USGA - GREEN SECTION RESEARCH

PROJECT: Evaluation of Management Factors Affecting Volatile and Dislodgeable Foliar Residues of Turfgrass Pesticides

ANNUAL REPORT: (11/1/95 - 10/31/96)

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EXECUTIVE SUMMARY

Accomplishments.

This year, we have completed all the method development for the determination of 13 turfgrass pesticides in three separate multiresidue analyses. All experiments and field samples have been collected. A total of 13 separate experiments have been conducted and a total of 585 samples have been collected. Residue analysis of this sample set is 80% completed. We have determined that the critical vapor pressure below which no turfgrass pesticide will volatilize to the extent that it results in an inhalation HQ greater than 1.0 to be between 3.3×10^{-6} to 5.6×10^{-5} mm Hg (Objective 1.1). We have determined the critical OPP RfD above which no tufgrass pesticide will result in a dermal HQ greater than 1.0 to be between 0.005 to 0.013 (Objective 1.3). We have collected appropriate weather data with this residue data set and have met with Dr. D. Haith, Dept. Agric. Eng., Cornell University, who has agreed to cooperate with us by modeling this data into a temperature dependent algorithm that will determine the critical surface temperature below which no volatile turfgrass pesticide will result in an inhalation HQ greater than 1.0 (Objective 1.2). This model will be available Spring/Summer 1997.

Two applications of the spreader/stricker adjuvant, Exhalt 800, have been made to determine if such ammedments can attenuate the exposure levels determined previously for the organophosphate insecticides. These data are currently being analyzed (residue data set 50% completed).

In summary, we have shown that organophosphate insecticides that possess high toxicity and volatility may result in exposure situations that cannot be deemed completely safe as judged by the USEPA Hazard Quotient determination. This assessment, however, must be viewed in terms of the assumptions that were used in making these estimations. In all instances, maximum pesticide concentrations were used for the entire 4 hour exposure period, maximum rates for pesticide applications were used, and dermal transfer coefficients and dermal permeability factors were taken from non-turfgrass situations that are likely to exceed those that would take place on a golf course. Because of this, we view such estimates as *worst case scenarios*. In order to more accurately predict the health implications of pesticide exposure to golfers, a relevant dosimetry evaluation of golfers, playing golf on a golf course, needs to be carried out. With more accurate exposure estimates, it is our belief that the exposure levels reported in this report will be found to be in excess of the true exposure to pesticides on a golf course.

Percentage Time Effort.

J.M. Clark, Ph.D. - Principal Investigator - 10% time commitment; G.R. Roy, B.S. - M.S. Candidate - 100% of ½ time position; J.D. Doherty, M.S. - Pesticide Analyst - 100% of full time position; G. Martin - Undergraduate Work-Study Student and Summer Part-Time Employee - 20 hrs/week fall/spring semesters, 40 hr/wk summer; A. Curtis, B.S. - Pesticide Analyst - 5% time commitment.

Budget.

See Attachment 1.

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PREVIOUS WORK

Volatilization can be a major route of pesticide loss following application to turfgrass areas. Consequently, a significant portion of applied pesticide may be available for human exposure via volatile and dislodgeable residues. In previous USGA-funded research carried out by this laboratory, volatile and dislodgeable residues were determined following application of triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl) butanone], MCPP [(+/-)-2-(4-chloro-2-methylphenoxy) propionic acid], trichlorfon (dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate) and isazafos (*0-5*-chloro-1-isopropyl-1*H*-1,2,4-triazol-3-yl *0,0*-diethylphosphorothioate) to an established plot of 'Penncross' creeping bentgrass (*Agrostis palustris* Huds.). For each application, a 10-m radius plot was sprayed and the Theoretical Profile Shape (TPS) method of Wilson was used to estimate volatile flux. Dislodgeable residues were concurrently determined by wiping treated turfgrass with a water dampened piece of cheesecloth.

Less than 8% of the total applied triadimefon was measured as volatile residues with nearly all volatilization loss occurring within 5 to 7 d of application. Diurnal patterns of triadimefon volatilization were evident. Mid-day (11-1500 h) triadimefon volatile flux on Days 2 (4.6 g ha^{-2} h^{-1}) and 3 (2.4 g ha^{-2} h^{-1}) was 2 and 1.4 times, respectively, greater than the average of morning and late afternoon volatile flux on these respective days. Less than 1% of the total applied MCPP was measured as volatile residue. Volatile MCPP residues decreased over time to nondetectable levels by Day 5. Both triadimefon and MCPP dislodgeable residues were greatest on Day 1 following application and dissipated over time. By Day 5, triadimefon dislodgeable residues decreased to 0.04% of the initial residue level immediately following application and MCPP dislodgeable residues were nondetectable.

For trichlorfon and isazafos applications, less than 12% of applied insecticides were lost as measured volatile resides during the experimental sampling periods. Volatile loss declined in a diphasic pattern with most loss occurring within 5 to 7 d application. Irrigation greatly reduced initial volatile and dislodgeable residues. Subsequent volatile and dislodgeable residues, however, increased substantially on Days 2 and 3 compared with residues levels in the absence of irrigation. Trichlorfon dislodgeable residues never exceeded 1% of applied compound in the absence of irrigation, whereas with irrigation, trichlorfon, and isazafos dislodgeable residues were never greater than 0.5% of applied compound. Irrigation increased the transformation of trichlorfon to DDVP (2,2-dichlorovinyl dimethyl phosphate), a more toxic insecticide.

Inhalation and dermal exposures were estimated using measured air concentrations and dislodgeable residues, respectively, and hazard quotients (HQs) were calculated for both volatile and dislodgeable residues of each pesticide (Fig. 1). Exposures (i.e., doses) divided by reference doses (RfDs) resulted in hazard quotients (HQs). A HQ less than 1 indicated that the residue level is below a concentration that might reasonably be expected to cause adverse effects in humans.

Triadimefon and MCPP volatile and dislodgeable residues resulted in HQs below 1.0 throughout the entire 15 d experimental period indicating that exposures were below any level expected to cause adverse health effects.

Calculated inhalation HQs for volatile residues were equal to or less than 1 for all sampling periods except Days 1 (HQ = 5.0), 2 (HQ =4.5) and 3 (HQ=1.5) following isazafos application. Calculated dermal HQs from dislodgeable residues were equal to or less than 1 for each sampling period except

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for DDVP on Day 2 (HQ = 4.6) when trichlorfon application was followed by irrigation, and on Days 2 (HQ = 14.3) and 3 (HQ = 5.7) following isazafos application.

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Objective 1 (Year 1).

1.1 Determine a critical vapor pressure below which no turfgrass pesticide will volatilize to the extent that it results in an inhalation HQ of greater than 1.0.

1.2 For those pesticides of intermediate vapor pressure, determine the critical surface temperature below which no compound results in an inhalation HQ of greater than 1.0.

1.3 Define the critical RfD above which no pesticide will result in a dermal HQ of greater than 1.0.

Progress in Completing Objective 1.

During the summer and fall of 1995 and spring of 1996, four replicate applications of eight pesticides have been made (i.e., chlorthalonil, iprodione, propiconizole, thiophanate methyl, cyfluthrin, trichlorfon, bendiocarb, carbaryl). The remaining five pesticides (i.e., ethoprop, diazinon, isazafos, chlorpyrifos, isofenphos) have been applied in five separate applications. Physical and toxicological characteristics of each pesticide are given in Table 1. After each application, samples were taken for a one week period. This has resulted in the collection of approximately 585 residue samples. These samples are 80% analyzed according to methods developed by M.P.A.L. over the past 15 months (see multiresidue analysis section below and Fig. 2 and Table 2).

