USDA/ GREEN SECTION RESEARCH

Evaluation of Managment Factors Affecting Volatile Loss and Dislodgeable Foliar Residues

February 1, 1995 through Nov. 1, 1995

Annual Report

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EXECUTIVE SUMMARY

Volatile and dislodgeable samples and weather data have been collected for the completion of Objective 1 "Development of a best management system for screening turfgrass pesticides for potential volatiles and dislodgeable foliar residues." To date, 450 samples and weather data were collected from June to November, 1995. Samples have been concentrated and stored in a freezer for analysis that is currently being carried out.

Analytical methods have been developed that allow multiple residues to be determined in each of three groups of pesticides that are applied together: Group 1 (Diazinon, Etoprop, Chlorpyrifos, Isazofos, Isofenphos); Group 2 (Trichofon, DDVP, Carbaryl, Bendiocarb, Cyfluthrin); Group 3 (Chlorthalonil, Propiconizol, Iprodione, Thiophanate methyl).

Two additional 10m radius turfgrass plots were established in September in order to complete Objective 3 in the third year of funding of the current proposal.

Dr. D. Haith, Cornell Univ., has been brought onto the project to provide his expertise in developing on algorthum relating HQs, volatility, temperature, and relative humidity for use as a "best management" tool for superintendents in the proper selection of pesticides to avoid golfer exposure.

PROGRESS AND RESULTS

I. *ANALYTICAL AND LABORATORY TECHNIQUES*

A. Academics and Related Work Experience (Gerard R. Roy, Masters Candidate, Department of Entomology).

Academic courses taken and presently enrolled in (*):

Organic Chemistry	Descriptive Inorganic Chemistry
Quantitative Analysis	Biostatistics
Methods of Environmental Toxicology and Chemistry	
Toxicology of Insecticides *	

From October of 1991 through January of 1994, Mr. Roy worked as a laboratory technician for Tighe & Bond Inc., Westfield, MA where he was responsible for sample preparation and quality control/ quality assurance (QC/QA) aspects in the quantitation of metals and organic compounds in a variety of environmental matrices including waste water, drinking water, soils, and sludges. Mr. Roy was employed by the Massachusetts Pesticide Analysis Laboratory beginning in September 1993 through the present, where he performed method development, sample preparation, QA/QC, and sample analysis, of a wide range of pesticides.

From March 1 through Nov 1, 100% of Mr. Roy's time has been devoted to the project (i.e.,. USGA/MPAL). A XAD-4 resin from Rohm and Haas was selected for the collection of volatile pesticides residues from air and Fisher's analytical-grade cheesecloth was selected to collect pesticide residues from turf[6]. Method development for pesticide analyses from these two matrices has been pursued. During this initial period, many aspects of site management, sampling, pesticide analytical chemistry, and chromatography have been acquired.

B. Instrumentation.

1. Gas Chromatography (GC) . Nine of the fourteen pesticides can be analyzed by GC. Two GC systems utilizing three different detectors; flame photometric detection (FPD), thermal selective detection (TSD), and the HALL elctroconductivty detector, have been employed to accomplish these analysis [1,2,6].

2. High Pressure Liquid Chromatography (HPLC). Two HPLC systems, utilizing two different detectors; Fluorescence, and Ultraviolet (UV), have been employed for the analysis of the remaining pesticides [7,8]. A variety of analytical columns and mobile phases under both normal and reverse phase conditions are presently being evaluated.

C. Sample Preparation Techniques.

1. All compounds are amenable to extraction by acetone from both the XAD-4 resin and cheesecloth. The compounds are stable in acetone in which they are stored until the analyses are performed. Most interfering environmental contaminations are circumvented by using the selectivity of the GC and HPLC detectors described above. To reach acceptable detection limits, samples must be concentrated without the loss of any compound[6].

2. Derivatization. Derivatization of the two carbamate insecticides; carbaryl, and bendiocarb will be performed by adding a flourescent mercapto-ethenol group in order to take advantage of the sensitive and selective HPLC system with fluorescence detection[7]. This system will eliminate any co-eluting contaminants that create a problem using HPLC with these environmental matrices.

