH_4NO_3$ | 34-N | 410 | 0 | 0 | 9 | 150 |
| | | | 20-20-20 | 34-N | | | | | |
| | | | CTH[3] | 18.78 | | | | | |
| | | | 20-20-20 | 2-N | | | | | |
| | | | urea[3] | 20-N | | | | | |
| 10-12-95 | 1 | 35 | urea[3] | 29-N | 250 | 0 | 0 | 4 | 139 |
| | 2 | 91 | CTH | 9.39 | 220 | 0 | 0 | 9 | 126 |

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

Influence of Management practices on Pesticide Movement from Simulated Fairways.
At 24, 48, and 96 HAT the plots received only simulated storm events at averages of 5.0, 5.0, and 2.4 cm, respectively. Only samples collected over the first 192 HAT contained

concentrations of the pesticides above the MDC of 1 μg $L^{-1}$ . The fraction of water leaving the plots for all experiments at 24, 48, 96, and 192 HAT was 44.8, 72.1, 40.0, and 35.5%, respectively. The highest concentrations of pesticides in the runoff water occurred during the first rainfall event applied at 24 HAT.

The fraction of applied analytes that were transported in the runoff water correlated closely to the log of the water solubility (pSw) and the log of the octanol:water partition coefficient (pKow) (Equation 1) for the analytes (TABLE 7).

Equation 1.

$$pK_{ow} = \frac{pS_w - 4.184}{-0.922}$$

$pS_w$=log water solubility ($S_w$) in ppm

The $r^2$ for the quadratic equations for the resulting graphs of % applied analyte transported against the pSw or pKow for the analyte were 0.91 and 0.97, respectively. For practical purposes the data indicate that the higher the water solubility of the analyte the greater potential for analyte movement in surface water runoff. This prognosis is illustrated in results presented in TABLE 7.

TABLE 7. Relationship between % transported and pKow and log water solubility (pSw ppm) for nine analytes applied as a broadcast application.

| Analyte | % Transported | pSw (ppm) | pKow |
|---|---|---|---|
| Nitrate | 16.4 | 6.00 | -1.97 |
| Dicamba-DMA | 14.6 | 5.82 | -1.82 |
| Mecoprop-DMA | 14.4 | 5.48 | -1.77 |
| 2,4-D-DMA | 9.6 | 5.09 | -1.40 |
| Chlorothalonil | 0.8 | 2.78 | 1.53 |
| Dithiopyr | 1.9 | -1.00 | 4.70 |
| Chlorpyrifos | 0.1 | -1.48 | 4.97 |
| Benefin | 0.01 | -1.60 | 5.62 |
| Pendimethalin | 0.01 | -1.85 | 5.11 |

| Y | X | Equation | $R^2$ |
|---|---|---|---|
| % transported | pSw | $y = a + bx + cx^2$ | 0.91 |
| % transported | pKow | $y = a - bx - cx^2$ | 0.97 |

The highest percentage of applied analytes transported from the treated plots have the highest water solubility. As much as 32.5, 16.4, 14.6, 14.4, and 9.6% of the applied trichlorphon, nitrate, dicamba, mecoprop, and 2,4-D were transported from the plots treated during the summer months. Less than 1% of the applied chlorothalonil, chlorpyrifos, benefin, and pendimethalin was transported from actively growing sod. These analytes are only slightly soluble in water (TABLE 8).