RESULTS

MATERIALS AND METHODS

A. Chemicals

1. Analytical Standards

The following standards were received from the EPA (Beltsville, MD). Bendiocarb (2,3-isopropylidenedioxyphenyl methylcarbamate, 99.8 % pure. Carbaryl (1-naphthyl methylcarbamate), 99 % pure. Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate), 99 % pure. Chlorothalonil (tetrachloroisophthalonitrile), 97.7 % pure. Cyfluthrin ((RS)-α-cyano-4-fluoro-3-phenoxybenzyl (1RS,3RS;1RS.3SR)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, 50.4 % pure. Diazinon (O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate), 96.7 % pure. Ethoprophos (O-ethyl S,S-dipropyl phosphorodithioate), 98 % pure. Ipridione (3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide), 97 % pure. Isazafos (O-5-chloro-1-isopropyl-1H-1,2,4-triazol-3-yl O,O-diethylphosphorothioate), 93.6 % pure. Isofenphos

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(O-ethyl O-2 isopropoxycarbonylphenyl isopropylphosphoroamidathioate; isopropyl O-(ethoxy-N-isopropylamino(thiophosphoryl))salicylate), 92.2 % pure. Thiophanate-Methyl (dimethyl 4,4'-(o-phenylene)bis(3-thioallophanate), 99.9 % pure. Trichlorfon (dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate), 98.1 % pure, and its hydrolysis product Dichlorvos (2,2-dichlorovinyl dimethyl phoshate.) (DDVP), 99 % pure. Ethoprophos (O-ethyl S,S-dipropyl phosphorodithioate), 97 % pure, was recieved from Chem Services (Chem Services, West Chester, PA). Propiconizole ((±)-1-(2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmetyl)-1H-1,2,4-triazole), 99 % pure, was obtained from Riedel-De Haen (Seelze-Hannover, Germany).

2. Formulations

Commercial pesticide formulations applied during the study included: Turcam, 76% bendiocarb active ingredient, (Nor-Am Chemical Co., Wilmington, DE); Sevin 4F, 41.2% carbaryl active ingredient (Lesco Inc., Rocky River, OH); Dursban Pro2E, 44.9% chlorpyrifos active ingredient (DowElanco, Indianapolis, IN); Daconil 2787, 40.4% chlorthalonil active ingredient (ISK Biotech Corp., Mentor, OH); Tempo 20WP, 20% cyfluthrin active ingredient (Miles Inc., Kansas City, MO); Diazinon AG500, 48% diazinon active ingredient (Ciba Geigy Corp., Greensboro, NC); Mocap, 69.6% ethoprophos active ingredient (Rhone-Poulenc Ag. Co., Research Triangle Park, NC); Chipco 26019, 23.3% ipridione active ingredient (Rhone-Poulenc Ag. Co., Research Triangle Park, NC); Triumph 4E, 46.8% isazafos active ingredient (Ciba Geigy Corp., Greensboro, NC); Oftonol 2, 22.2% isofenphos active ingredient (Miles Inc., Kansas City, MO); 3336-F, 46.2% thiophanate-methyl active ingredient (W.A. Cleary Chemical Corp., Somerset, NJ); Proxol 80SP, 80% trichlorofon active ingredient (Nor-Am Chemical Co., Wilmington, DE); Banner, 14.3% propiconizole active ingredient (Ciba Geigy Corp., Greensboro, NC);

3. Solvents and Reagents

All solvents were purchased from Fisher Scientific Company (Springfield, NJ); acetone (optima), methanol (MeOH, HPLC grade), acetonitrile (HPLC grade). Sodium hydroxide (NaOH), boric acid, phosphoric acid (H_3PO_4), and o-phthalaldehyde (OPA reagent) were purchased from Fisher Scientific Company (Springfield, NJ). 2-mercaptoethenol, 1-decanesulfonate sodium salt, and triethylamine were purchased from Aldrich Chemical Company (Milwaukee, WI).

B. Method Development

1. Parameters for the Theoretical Profile Shape (TPS) Method

The TPS method uses a trajectory simulation model to predict the source flux ($F_z(0)$) from the center of a circular plot. The horizontal flux is defined as the product of the mean air concentration (c) and wind speed (s) measured in the center of the plot at a specified height above the plots surface (ZINST) divided by the normalized horizontal flux (NHF) (Eqn. 1). To determine NHF and ZINST, a trajectory simulation model (Three - Dimensional Lagrangian Stochastic model (LS)) was used to predict the trajectory of large numbers of particles in vertical and horizontal directions. The particles were assumed to be neutral and originate from a uniform and circular source. Plots of NHF versus height above the surface were made for three atmospheric conditions; stable, unstable, and neutral. For a given plot radius and roughness height, there is a height above the surface (ZINST) were the NHF value is only slightly dependent on atmospheric conditions. At this height,

the plots of the three atmospheric conditions (stable, instable, neutral) most closely intersect. In this fashion, source flux from a chemically treated plot (F_z (0)) can be estimated by measuring air concentration (c) and wind speed (s) at ZINST and using Wilson's predicted NHF value (Eqn. 1).

$$F_Z(0)_{Field} = sc_{field}/NHF) \quad [1]$$

Wilson (1991) determined that for our 10 m radius turfgrass plot with a roughness height of 0.2 cm, ZINST was equal to 70 cm. NHF was determined to be 2.0 during stable conditions, and 2.9 during unstable and neutral conditions.

2. Preparation of XAD-4 Resin

Before field use, the XAD-4 resin had to be thoroughly cleaned to remove any impurities that would be co-extracted with the pesticides and cause interferences during instrumental analysis. In addition, XAD-4 resin is shipped and stored with a wettable form of sodium chloride and sodium carbonate salts (pH= 10.6) to retard microbial growth. Trichlorfon, bendiocarb, and carbaryl are degraded rapidly under alkaline conditions. Thus, the pH of the resin must be neutralized prior to use. To accomplish this, 1.5 L of resin is placed in a 2.0 L Erlenmeyer flask, which is then filled with distilled water. The beads are mixed thoroughly using a magnetic stir plate. The pH of the resin in distilled water is then adjusted to $\approx$ 4.5 by the dropwise addition of a 40% HCl solution and stirred for one hour. The resin is then soxhlet-extracted for 8 to 10 hours with acetone and air dried.

3. Extraction Procedures

Amberlite polymeric resin (XAD-4, 20/50 mesh, Rohm and Haas, Philadelphia, PA) is a divinyl benzene polymer that is used to remove organic compounds from air and aqueous solutions (Rohm and Haas, 1993). The volatile pesticide residues in this study were removed from the ambient air by collection onto XAD-4 resin. Trapped residues are removed quantitatively from the resin by extraction with acetone. Approximately 120 ml of XAD-4 resin is used for each volatile sample. The resin is placed in a 500 ml Erlenmeyer flask, 200 mls of acetone is added and flask is shaken for one hour on a wrist action shaker. The slurry of resin and solvent is filtered through a Whatman # 1 filter paper supported in a large glass funnel, and the eluent collected in a 500 ml glass amber jar. The resin is rinsed with 2 x 50 ml aliquots of acetone and the eluents pooled. Dislodgeable foliar residues are taken with dampened 8.9 x 8.9 cm pieces of cheesecloth pre-extracted with acetone (Fisher Scientific, NJ). The cheesecloth is placed in a 500 ml Erlenmeyer flask, 150 mls of acetone is added, and the flask is shaken for one hour on a wrist action shaker. The solvent extract is filtered through a Whatman # 1 filter paper supported by a glass funnel. The eluent is collected in a 500 ml glass amber jar. The cheesecloth is additionally rinsed with 2 x 50 ml aliquots of acetone that are pooled with the previous eluent.