D. Sample Analysis.

Once the sample is prepared and injected into an instrument, the pesticide of interest must then be correctly identified and quantitatively assessed. The concepts of standard curves, daily spikes, daily blanks, storage spikes, replicate treatments, internal and external standards have been studied and incorporated into routine sample analysis under DFA/MPAL SOP's (see MPAL SOP plan)[6].

Spectra-physics integration and data acquisition software packages are available on IBM computers at MPAL. The proper operation of this system allows the data chromatograms to be

more accurately evaluated and easily stored for future publication. *Microsoft Word* and *Chemtext* are word processing programs that allow rapid text production and data reduction processes and are currently available at MPAL.

II. *FIELD SAMPLING TECHNIQUES*

A. Experimental Theory.

1. Measurement of Volatile Pesticide Residues in Air. The rate of volatile pesticide loss from the treated turf is measured with J.D. Wilson's Trajectory Simulation Method (TSM)[3]. A high volume air sampler is suspended at a predetermined height (ZINST) in the center of a circular plot. As air is pulled through the collector (*ca.* 25 cubic feet per minute), the pesticide vapors recondense onto a XAD-4 resin trap. Extraction of the pesticide from the trap resin with acetone will give the concentration of the pesticide at that one height. The actual ZINST is determined using a meteorological modeling system and is dependent upon the radius of the plot and the roughness height of the turf[3]. Dr. Wilson has determined ZINST to be 70 cm for our plots (10 m radius) at a roughness height of 0.2 cm for turfgrass cut at a height of 0.5 inches[6].

2. Measurement of Dislodgeable Pesticide Residues. The dislodgeable residue method used in the past by our laboratory was reviewed, and an alternative method which is more representative of human exposure on a golf course was chosen [10,11]. A one square foot area of pesticide-treated turf is wiped with a piece of water-dampened, pre-extracted, cheesecloth.

Similar to the resin, extraction of the cheesecloth with acetone , followed by a concentration step, will give the concentration of the dislodgeable residues available at that time[6].

B. Preparation/Maintenance of Experimental Turf Plots.

1. Initializing and Maintaining Turf. The University of Massachusetts Turf Farm is located in South Deerfield, MA. In May of 1991, approximately 0.5 acres of turf was desodded, tilled, raked and prepared for seeding. On June 17, 1991, the plot was seeded with Penncross creeping bentgrass. The plot has since been clipped at a height of 1/2 inch. Maintenance has simulated that of a golf course fairway with mowing three times a week and watering and pesticide applications (i.e., pesticides of non-interest to the study) as needed. In September of 1995, two additional plots were established in the same fashion described above, in order to carry out the third objective of this study which will take place in the third year of our current proposal.

2. Application of Pesticides of Interest. Application of the pesticides are done in three groups. Group 1 consists of five organophospate insecticides (e.g., chlorpyrifos, diazinon, ethoprop, isazofos, isofenphos). Group 2 consists of two organophosphates (e.g., trichlorfon, DDVP), a pyrethroid (cyfluthrin), and two carbamates (e.g., bendiocarb, carbaryl). Group 3 consists of four fungicides (e.g., iprodione, chlorthalonil, propiconizole, thiophanatemethyl). Analytical methodologies and compatibility were the major factors in determining this particular grouping scheme. The first application of group 1 pesticides took place on June 14, 1995. A tank mix of the compounds contained in group 1 was prepared using the following maximum