TABLE 8. 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 $ha^{-1}$) | (%) | (ppb) |
| Nitrate-N | 24.4 | 16.4 | 12,500 |
| Nitrate-N D[1] | 24.4 | 64.2 | 24,812 |
| Dicamba-DMA | 0.56 | 14.6 | 360 |
| Dicamba-DMA D[1] | 0.56 | 37.3 | 752 |
| Mecoprop-DMA | 1.68 | 14.4 | 810 |
| Mecoprop-DMA D[1] | 1.68 | 23.5 | 1,369 |
| 2,4-D-DMA | 2.24 | 9.6 | 800 |
| 2,4-D-DMA D[1] | 2.24 | 26.0 | 1,959 |
| 2,4-D-LVE | 2.24 | 9.1 | 812 |
| 2,4-D-DMA P[2] | 2.24 | 1.3 | 158 |
| 2,4-D-DMA B[3] | 2.24 | 7.6 | 495 |
| Trichlorphon[4] | 9.15 | 32.5 | 13,960 |
| Trichlorphon[4] P[2] | 9.15 | 6.2 | 2,660 |
| Chlorothalonil[5] | 9.50 | 0.8 | 290 |
| Chlorpyrifos[6] | 1.12 | 0.1 | 19 |
| Dithiopyr | 0.56 | 2.3 | 39 |
| Dithiopyr-G[7] | 0.56 | 1.0 | 26 |
| Benefin | 1.70 | 0.01 | 3 |
| Benefin-G[7] | 1.70 | 0.01 | 6 |
| Pendimethalin | 1.70 | 0.01 | 9 |
| Pendimethalin-G[7] | 1.70 | 0.01 | 2 |

[1] D = applied to dormant bermudagrass.
[2] P = pressure injection application.
[3] B = 2 m buffer strip between treatment and collection; 75% plot treatment.
[4] Trichlorphon + dichlorvos metabolite.
[5] Total for chlorothalonil and OH-chlorothalonil.
[6] Total for chlorpyrifos and OH-chlorpyrifos.
[7] G = granule application.

Application of the analytes to dormant sod greatly increased the fraction of applied analyte to be transported from the plots (TABLE 8). Transport of nitrate, dicamba, mecoprop, and 2,4-D increased to 64.2, 37.3, 23,5, and 26.0 % of the applied analyte, respectively. Application of the ester formulation (LVE) did not reduce the fraction of 2,4-D transported compared to the amine formulation (DMA) (TABLE 8). Additionally, granule formulations of pendimethalin dithiopyr and benefin did not decrease the fraction of these analytes transported compared to the emulsifiable concentrate formulation applied as a liquid (TABLE 8). Finally, pressure injection of 2,4-D and trichlorphon greatly reduced the fraction of these analytes transported from the nondormant sod compared to the broadcast application technique of these analytes. Pressure injection of 2,4-D (DMA) reduced the transport of 2,4-D by 7 fold and trichlorphon was reduced 5.2 fold compared to broadcast application (TABLE 8). Including a 25% area buffer strip between the treated area and the sample collection area did not, significantly, reduce 2,4-D transported, based on fraction of applied, from the plots. The concentration of 2,4-D in the water collected from the treatment with a buffer strip, at 24 HAT, was ca. one-half as high as compared to the treatment, without a buffer strip (TABLE 8). This is explained, in part by the fact that 25% less analyte was applied to the plot with the (2.0 m) buffer strip.

**Potential Reentry Exposure to Pesticides.**

FIGURE 6 shows the residue levels of dicamba, 2,4-D, and mecoprop detected on the fabric (mg). Almost all of the detected residues were from samples taken up to 6 HAT. Very little herbicide residue was found on the fabric samples taken following 6 HAT. The relative quantities of mecoprop, 2,4-D, and dicamba recovered were proportional to the respective rates at which they were applied to the turf (i.e. mecoprop>2,4-D>dicamba). The residue recovered from the filter paper (represents skin) is shown in FIGURE 7. It should be noted that the y-axis units are reduced by a factor of 10 compared to FIGURE 6. The data indicate that there is very little residue on the filter paper after the 0 HAT sampling period. These data indicate that the risk for potential skin exposure, to the herbicides, is greatest immediately following application and there is very little risk of exposure when kneeling on a green at periods of 6 HAT or longer. The combined residues on the fabric and the filter paper from samples taken at 0 and 6 HAT accounted for 95% of the total quantity of each herbicide recovered over the 102-hr sampling period. The sum of each herbicide found on the fabric and filter paper would represent an absolute maximum-potential exposure for the golfer assuming all of the herbicide on the fabric would rub on the golfer's knee while walking.