Extracts for both the resin and cheesecloth are concentrated by vacuum in a hot water bath (45° C) and further reduced to 10 ml under a gentle stream of nitrogen. In addition, non-fortified resin and cheesecloth were extracted using the same procedures described above to determine if there would be any interferences during the instrumental analysis.

4. Tank Mixtures

The 13 pesticides of interest in this study were placed into three separate groups (i.e., Group 1, Group 2, Group 3). The pesticides in each group were combined in a tank mixture and applied simultaneously. The rational used for the groupings is that the pesticide formulations must be compatible when preparing the tank mix for application. For example, formulation types, such as emulsifiable concentrates, were applied together. The same is true for the other formulation types (e.g., flowables and wettable powders). Jar tests were performed by mixing proportional amounts of each formulation with water in a one liter jar and shaking thoroughly. After allowing the mixture to settle, the contents in the jar were inspected for stable emulsions or unacceptable separations. No emulsions or separations were observed in the above groupings.

C. Multiresidue Analysis of Pesticides

1. Group 1 (Chlorpyrifos, Diazinon, Ethoprop, Isazafos, Isofenphos)

Group 1 consists of five organophosphorous insecticides. They are all thermally stable and can be analyzed simultaneously using gas chromatography (GC). Due to their common phosphorous groupings, all pesticides in Group 1 can be detected using a flame photometric detector (FPD) in the phosphorous mode. Using a non-polar liquid phase, they can be completely resolved and quantitated utilizing the concepts of analytical standards, matching retention times, linear curves, matrix and storage spike recoveries, and matrix blanks as discussed below and as published by Murphy et al., (1996).

a. Sample Extraction. The volatile and dislodgeable samples were extracted with acetone and concentrated according to the methods previously described. The final volume of the samples is dependent on the levels of analytes in the sample. The volume is adjusted so as the concentration of the analyte in the sample is within the linear range of the analysis. However, samples were not concentrated to a final volume less than 10 mls. Volumes less than 10 mls can contain high percentages of water that were present in the air and turfgrass during sampling. Injection of water onto the liquid phase of the GC column leads to column degradation and is not recommended.

b. Sample Cleanup. There were no interferences from either sample collector (i.e., resin or cheesecloth) and no interferences from the two environmental matrices (i.e., air and turfgrass). Therefore, no additional cleanup steps were required with the Group 1 insecticides. This is primarily due to the selectivity of the FPD (phosphorous mode) used in the gas chromatographic analysis of these organophosphorous insecticides.

c. Instrumental Analysis. A Hewlett Packard gas chromatograph (model 5890), equipped with an FPD and a RTX-1 column (crossbound 100% dimethyl polysiloxane, 0.32 mm I.D, 1.5 μ film thickness, and 30 m length, (Restek Corp., Bellefonte, PA) was used for the separation and detection of Group 1 insecticides. Chromatograms were obtained using a Chrom Jet SP4400 integrator (Thermo Separations Product, Riviera Beach, FL). The computer software program used in quantitation was WINner on Windows® (Thermo Separations Product, Riviera Beach, FL). The following instrument settings were used: injector port temperature 250° C, detector temperature 300° C, initial column temperature 180° C held for 1 minute, raised to 240° C at a

rate of 10° C/ min, raised to 280° C at a rate of 20° C/ min. Carrier gas used was helium (He) at a flow rate of 5 ml/min. A septum purge was introduced at 0.8 min into each chromatographic run. Sample (2.0 µl) was injected into the GC using an Hewlett Packard model 7673A autosampler.

d. Detection Limit and Linear Working range. The linear working range for Group 1 insecticides was determined to be 0.5 ug/ml to 10 ug/ml with average correlation coefficient (r) of 0.9995. At the low end of the working range (0.5 ug/ml), the detection limit of the organophosphorous insecticides was 25 ng/m^3 of ambient air and 50 ug/m^2 of turfgrass.

2. Group 2 (Bendiocarb, Carbaryl, Cyfluthrin, Trichlorfon, Dichlorvos)

Group 2 consists of five insecticides; two methyl carbamates (i.e., bendiocarb, carbaryl), a pyrethroid (i.e., cyfluthrin), and an organophosphate (i.e., trichlorfon) and its principal metabolite, dichlorvos. Within this group, there are significant differences in physical characteristics (e.g., water solubilities, thermal stabilities) that prohibit these compounds from being simultaneously analyzed. Thus, three analytical methods have been developed to analyze the Group 2 insecticides.

2.1. Bendiocarb, Carbaryl

Bendiocarb and carbaryl are both methyl carbamates and can be simultaneously analyzed by HPLC following the methods of Dong (1990). This involves the separation of bendiocarb and carbaryl by HPLC, followed by a post column derivitization step that is specific for methyl carbamates, and subsequent fluorescence detection.

a. Sample Extraction. Both volatile and dislodgeable samples were extracted with acetone and concentrated according to the methods previously described. The final volume of the sample is empirical and, as previously discussed, the minimum final volume should be 10 mls or greater. For the analysis of bendiocarb and carbaryl, a 1.0 ml aliquot is removed from the final volume of the sample extract and placed into a graduated test tube. The aliquot was reduced under a gentle stream of nitrogen to near dryness (e.g., 0.1 ml). The sample is then rediluted with a $MeOH/H_2O$ (50/50) solution. Again, the final volume of the dilution is empirical and depends on the level of analyts in solution.

b. Sample Cleanup. Due to the selectivity of the post column derivitization and fluorescence detector used in this method, no additional sample cleanup steps were required.

c. HPLC Analysis. The reagents used in this analysis includes the following; mobil phase (50/50 MeOH / H_2O), NaOH (0.05 M), and the derivitization reagent (OPA). OPA reagent is a 0.05 M sodium borate buffer solution (pH 9.1) containing 500 mg/l o-phthalaldyhyde and 0.1% 2-mercaptoethenol. The HPLC system component settings utilized in this method consist of the following: the mobil phase pump is a Kratos Spectraflow 400 (Perkin Elmer Corp., Norwalk, CT) pumping at a rate of 1.0 ml/min. The HPLC column is a Waters u bondpack C18 - 3.9 x 300 mm (Waters, Milford. MA). The OPA reagent and NaOH solutions are pumped metered by a Milton Roy pump (Milton Roy, Riviera Beach, FL) at a flow of 0.1 ml/min. The NaOH is also heated to 90° C and the OPA is heated to 40° C. The detector is a Kratos Spectraflow 980 Fluorescence detector (Perkin Elmer Corp., Norwalk, CT). The detector monitored the excitation wavelength of 230 nm with the emission wavelength set at 418 nm. Autosampler injections (100

µl) were performed using a Perkin-Elmer ISS-100 (Perkin Elmer Corp., Norwalk, CT). The software package used for integration and quantitation is Perkin Elmer Nelson, model 1020 (Perkin Elmer Corp., Norwalk, CT).

d. Detection Limit and Linear Working Range. The linear working range for bendiocarb and carbaryl was determined to be 0.05 ug/ml to 5.0 ug/ml with an average correlation coefficient (r) of 0.9994. At the low end of the working range (0.05 ug/ml), the detection limit of the methyl carbamate insecticides was 2.5 ng/m^3 of ambient air and 5.0 ug/m^2 of turfgrass.