recommended rates on turf grass; 3.0 fl.oz./1000 sq. ft. of Diazinon, 3.0 fl.oz./1000 sq.ft. of Mocap, 1.5 fl.oz./1000sq.ft. of Triumph, 5.0 fl.oz./1000 sq.ft. of Dursban, and 3.0 fl.oz./1000 sq.ft. of Oftonol. These products were applied to a 10 m radius plot using a fifteen foot, twelve nozzle, spray boom in four gallons of water per 1000 sq.ft. The compounds were then watered in (*ca.* 0.25 inches) using the facilities irrigation system. Volatile and dislodgeable residue sampling started after application and continued for seven days according to the sampling schedule (see section II. D). For the first application a pre-application, sample was taken. For subsequent applications, the last samples taken on the last day of the previously applied group of compounds will serve as the pre-application sample. One week later, group 2 was applied at the following maximum recommended rates on turf grass; 3.75 oz./1000 sq.ft. of Proxol, 2.0 oz./1000 sq.ft. of Turcam, 5.0 g/1000 sq.ft. of Tempo, and 1.5 fl.oz./1000 sq.ft. of Sevin, using the same spray boom, and following the same sampling schedule. On week later, group 3 was applied at the following rates, 4.0 fl.oz./1000 sq.ft. of Banner, 11.0 fl.oz./1000 sq.ft. of Daconil, 10.0 fl.oz./1000 sq.ft. of 336-F, and 8.0 fl.oz./1000 sq.ft. of Chipco. Following this schedule, a complete set of turfgrass pesticides will be applied every three weeks, weather permitting. These applications have continued throughout the summer months and will continue into the fall of 1995. Depending on the data evaluation, further applications may be done in the spring of 1996.

C. Meteorological Data Capture.

A Campbell CR10 Weather Station was set up in the southwest corner of the plot, which is normally downwind of the high volume air sampler. Wind speed, wind direction, surface and

air temperature, solar radiation, and rainfall are sensored every minute and a sixty minute average of the data is collected in a storage module. In addition, soil moisture and relative humidity were measured by another group of researches using the adjacent plot is at our disposal. After the sampling period, the storage module is disconnected, brought back to the laboratory, and the weather data transferred to an IBM computer for permanent storage and analysis.

D. Sampling Schedule.

VOLATILES

Day 1	Days 2 and 3	Days 5 and 7
8 - 9 a.m	7 - 11 a.m	11 a.m. - 3 p.m.
9 - 11 a.m.	11 a.m. - 3 p.m.	11 a.m. - 3 p.m.
11 a.m. - 3 p.m.	3 - 7 p.m.	----------
3 - 7 p.m.	----------	----------

DISLODGEABLES

Day 1	Days 2, 3, 5, and 7
8:15 a.m. (15min post application)	all samples taken at 12 noon
1 p.m. (5 hours post application)	
4 p.m. (8 hours post application)	

III. *RESULTS*

A. Method Development.

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

a. Extracting and Concentrating Samples. 120 ml of XAD-4 resin amended with group 1 pesticides (10 and 20 ppm) was extracted with 250 ml of acetone. The flask containing the resin/acetone mixture was agitated on a wrist-action shaker for one hour. The slurry of resin and acetone was filtered through a Whatman #1 filter paper and the eluent collected into a 500 ml round bottom flask. The resin was rinsed with 2 x 50 ml of acetone and the eluents pooled. Samples were concentrated by vacuum in a hot water bath and further concentrated down to 5 mls under a gentle stream of nitrogen. The samples at this point are ready for injection onto the GC.

The same extraction and concentration procedure was used for the cheesecloth with the exception of only 150 mls of acetone is needed for the extraction.

b. Sample Cleanup. No cleanup steps needed for the group 1 compounds due to the selectivity of the GC detector (TSD).

c. GC Analysis. A Varian 3400 GC with a DB - 5 (30 m x 0.541 mm) column with a TSD detector was used for the quantitation of group 1 pesticides. The following instrument settings were used: injector port 250° C, detector 300°C, initial column temperature 100° C for 1 min increasing to 200° C at a rate of 15° C/min., holding for 3 min, and increasing to 250° C at a

rate of 15° C/min and holding for 2 min. This temperature program allowed for good separation of the compounds in group 1. The 5/1 signal to noise detection limit was 0.5 ug/ml (0.5 ppm) and extraction efficiencies from the resin ranged from 90 - 100%, with an average of 96% +/- 3.3.

d. Additional Method Development. Method development is ongoing for group 1. Experiments with different internal standards such as triphenyl phosphate will be evaluated as well as a different GC system and detector (HP5890- FPD) in an attempt to increase recoveries and decrease detection limits.