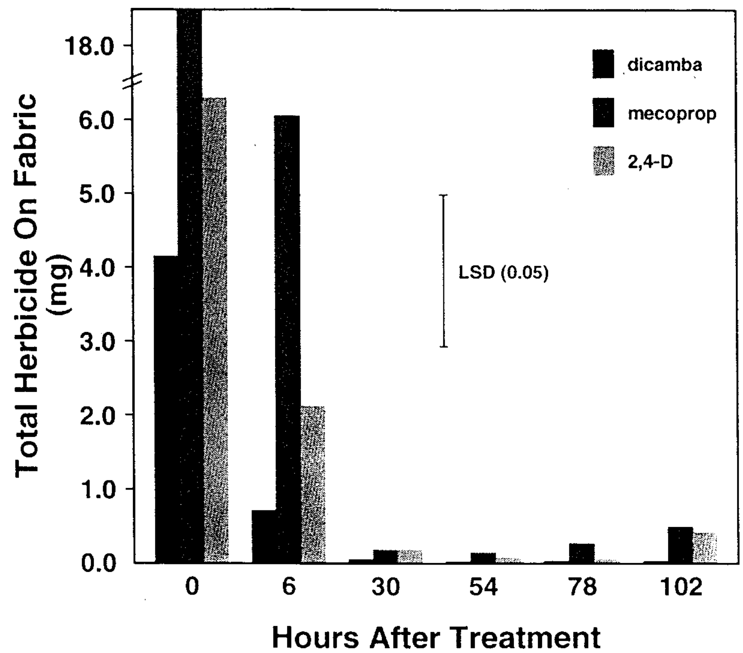


FIGURE 6. Total herbicide (mg) residues on fabric (simulation of trousers) following exposure to treated turfgrass.

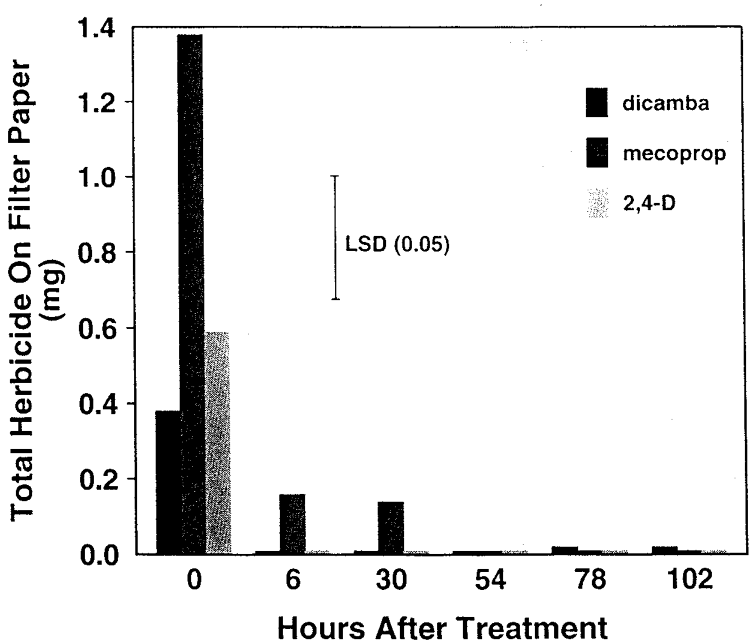


FIGURE 7. Total herbicide (mg) residues on filter paper (simulation of golfer's skin) following exposure to treated turfgrass.

Assuming that the quantity of herbicides on the filter paper (FIGURE 7) represents potential exposure for the golfer, these quantities of the herbicides should not pose a risk to the golfer. The World Health Organization has determined the levels of exposure, to these herbicides, that do not produce effects on non-human animals (TABLE 9). The NOEL (No Observed Effect Level) is the highest level, determined from a series of test exposures on non-humans, at which no health effects were observed.