2.2. Trichlorfon and Dichlorvos (DDVP)

Trichlorfon is also an organophosporous insecticide that converts to DDVP through a dehydrochlorination process (Aktar, 1982). It has also been shown that conversion to DDVP in the field is dependent on irrigation and rainfall (Murphy, 1991). Although DDVP was not directly applied in this study, its levels were monitored because DDVP is more toxic than trichlorfon and highly volatile (V.P. = 1.6×10^{-2} mm Hg). Trichlorfon and DDVP share a phosphorous grouping that allows both insecticides to be analyzed simultaneously by GC with an FPD in the phosphorous mode.

a. Sample Extraction. Both volatile and dislodgeable samples were extracted with acetone and concentrated according to the methods previously described. Again, the final volume of the extract is empirical but should be no lower than 10 mls.

b. Sample Cleanup. No interferences from either the sample collectors or the environmental matrices were observed during this analysis. Thus, no additional cleanup procedures were necessary for this analysis.

c. Instrumental Analysis. The instrumentation and methods used to identify and quantitify trichlorfon and DDVP were the same as previously described for the Group 1 insecticides. Different instrument settings and column were necessary however, because trichlorfon can undergo degradation in the injection port and on the column. It was observed during method development that typical injection port temperatures of 250° C caused considerable degradation of trichlorfon. This degradation was significantly reduced when injection port temperatures were lowered to 130° C. In addition, column temperatures were kept at or below 130° C until trichlorfon eluted from the column. The temperature program used for this analysis was as follows; initial column temperature of 50° C held for one minute, raised to 125° C at a rate of 10° C/min and held for one minute, raised to 220° C at a rate of 30° C/min. It was also observed that trichlorfon degraded less when the time on the column was reduced. To accomplish this process, a short five meter HP-1 column (methyl silicone gum, 5 m x 0.53 mm I.D with a 2.65 um film thickness, Hewlett Packard, Rockville, MD) was used. Accumulation of contamination in the injection port from previous injections also enhanced trichlorfon degradation. Thus, keeping the injection port clean was critical in minimizing degradation. This was accomplished by removing the injection port sleeve and sonicating it in a solution of acetone for 15 minutes and placing it back into the GC injection port.

d. Detection Limit and Linear Working Range. The linear working range for the quantitative determination of trichlorfon and DDVP residues was determined to be 0.5 ug/ml to 10 ug/ml with an average correlation coefficient of 0.9997. At the low end of the range (i.e., 0.5 ug/ml), the detection limit of these insecticides was 25 ng/m^3 of ambient air and 50 ug/m^2 of turfgrass.

2.3. Cyfluthrin.

Cyfluthrin is a mixture of four diastereoisomeric pairs of enantiomers that can be separated and quantitated using GC with a mass selective detector (MS).

a. Sample Extraction. The volatile and dislodgeable samples were extracted with acetone and concentrated according to the methods previously described.

b. Sample Cleanup. No additional sample cleanup procedures were required for this analysis.

c. Instrumental Analysis. A Hewlett Packard model 5890 Series II GC, equipped with a 30 m DB-5 column with a 0.25 μ film thickness and 0.25 mm I.D. (J & W Scientific, Folsom, CA), was used in this analysis. The following temperature program was used; initial temperature of 200° C held for 1 minute, raised to 275° C at a rate of 15° C/min and held for 9 minutes. The injection port temperature was 250° C and the detector temperature was 280° C. The detector is an Hewlett Packard 5971 Mass Selective Detector, operated in the selective ion monitoring mode (SIM). Of the many mass ions produced by the source of the MS detector from cyfluthrin, four mass ions were selected to monitor and quanititate cyfluthrin in the field samples. The molecular weight of the four mass ions monitored were; 163, 199, 206, 226. These mass ions are both abundant and unique for cyfluthrin. A septum purge was introduced at 1.0 minutes into each chromatographic run. Autosampler injections volumes were set at 2.0 μls.

d. Detection Limit and Linear Working Range. The linear working range for cyfluthrin was determined to be 0.5 ug/ml to 5.0 ug/ml with an average correlation coefficient of 0.9973. At the low end of the working range (i.e., 0.5 ug/ml), the detection limit of cyfluthrin is 25 ng/m^3 of ambient air and 50 ug/m^2 of turfgrass.

3. Group 3 (Chlorthalonil, Ipridione, Propiconizole, Thiophanate Methyl)

Group 3 consists of four fungicides. Chlorthalonil, ipridione, and propiconizole are amenable to separation and analysis by GC techniques. In addition, these three fungicides all possess chlorine atoms that can be detected and quantitated utilizing an electrolytic conductivity detector (ELCD) operated in the halogen mode. Thiophanate methyl is not amenable to GC analysis but can be analyzed by HPLC according to the methods of Gilvydis et al. (1990).

3.1. Chlorthalonil, Ipridione, Propiconizole

a. Sample Extraction. Both volatile and dislodgeable samples were extracted with acetone and concentrated according to the methods previously described. Again, the final volume of the extract is empirical but should be no lower than 10 mls.

b. Sample Cleanup. No interferences from either the sample collectors or environmental matrices were observed during this analysis. Thus, no additional cleanup procedures were necessary for this analysis.

c. Instrumental Analysis. A Hewlett Packard model 5890 Series II GC, equipped with an HP-50+ column (cross-linked 50% phenyl methyl silicone, 15 m x 0.53 mm I.D., 1.0 film thickness,

Hewlett Packard, Rockville, MD), was used for this analysis. The following temperature program was used to separate the three fungicides; initial temperature 120°C held for 1 minute, raised to 230°C at a rate of 15°C/min and held for 3 minutes, raised to 260°C at a rate of 10°C/min and held for 2 minutes. Injection port temperature was 250°C. A septum purge was introduced at 1 minute into each chromatographic run. Sample injection volumes of 2.0 µl were made manually. The detector used was a Model 4420 ELCD (O.I Corporation, College Station, TX) operated in the halogen mode. The reaction temperature was 900°C.

d. Detection Limit and Linear Working Range. The linear working range for chlorthalonil, ipridione, and propiconizole was determined to be 0.5 ug/ml to 5.0 ug/ml with an average correlation coefficient of 0.9998. At the low end of the working range (i.e., 0.5 ug/ml), the detection limits for these fungicides were 25 ng/m^3 of ambient air and 50 ug/m^2 of turfgrass.

3.2. Thiophanate methyl.

a. Sample Extraction. Both volatile and dislodgeable samples were extracted with acetone and concentrated according to the methods previously described. The final volume of the sample is empirical but, as previously discussed, it should be at least 10 mls. For the analysis of thiophanate methyl, a 1.0 ml aliquot is removed from the final volume of sample extract and placed into a graduated test tube. The aliquot is reduced under a gentle stream of nitrogen to near dryness (e.g., 0.1 ml). The reduced sample is then rediluted by the addition of an ion pairing/MeOH (60/40) solution (i.e., mobil phase for HPLC analysis, see below). Again, the final volume of the dilution is empirical but depends on the level of analyte in solution.

b. Sample Cleanup. No interferences from either the sample collectors or the environmental matrices were observed during this analysis. Thus, no additional cleanup procedures were required for this analysis.

c. HPLC Analysis. The HPLC system used for this analysis consists of a Waters 966 photodiode array, 600E system controller, 717 autosampler, and Millenium software package (Waters, Milford, MA). Reagents and solvents used for this analysis are ; LC ion-pairing solution, which consists of 1.0 g 1-decanesulfonate sodium salt, 10 ml triethylamine, 7 ml of a concentrated phosphoric acid (H_3PO_4) solution diluted to 1 ml with LC grade water. LC mobil phase, which consists of 60 parts ion-pairing solution and 40 parts MeOH. Further method development is ongoing.