TABLE 9. Maximum No Observed Effect Level (NOEL) (mg/kg) for dicamba, mecoprop, and 2,4-D established by World Health Organization and the NOEL (mg) for James.

| Herbicide | Maximum NOEL (mg/kg body wt.) | NOEL for James (mg) |
|---|---|---|
| dicamba | 5 | 324.5 |
| mecoprop | 50 | 3,245.0 |
| 2,4-D | 10 | 649.0 |

Considering the established NOEL for James (TABLE 9) who weighed 64.5 kg, he could kneel down on freshly treated turf, to align a putt and the residue that would accumulate on the skin area (represented by the filter paper) of his knee (FIGURE 7) would be considerably lower than the NOEL. If the golfer waited 6 HAT, with these herbicides, the level of potential exposure would be reduced to nearly zero. Assuming that the herbicide on the filter paper represents skin exposure, James could kneel on greens, at 0 HAT, the following number of times before the potential exposure level would be equal to his NOEL: dicamba-863; mecoprop-2,350; and 2,4-D-1,109 times (TABLE 10). This would result in a very high golfing score. At 6 HAT these numbers would approach infinity since nearly 0 mg of the herbicides were found on the filter paper (FIGURE 7).

TABLE 10. Total number of times James can align for putting before potentially receiving skin exposure (filter paper) equal to NOEL.

| HAT[1] | dicamba | mecoprop | 2,4-D |
|---|---|---|---|
| 0 | 863 | 2,350 | 1,109 |
| 6 | 40,563 | 19,908 | 92,714 |
| 30 | 46,357 | 24,037 | 92,714 |
| 54 | 46,357 | 1,622,50 | 324,500 |
| 78 | 17,079 | 3,245,000 | 324,500 |
| 102 | 3,245,000 | 3,245,000 | 324,500 |

[1] Hours after treatment

Results of this research indicate that, under these conditions, a golfer is not at risk when kneeling on a golf course green (or 18 greens), at 0 or 6 hours after treatment with these herbicides, to align a putt. However, wisdom dictates that the golfer should not kneel on a green immediately after treatment with pesticides.

## CONCLUSIONS

Pesticides begin to disperse from the target area immediately after application. Partitioning of the pesticides in the environment and potential loss of pesticides to groundwater and surface water is determined by innumerable interacting factors and conditions. The potential for pesticides to leach to ground water depends on the: 1) properties of the chemical, 2) properties of the soil, 3) application conditions, and 4) climatic conditions. Chemicals found most often in ground water had many of the following characteristics: 1) highly mobile in soil leaching studies [high Rf values], 2) low retention by soil in adsorption studies [low $K_{OC}$ values], 3) applied at moderate to high rates over large hectarage, and 4) moderate to long lived in the environment (half-lives of 30 days or longer).

Previously obtained data from the greenhouse and outside lysimeter experiments indicated that only small quantities of the herbicides applied in that research were transported from the lysimeters (See 1994 Final Report). In that research, the analyte concentrations in the effluent water from the lysimeters were near the minimum detectible concentration (MDC) established for our methods of analyte extraction and analyses (1 $\mu g\ L^{-1}$). Therefore, if the analyte concentration is slightly above this level the data are a real number. If the concentration is slightly below the minimum detectable concentration, the data becomes zero. This allows for a large error term that will mask small differences that might be attributed to the differences in rooting mixtures or grass species.

The Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) model was used to predict the potential for 2,4-D to be transported from the lysimeters subtending bermudagrass in the greenhouse. The prediction of transport was compared with data on 2,4-D transport during a 1991 greenhouse lysimeter experiment. The GLEAMS model, with the defined parameters of that study, overestimated the actual 2,4-D transported from the lysimeters through the two rooting-media profiles used in these experiments. The GLEAMS model data inferred that the increased level of sphagnum peat moss in the rooting medium should reduce the 2,4-D concentration in the aqueous effluent. Since the observed levels of 2,4-D were near the MDC, for that experiment, it was impossible to determine an influence of the increased organic matter content, in the rooting media, on 2,4-D transported in the aqueous effluent. The inclusion of the thatch layer in the GLEAMS model did not alter the predicted transport of 2,4-D in the aqueous effluent from the 85:15 rooting media compared to noninclusion. The probable reason for no significant influence expressed by the thatch layer is due to the very thin thatch layer (1.40 cm) and due to the limited increase in organic matter used for this layer compared to the rooting media (5.80 vs 2.26%). Even though the GLEAMS model greatly overestimated the observed herbicide load, the maximum predicted concentration of 48 $\mu L^{-1}$ is less than the recommended MCL standard (70 $\mu L^{-1}$) for 2,4-D. Therefore, we havE undertaken a number of research projects that assist in resolving the differences between the GLEAMS model prediction of transport and the actual data obtained from the lysimeters. These data will be reported in the 1996 annual report.

Interest in the influence of MeBr on the environment has increased due to the influence of methane and MeBr on the ozone layer in addition to the general toxicity of MeBr and Br to animals. There are few reports on the transport of MeBr and Br through soil following treatment with MeBr. To place an importance on the reported concentrations and quantities of

MeBr and Br escaping into the environment by transport from fumigated greens is complicated by the fact that there are no published drinking water regulations or health advisories for these analytes in potable water systems. However, based on the very small fraction of the applied MeBr that we determined to be transported through the soil system, it is probably of minor importance compared to the released gas following fumigation. However, recent indications are that EPA is presently in the process of mandating the phasing-out of the use of MeBr. These data were submitted the program of Pesticide Impact Assessment Program for consideration.

In our recent proposal that is being funded by USGA, we proposed to determine management strategies that will reduce the risk of pesticides moving from the site of application. Pressure injection, of pesticides that are effective in the soil, has potential for risk reduction. We conducted several trial experiments during August 1995 to determine the potential for reducing quantity of pesticides in runoff water following application. Pressure injection could reduce the amount in the runoff but could result in increased movement through the soil. Therefore, we used our outside lysimeter facility to compare application methods on trichlorphon transport through the lysimeter system. The preliminary data, presented in TABLE 3, indicate that trichlorphon transport was greater from the broadcast (BDCST) application compared to pressure injection (PI) and the concentration trichlorphon in leachate from both applications was higher than received for other analytes. The research was conducted using 4 replications for each treatment (BDCST vs PI). The difference was consistent for all replications and Student's T test indicated significant (P=.05) differences at all sampling periods for both the concentration and fraction transported. However, this experiment was conducted only once and will be repeated, therefore, the data are only considered as indications until experimental error can be determined.

Data from the runoff plots are probably the first data of this type to be obtained from the Piedmont region including turfgrass as a cover. Watschke, Harrison, and Hamilton 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. Our system developed in the Piedmont on a kaolinite-clay loam soil resulted in at least 40-70% of the rainfall (3.3 cm $hr^{-1}$) to leave the plots as surface runoff. Additionally, this water contained moderately high concentrations of the treatment pesticides 2,4-D, mecoprop, and dicamba at 24 and 48 HAT. The concentrations of 2,4-D in the runoff water was a factor above the recommended MCL (See 1994 final report for data from preliminary experiments). These preliminary data indicated that there is a need for additional research on determining the potential for pesticides to occur in surface water runoff from the treated plots and determine potential management practices that could reduce the risk of pesticides in the runoff water.