4. Extraction Efficiency Studies

To ensure all pesticides were ammenable to the methods previously described, extraction efficiency studies were performed. Both the XAD - 4 resin and cheesecloth were ammended with the Group 1 mixture of pesticides at the following levels; 10 ug, 100 ug, and 1000 ug. The resin and cheesecloth were then extracted and analyzed as previously described. Group 2 and Group 3 were carried out in exactly the same manner.

The results from these studies are listed in table 2 as the average percent recovery for each pesticide for both XAD -4 resin and cheesecloth. The recoveries range from 68 % (chlorthalonil, cheesecloth) to 105 % (bendiocarb, cheesecloth). Both cyfluthrin and thiophanate methyl are still under investigation.

Sample Inhalation Calculation

Air Concentration x Moderate Breathing Rate x 4h / 70 kg = Dose

(ug/m^3) ($2.5\ m^3$ / h) (ug/kg)

Dose / Reference Dose = Hazard Quotient

(ug/kg) [ug/(kg.d)]

Sample Dermal Calculation

Dermal Exposure / 70 kg x Dermal Permeability[a] = Dose

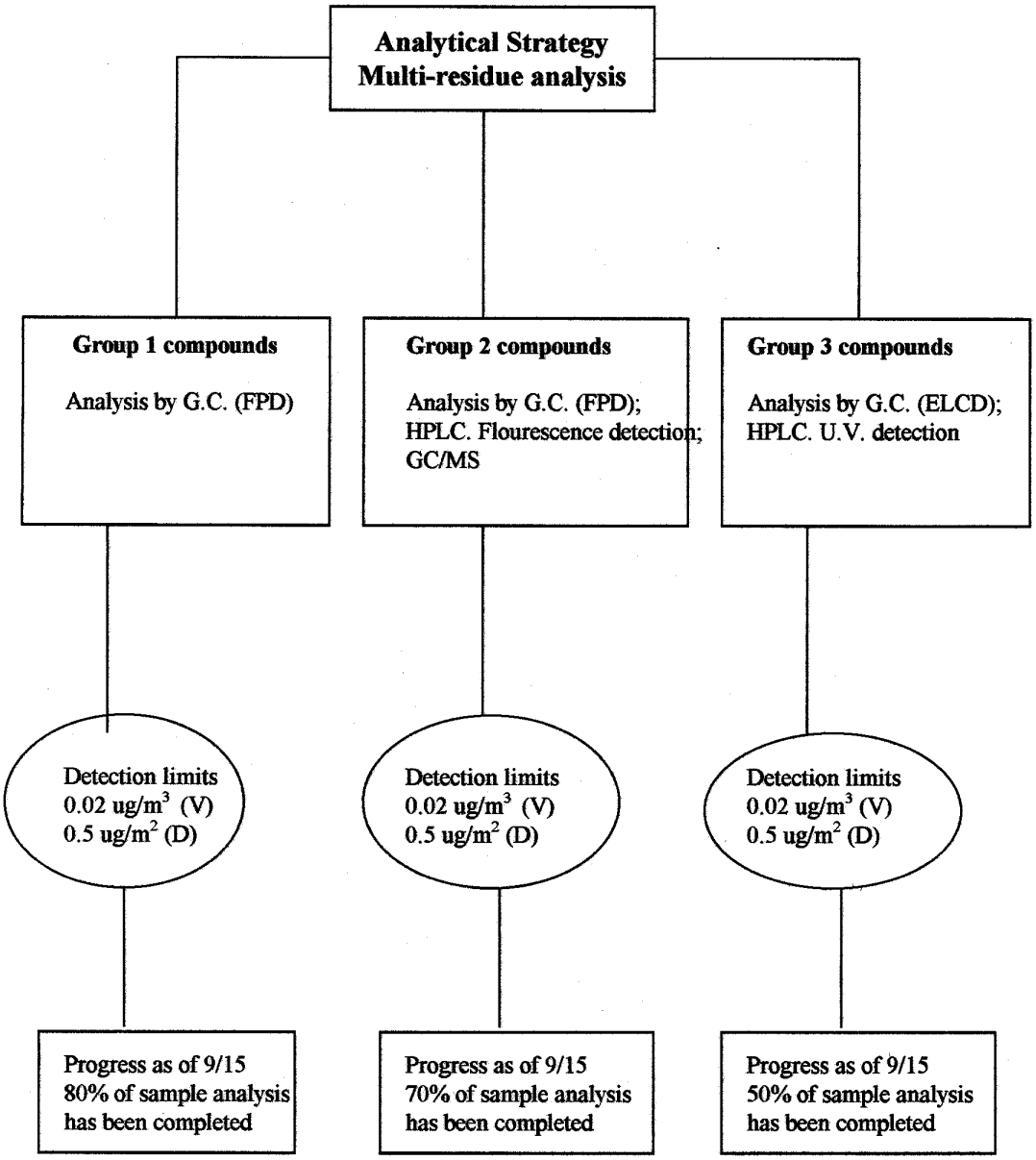
(mg) (o.1) (mg/kg)

Dose / Reference Dose x 1000 ug/mg = Hazard Quotient

(mg/kg) [ug/(kg.d)]

[a] Akin, E.W. EPA Memorandum, 1990.

Figure 1: Example of the procedures used to calculate a dose from both dermal and volatile residues, and how to calculate a hazard quotient from the dose.



Group 1 = Ethoprop; Diazinon; Isazafos; Chlorpyrifos; Isofenphos

Group 2 = Trichlorfon /DDVP; Bendiocarb; Carbaryl; Cyfluthrin

Group 3 = Chlorothalanil; Propiconizole; Ipridione; Thiophanate-Methyl

Figure 2: Analytical strategy for multiresidue analysis.

Table 1: Physical and Toxicological Properties of Turfgrass Pesticides.

Pesticides	Molecular Weight[a]	Vapor Pressure[a] (mmHg)	Water Solubility[a] (PPM)	NOEL[b] (mg/kg/day)	uncertainty factor[b]	OPP RfD[b] (mg/kg/day)
Insecticides						
Organophosphates						
DDVP	221.0	1.6 E-2	8000	0.05	100	0.0005
Ethoprop	242.3	3.5 E-4	750	0.015	1000	0.000015
Diazinon	304.4	9.0 E-5	60	0.009	100	0.00009
Isazofos	313.7	5.6 E-5	168	nd[c]	100	0.00002
Chlorpyrifos	350.6	2.0 E-5	1.4	0.03	10	0.003
Trichlorofon	257.4	3.8 E-6	120000	nd[c]	100	0.002
Isofenphos	345.4	3.3 E-6	18	0.05	100	0.0005
Carbamates						
Bendiocarb	223.2	3.4 E-6	280	0.5	100	0.005
Carbaryl	201.2	3.1 E-7	120	1.43	100	0.014
Pyrethroids						
Cyfluthrin	434.3	2.0 E-9	0.002	2.5	100	0.025
Contact Fungicide						
Chlorthalonil	265.9	5.7 E-7	0.9	1.5	100	0.015
Systemic Fungicides						
Propiconizole	342.2	4.2 E-7	100	1.25	100	0.0125
Thiophanate Methyl	342.4	7.1 E-8	0	8.0	100	0.08
Ipridione	330.2	3.8 E-9	13	6.1	100	0.061

[a] Molecular weights, vapor pressures, and water solubilities were taken from The Pesticide Manual, Tenth Edition (1994).

[b]Toxicological data and RfD values were taken from USEPA the Office of Pesticide programs reference dose tracking report 4/14/95.

[c]No data avialable.

Table 2: Average % recoveries of extraction efficiency studies from XAD - 4 resin and cheesecloth

Pesticide	Extraction Efficiencies (% recoveries)	
	XAD - 4 Resin	Cheesecloth
Group 1		
Ethoprop	97.0	88.1
Diazinon	99.0	88.8
Isazafos	96.0	90.0
Chlorpyrifos	99.0	87.5
Isofenphos	91.2	92.5
Group 2		
Bendiocarb	89.0	105
Carbaryl	89.0	105
Trichlorfon	95.2	88.3
DDVP	82.9	75.5
Cyfluthrin	n/a[a]	n/a[a]
Group 3		
Chlorthalonil	70.0	68.0
Ipridione	99.2	85.2
Propiconizole	89.1	90.8
Thiophanate methyl	n/a[a]	n/a[a]

[a]n/a = Still under investigation.

FIELD DATA

The measured air concentrations were used to calculate inhalation hazard quotients (IHQs) for all 13 pesticides used in this study. The pesticides were grouped into three vapor pressure categories: those of high vapor pressure (> 1.0×10^{-5} mm Hg, Table 3A), intermediate vapor pressure (< 1.0×10^{-5} to > 1.0×10^{-7} mm Hg, Table 3B), and low vapor pressure (< 1.0×10^{-7} mm Hg, Table 3C). Those pesticides of intermediate and low vapor pressures never resulted in an IHQ greater than 1.0 under any circumstances (Tables 3B & C). Those pesticides of high vapor pressure showed IHQs greater than 1.0 (Table 3A). Ethoprop, isazafos, and diazinon had IHQs greater than 1.0 through day 3. The maximum IHQs all occurred on day 1, and were below 1.0 after day 3. Chlorpyrifos, which is in the high vapor pressure category, had a maximum IHQ of 0.1 on day 2. This is due to the high RfD value of chlorpyrifos compared to the other organophosphorous insecticides. DDVP, which is the hydrolytic metabolite of trichlorfon, has the highest vapor pressure, but does not result in IHQs greater than 1.0. This is primarily a factor of the rate at which DDVP is forming. At slow rates of formation, it will not accumulate on the turfgrass to the extent that it results in an IHQ greater 1.0.

Dislodgeable foliar residues were used to calculate dermal hazard quotients (DHQs) for the 13 pesticides in this study (Table 4). Ethoprop, isazafos, diazinon, isofenphos, trichlorfon, chlorpyrifos, and bendicarb had DHQs greater than 1.0 on day 1 (15 min. post application). However, only ethoprop, isazafos, and diazinon had DHQs greater than 1.0 through day 1 (8 hr. post application). Only ethoprop and isazafos had DHQs greater than 1.0 through day 3. In general, most DHQs were below 1.0 by five hours post-application. The exceptions were ethoprop, isazafos, and diazinon, which have the lowest RfDs (highest toxicity rating).

From this data set, we have determined that the critical vapor pressure below which no turfgrass pesticides will volatilize to the extent that it results in an inhalation HQ greater than 1.0 to be between 3.3×10^{-6} mm Hg (see isofenphos vapor pressure, Table 1 and isofenphos IHQ, Table 3B) to 5.6×10^{-5} mm Hg (see isazafos vapor pressure, Table 1 and isazafos IHQ, Table 3A) (Objective1.1). Similarly, we have determined the critical OPP RfD above which no turfgrass pesticide will result in a dermal HQ greater than 1.0 to be between 0.005 (see bendicarb OPP RfD, Table 1 and bendiocarb DHQ, Table 4) to 0.013 (see propiconizole OPP RfD, Table 1 and propiconizole DHQ, Table 4) (Objective 1.3).

The completion of Objective 1.2 will allow us to provide the golf course superintendents with a method by which they can easily assess the potential for there being an exposure hazard involved in applying a particular compound at a particular time in a particular fashion. This method will be developed in collaboration with Dr. Doug Haith of Cornell University. Dr. Haith is experienced in the modeling of pesticides in the environment and with his assistance we will develop a simple algorithm to aid pesticide applicators in their selection of turfgrass pesticides. This model will be available spring/summer 1997.

Objective 2 (year 2).

2.1 Evaluation of selective turfgrass management practices to minimize potential volatile and foliar residues of turfgrass pesticides.

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Table 3A: Inhalation hazard quotients (IHQs) for turfgrass pesticides in the high vapor pressure group (i.e., vapor pressures > 1.0×10^{-5} mm Hg).

Pesticide	Day 1 (IHQs)	Day 2 (IHQs)	Day 3 (IHQs)
DDVP *	0.06	0.04	0.02
Ethoprop	50	26	1.2
Diazinon	3.3	2.4	1.2
Isazafos	8.6	6.7	3.4
Chlorpyrifos	0.09	0.1	0.04

* DDVP was not applied,but is the breakdown product of trichlofon.

Table 3B: Inhalation hazard quotients (IHQs) for turfgrass pesticides in the intermediate vapor pressure group (i.e., vapor pressures between 1.0×10^{-5} mm Hg and 1.0×10^{-7} mm Hg).

Pesticide	Day 1 (IHQs)	Day 2 (IHQs)	Day 3 (IHQs)
Trichlorfon	0.02	0.004	0.004
Bendiocarb	0.02	0.002	0.002
Isofenphos	n/d	0.02	n/d
Chlorthalonil	0.001	0.001	0.0003
Propiconizole	n/d	n/d	n/d
Carbaryl	0.0005	0.0001	0.00004

n/d = non - detected.

Table 3C: Inhalation hazard quotients (IHQs) for those turfgrass pesticides in the low vapor pressure group (i.e., vapor pressures < 1.0×10^{-7} mmHg).

Pesticide	Day 1 (IHQs)	Day 2 (IHQs)	Day 3 (IHQs)
Thiophanate-Methyl	n/d	n/d	n/d
Ipridione	n/d	n/d	n/d
Cyfluthrin	n/d	n/d	n/d

n/d = non - detected.
note: The IHQs reported in tables 3A-3C are the maximum daily IHQs measured, all of which occured during the 11:00 A.M to 3:00 P.M sampling period.

Table 4: Dermal hazard quotients (DHQs) for turfgrass pesticides listed with increasing RfDs from top to bottom Through day 3 post application.