Data for 9 analytes were used for developing a regression curve of fraction of applied analyte transported from the treated plots against the log of the water solubility (pSw) for the analyte and the log of the octanol:water partition coefficient (pKow) (TABLE 6). There was a high correlation for the quadratic curves from the data on fraction of analyte transported to pKow and pSw ($r^2$=0.97 and 0.91). The analyte transport data for all analytes and management systems researched in this study are presented on TABLE 6. The treatments for the research were replicated 9 times and some of the experiments were repeated and some will be repeated. The data should be interpreted as preliminary since there are no statistics included. However, trends are obvious and should be considered as valid. Analytes applied to dormant sod resulted in the highest analyte transport from the plots. As much as 64,2, 37.3, 26.0, and 23.5% of the applied nitrate, dicamba, 2,4-D, and mecoprop, respectively, were transported in the runoff water from the treated dormant plots. Thirty two percent of the trichlorphon and more than 10% of the dicamba, nitrate, mecoprop were transported from the treated sites. Very little of the less water soluble analytes; benefin, pendimethalin, chlorpyrifos, and chlorothalonil; were transported from the treated site. Pressure injection decreased the fraction of 2,4-D and trichlorphon transported from the treated sites by 7.4X and 5.2X. It is realized that 2,4-D would seldom be effective if pressure injected. Its use in this instance was as a water soluble analyte that occurred in fairly high concentrations in runoff water from plots treated with 2,4-D DMA. Analytes of similar solubility in water would be expected to give similar results.

Finally, the inclusion of a buffer strip between the area treated with 2,4-D DMA did not significantly reduce (9.9 to 7.6%) the fraction of applied 2,4-D transported from the plots (TABLE 8). Buffer strips are effective in screening particulate movement in water. However, the water soluble analytes are in solution and a buffer strip would not be expected to lower the fraction of applied analyte moving from the treated plots. However, the concentration in the runoff water would be decreased due to the reduction in treated area in the runoff plots.

The minimum difference in the fraction of 2,4-D LVE and 2,4-D DMA transported from the treated sites was surprising and can not be explained. 2,4-D LVE is only slightly soluble in water whereas the amine salt formulation (DMA) is very soluble in water. The 2,4-D LVE experiment was not repeated and will be repeated next summer. However, our system of treatment and analyses should not result in a major experimental error.

Data on the transport of the analytes from the practice greens at the Town and Country Club golf course agree very closely to data obtained for chlorothalonil, chlorpyrifos, and nitrate in leachate from the lysimeter studies. Nitrate and OH-chlorothalonil are commonly found in the leachate from the greenhouse and outside lysimeters treated with chlorothalonil, chlorpyrifos, and nitrate. Only trace quantities of chlorothalonil, chlorpyrifos, and OH-chlorpyrifos were determined in the leachate. The additive for chlorothalonil and OH-chlorothalonil in the leachate from the lysimeters was less than 1% of the applied chlorothalonil over the collection period.

To place a risk on the quantities of analytes in the runoff water is impossible and to imply that experimental plots duplicate the action of an actual rainstorm is not reasonable. It must be realized that the runoff water will probably be diluted several fold prior to reaching potable water systems. Additionally, the simulated rainfall was instantly turned on at maximum intensity as compared to a natural rainfall event which most probably would gradually attain maximum intensity over a period of time. However, these data would indicate that precautions must be exercised when applying water-soluble pesticides to golf course fairways in the Piedmont region, having at least a 5% slope. Risk reduction should be the objective of all management programs and the implications from this research should be important in developing those programs.

The results from the research project conducted to determine the potential exposure for a golfer kneeling on a golf course green treated with certain herbicides, indicate that the golfer is exposed to very small quantities of herbicide from this activity. Assuming that the quantity of herbicides on the filter paper represents potential exposure for the golfer, these quantities of the herbicides should not pose a risk to the golfer. The World Health Organization has determined the NOEL (No Observed Effect Level) for these herbicides (TABLE 9). Considering the established NOEL for James, the average golfer, who weighs 64.5 kg, he could kneel down on freshly treated turf, to align a putt and the residue that would accumulate on the skin area (represented by the filter paper) of his knee would be considerably lower than the NOEL. Assuming that the herbicide on the filter paper represents skin exposure, James could kneel on greens at 0 HAT, the following number of times before the potential exposure level would be equal to his NOEL: dicamba-863; mecoprop-2,350; and 2,4-D-1,109 times. This would result in a very high golfing score. At 6 HAT these number approach infinity since nearly 0 mg of the herbicides were found on the filter paper.

**1994-1995 PUBLICATIONS FROM RESEARCH ON FATE OF PESTICIDES**


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