Pesticide	RfD (mg/kg/day)	Day 1 (DHQs)			Day 2 (DHQs)	Day 3 (DHQs)
		15 Minutes	5 Hours	8 Hours	12:00 A.M	12:00 A.M
Ethoprop	0.000015	160	16.4	13.5	2.3	3.4
Isazafos	0.00002	105	11.7	9.7	1.6	2.1
Diazinon	0.00009	30	2.8	2.2	0.4	0.5
Isofenphos	0.0005	3.2	0.5	0.5	0.1	0.1
DDVP	0.0005	0.6	0.03	0.03	n/d[a]	n/d[a]
Trichlorfon	0.002	6.4	0.07	0.09	0.08	0.05
Chlorpyrifos	0.003	1.7	0.2	0.16	0.03	0.04
Bendiocarb	0.005	3.1	0.06	0.1	0.06	0.008
Propiconizole	0.0125	0.002	0.03	0.002	0.005	0.002
Carbaryl	0.014	0.3	0.008	0.01	0.006	0.0002
Cyfluthrin	0.025	---[b]	---[b]	---[b]	---[b]	---[b]
Ipridione	0.061	0.004	0.003	0.003	0.004	0.003
Thiophanate-methyl	0.08	---[b]	---[b]	---[b]	---[b]	---[b]

[a]n/d = not detected.

[b]. --- = no data available at this time.

Plans for Objective 2.

From objective 1, the problematic pesticides will be those compounds with high vapor pressure and, more importantly, those compounds that have low RfD values (i.e., high intrinsic toxicity). Compounds having these characteristics are the insecticides, particularly the organophosphorous insecticides (e.g., ethoprop, diazinon, isazafos, and trichlorfon/DDVP). Exposure to these compounds will be most affected by management practices and hence will be incorporated into objective 2 studies.

The above insecticides will be applied in the presence and the absence of adjuvants to two duplicate turfgrass plots that have been established. The two types of adjuvants to be used in this objective are: 1) Aqua Gro® -L, a non-ionic surfactant; and 2) Exhalt 800, an encapsulating spreader/sticker. The plots will be sampled, the samples analyzed, and the results calculated as previously outlined in objective 1. These applications are expected to take place in July and August of 1996.

To data, two duplicate turfgrass plots were established in the fall of 1995. The insecticides ethoprop, isazafos, and trichlorfon were chosen as the compounds from the screening that needed further research. These insecticides will be applied to the new plots in the presence and absence of the spreader/sticker agent, Exhalt 800, and then in the presence and absence of the wetting agent Aqua Gro® -L. Following the exact procedures as previously described, results from the two plots will be compared to determine if the addition of adjuvants to the tank mix can be used to mitigate human exposures. There have been two applications in the presence and absence of Exhalt 800 done in the late summer of 1996. Analytical results of these two collections are 50% completed on these samples.

Objective 3 (Year 3).

3.1 Determination of the importance of thatch accumulation on the dissipation of volatile and dislodgeable foliar residues of turfgrass pesticides.

Plans for Objective 3.

The pesticide(s) of interest will be simultaneously applied to two plots of turfgrass. One plot will be six years old and have developed a mature thatch layer, while the other will be less than two years old and have little thatch accumulation. In addition, a section of the mature thatch plot will be dethatched prior to application. Samples will be collected as previously described, and the influence of thatch on volatile and dislodgeable residues can be determined. Applications and sample collections will take place during the summer of 1997.

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Clark, J.M. 1996. Development and evaluation of pest management system for screening turfgrass pesticides for potential volatility and dislodgeable residues. 1996 Turfgrass Field Day Book. CFNR, UMass-Amherst, pp. 47-50.

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ATTACHMENT 1

DATE RUN 10/05/96
TIME RUN 16:40:15
FY=97 CC=A1
FBM090 - A1

UNIVERSITY OF MASSACHUSETTS
FINANCIAL RECORDS SYSTEM
AMHERST CAMPUS
ACCOUNT STATEMENT IN WHOLE DOLLARS FOR 10/04/96
FBM090/091 REP DISTR = 5025600421

REPORT PAGE 125
PROGRAM ID FBM0

ACCOUNT PAGE

TO: **CLARK, JOHN**
ENTOMOLOGY
ORG. NO.: **50 25 60 0421**

US GOLF ASSCO

ACCT: **5-20235**

EXP. DATE: **01/31/**

ACCOUNTANTS CODE:

SUB CODE	DESCRIPTION	BUDGETS ORIGINAL	BUDGETS REVISED	ACTUAL CURRENT MONTH	ACTUAL FISCAL YEAR	ACTUAL PROJECT YEAR	OPEN COMMITMENTS	BALANCE AVAILABLE	PE US
2600	BB-REG EMP-REL EXPEN		142-						
2621	OS-TVL-DOMESTIC		1,000					142-	
2641	IS-TVL-DOMESTIC		73			198		803	2
2645	IS-AUTO-DOMESTI		69			73			10
						69			10
	BB-REG EMP-REL EXPEN		1,000			340		660	3
2800	CC-SPECIAL EMPLOYEES	24,128	12,786					12,786	
2833	SEASN TEMP NON		33,655	2,064	8,256	26,087	7,568		10
3000	STUDENT PYROLL		16,770-					16,770-	
3010	STUDENT HOURLY		615			615			10
3020	CWS - MATCH		663			663			10
3030	CWS-POST MATCH		5,120			5,120			10
3120	GRAD ASST-RES		10,372	694	694	8,983	1,389		10
	CC-SPECIAL EMPLOYEES	24,128	46,441	2,758	8,950	41,468	8,957	3,984-	10
3200	DD-PENSION & INSURAN	182	125-					125-	
3270	UMEMPLOYMT COMP		75	6	25	75			10
3280	MEDICARE		378	30	120	378			10
3290	WORKERS COMP		41	15	41	41			10
	DD-PENSION & INSURAN	182	370	52	186	495		125-	13
3400	EE-ADMINISR EXPENSES		461					461	
3420	OFC & ADM EXP		39		4	39			10
	EE-ADMINISR EXPENSES		500		4	39		461	
3900	FF-FACILITY OPNL EXP		3,325-					3,325-	
3960	LAB SUPPLIES		250		7	144	106		10
3961	GASES&DEMURRAGE		127			127			10
4166	BOOK&PER NON-LI		617			617			10
4181	RESEARCH SUPL	11,379	26,076		1,097	20,182	131	5,763	7
4441	M&RM-EDUC/TECH		234			234			10
5303	RCHG-COPY SVC		240			240			10
5308	RCHG-RCS		107			107			10
5313	RCHG-CHEMISTRY		40				40		10
5315	RCHG-LIQUID GAS		4			4			10
5319	RCHG-ANIML CARE		932			932			10
5390	RCHG FAC OPN EX		26			26			10

00075

TO: **CLARK, JOHN**
ENTOMOLOGY
ORG. NO.: **50 25 60 0421**

US GOLF ASSCO

ACCT: **5-20235**

ACCOUNTANTS CODE: AP

SUB CODE	DESCRIPTION	BUDGETS ORIGINAL	BUDGETS REVISED	ACTUAL CURRENT MONTH	ACTUAL FISCAL YEAR	ACTUAL PROJECT YEAR	OPEN COMMITMENTS	BALANCE AVAILABLE	PERC USED
	FF-FACILITY OPNL EXP	11,379	25,329		1,104	22,614	277	2,438	90
6600	LL-LEASE,RENT,REPAIR		66-					66-	0
6820	EDUC EQT MAINT		66			66			100
	LL-LEASE,RENT,REPAIR					66		66-	0
8600	RR-BENEFIT PROGRAMS	1,190	1,419					1,419	0
8622	HEALTH INS PRO		1,045	110	110	1,045			100
	RR-BENEFIT PROGRAMS	1,190	2,464	110	110	1,045		1,419	42
	TOTAL DIRECT COST	36,879	76,104	2,920	10,354	66,065	9,234	805	99
9940	OVERHEAD	5,900	12,176	467	1,657	10,570		1,606	87
	TOTAL EXPENDITURES	42,779	88,280	3,387	12,010	76,636	9,234	2,411	97

00076

OPEN COMMITMENTS STATUS

ACCOUNT	REF. NO.	DATE	DESCRIPTION	ORIGINAL AMOUNT	LIQUIDATING EXPENDITURES	ADJUST-MENTS	CURRENT AMOUNT	
5-20235-4181	A538302	01/09	CC UNIV STORE	19.90	14.22		5.68	02/29/96
5-20235-3960	A564326	03/05	MERRIAM GRAVES	250.00		143.70-	106.30	07/26/96
5-20235-4181	A564321	03/29	INFOCUS SERVICES INC	125.00			125.00	03/29/96
5-20235-5313	A568306	04/04	GLASS BLOWING LAB	40.00			40.00	04/04/96
5-20235-2833	E329290	09/25	ROY,GERARD R	2,064.00		688.00-	1,376.00	10/03/96
5-20235-3120	E329290	09/24	ROY,GERARD R	2,083.20		694.40-	1,388.80	10/03/96
5-20235-2833	E830880	03/20	DOHERTY,JEFFERY J	16,168.00		9,976.00-	6,192.00	10/03/96
5-20235-4181	M041529	03/20	HADLEY GARDEN CENTER	853.32		853.32-		COMPLETED
5-20235-4181	Y042050	03/25	CAMPBELL SCIENTIFIC	364.06		364.06-		COMPLETED
			ACCOUNT TOTAL	21,967.48	14.22	12,719.48-	9,233.78	

TO: **CLARK, JOHN**
ENTOMOLOGY
ORG. NO.: **50 25 60 0421**

US GOLF ASSCO
ACCT: **5-20235**

EXP. DATE: **01/31/97**
ACCOUNTANTS CODE: AP

SUB CODE	DESCRIPTION	DATE	EC	REF1	REF2	REF3	6XJE 4/5X	OFFSET CHECK#	BUDGET ENTRIES	CURRENT REV/EXP	COMMITMENTS	BATCH ID
2833	DOHERTY,JEFFERY J	09/07	045	E830880		018383974		105525		344.00		APPA11
	DOHERTY,JEFFERY J	09/14	045	E830880		018383974		118430		344.00		APPA11
	DOHERTY,JEFFERY J	09/21	045	E830880		018383974		131809		344.00		APPA11
	DOHERTY,JEFFERY J	09/28	045	E830880		018383974		145653		344.00		APPA11
	ROY,GERARD R	09/01	045	E329290		034524387		314809		344.00		APPA11
	ROY,GERARD R	09/21	045	E329290		034524387		314809		172.00		APPA11
	ROY,GERARD R	09/28	045	E329290		034524387		326446		172.00		APPA11
	ROY,GERARD R	09/25	054	E329290		034524387					2,064.00	AP5087
	DOHERTY,JEFFERY J	09/07	055	E830880		018383974		105525			344.00-	APPA11
	DOHERTY,JEFFERY J	09/14	055	E830880		018383974		118430			344.00-	APPA11
	DOHERTY,JEFFERY J	09/21	055	E830880		018383974		131809			344.00-	APPA11
	DOHERTY,JEFFERY J	09/28	055	E830880		018383974		145653			344.00-	APPA11
	ROY,GERARD R	09/01	055	E329290		034524387		314809			344.00-	APPA11
	ROY,GERARD R	09/21	055	E329290		034524387		314809			172.00-	APPA11
	ROY,GERARD R	09/28	055	E329290		034524387		326446			172.00-	APPA11
2833	CM TOTAL SEASN TEMP NON									2,064.00		
3120	ROY,GERARD R	09/01	045	E329290		034524387		314809		347.20		APPA11
	ROY,GERARD R	09/21	045	E329290		034524387		314809		173.60		APPA11
	ROY,GERARD R	09/28	045	E329290		034524387		326446		173.60		APPA11
	ROY,GERARD R	09/24	054	E329290		034524387					2,083.20	AP5086
	ROY,GERARD R	09/01	055	E329290		034524387		314809			347.20-	APPA11
	ROY,GERARD R	09/21	055	E329290		034524387		314809			173.60-	APPA11
	ROY,GERARD R	09/28	055	E329290		034524387		326446			173.60-	APPA11
3120	CM TOTAL GRAD ASST-RES									694.40	1,388.80	
3270	U I FRINGE 09-96	10/03	068					0-10568-2125C		6.19		APUA11
3270	CM TOTAL UMEMPLOYMT COMP									6.19		
3280	DOHERTY,JEFFERY J	09/12	060	E830880		018383974	A	C1-0-10540-2123C		4.99		APMA11
	DOHERTY,JEFFERY J	09/19	060	E830880		018383974	A	C1-0-10540-2123C		4.99		APMA11
	DOHERTY,JEFFERY J	09/26	060	E830880		018383974	A	C1-0-10540-2123C		4.98		APMA11
	DOHERTY,JEFFERY J	10/03	060	E830880		018383974	A	C1-0-10540-2123C		4.99		APMA11
	ROY,GERARD R	09/26	060	E329290		034524387	A	C1-0-10540-2123C		2.49		APMA11
	ROY,GERARD R	09/26	060	E329290		034524387	A	C1-0-10540-2123C		4.99		APMA11
	ROY,GERARD R	10/03	060	E329290		034524387	A	C1-0-10540-2123C		2.50		APMA11
3280	CM TOTAL MEDICARE									29.93		
3290	WORK COMP 10-96	10/03	068					0-10549-2125C		15.48		APKA11
3290	CM TOTAL WORKERS COMP									15.48		
4181	HADLEY GARDEN CENTER	09/18	051	M041529	R045258	V0429879130					306.64-	AACETE
	CAMPBELL SCIENTIFIC	09/18	051	Y042050	R045657	V8703051571					50.12-	AACETE

00077

TO: **CLARK, JOHN**
ENTOMOLOGY
ORG. NO.: **50 25 60 0421**

US GOLF ASSCO

ACCT: **5-20235**

ACCOUNTANTS CODE: AP

SUB CODE	DESCRIPTION	DATE	EC	REF1	REF2	REF3	6XJE OFFSET 4/5X CHECK#	BUDGET ENTRIES	CURRENT REV/EXP	COMMITMENTS	BATCH ID
4181	HADLEY GARDEN CENTER	09/18	056	M041529	R045258	V0429879130				153.32	AACETE
	CAMPBELL SCIENTIFIC	09/18	056	Y042050	R045657	V8703051571				25.06	AACETE
4181	CM TOTAL RESEARCH SUPL									178.38-	
8622	ROY,GERARD R 00	09/21	060	E329291		034524387	0-14154-2125C		27.50		CVPA15
	ROY,GERARD R 00	09/21	060	E329291		034524387	0-14154-2125C		55.00		CVPA15
	ROY,GERARD R 00	09/28	060	E329291		034524387	0-14154-2125C		27.50		CVPA15
8622	CM TOTAL HEALTH INS PRO								110.00		
9940	OVERHEAD	10/05	068	OH00004			1-00035-0955C		467.20		COH001
9940	CM TOTAL OVERHEAD								467.20		
	*** ACCOUNT TOTAL ***								3,387.20	1,210.42	

82000