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

a. Extracting and Concentrating Samples. All pesticides in group 2 are also extracted with acetone. For trichlorfon and DDVP, aliquots are taken from the extraction solvent and evaporated to near dryness. After a solvent exchange to methylene chloride, the sample is ready for injection onto the GC. For carbaryl, bendiocarb, and cyfluthrin, aliquots are taken and evaporated to near dryness. After solvent exchange to 50/50 methanol/ deionized water solution the sample is ready for injection into the HPLC.

b. Sample Cleanup. No sample cleanup procedure need be done due to the selectivity of the GC (TSD) detector and the HPLC detector (fluorescence).

c. GC Analysis. Trichlorfon and DDVP will be analyzed by GC (Varian 3400). Exact GC conditions have not yet been determined. Extraction efficiencies and detection limits are still being evaluated. Cyfluthrin method development is ongoing. Cyfluthrin analysis by GC is still a

possibility if HPLC analysis with UV detection requires a cleanup step. A HP5890 II GC equipped with a Hall electroconductivity detector (ELCD) is likely to be the detector of choice.

d. HPLC Analysis. Carbaryl and Bendiocarb will be analyzed by HPLC with a post column derivitization with subsequent fluorescence detection[8]. The components of this HPLC system are as follows: Kratos Spectraflow 400 solvent delivery system, Kratos PCRS 520 reaction chamber, and a Spectaflow 980 programmable fluorescence detector. The mobile phase is 50/50 Methanol/deionized water, with a uBondpack C18 analytical column. The post column derivitization reaction causes carbamates to a fluoresce in the prescence of NaOH at 95° C and the reagents orthophtalaldyhyde (OPA) and mercaptoethenol at 40° C. The compounds will then be detected at an excitation wavelength of 230 nm. Extraction efficiencies and detection limits are still under investigation.

3. Group 3 (Chlorthalonil, Propiconizol, Iprodione, Thiophanate Methyl)

a. Extracting and Concentrating the Samples. Chlorthalonil, propiconizole and iprodione were amended on to the resin and cheesecloth at two concentrations in acetone (10 and 20 ppm). Group 3 pesticides were extracted in the same manner as the group 1 compounds, and with the exception of thiophanate methyl, will be concentrated in the same manner.

b. Sample Cleanup. With the possible exception of thiophanate methyl, no cleanup steps will be needed.

c. GC Analysis. Chlorthalonil, propiconizole, and iprodione are analyzed with a Varian 3400 GC equipped with a TSD detector and a DB - 5 analytical column. GC conditions were as

follows: injector temperature 250° C, detector temperature 300°C, temperature program 100° C to 250°C at a rate of 15° /min. Extraction efficiency recoveries averaged 89% +/- 15 with detection limits of 0.5 ppm. at a 5:1 signal to noise ratio.

d. Additional Method Development. Method development for thiophanate methyl is being currently evaluated. The only available methods are by HPLC (UV detection) which may require a cleanup step[8]. A Waters HPLC system equipped with a 996 Photodiode Array will be the next system evaluated for the analysis of thiophanate methyl.

e. Storage Conditions. Thiophanate methyl has been shown to be stable in acetone[8], so storage will not be a problem. Storage spikes will monitor its behavior.

B. *SAMPLE ANALYSIS*

Sample analysis has begun on the group 1 compounds. All current effort will be spent on method development and sample analysis. Sample collection is over until spring 1996. At the present time 450 samples have been collected, concentrated, and stored in a freezer on the premises of MPAL. Upon the completion of analysis of all the compounds , a determination will be made as to what and how much more data we will need to complete the first phase of the research.

IV. *PROPOSED RESEARCH SCHEDULE*

Objective 2. Evaluation of Selected Management Practices to Minimize Potential Volatile and Dislodgeable Foliar Residues of Turfgrass Pesticides (YEAR 2).

V. *TIME DEVOTED TO THE RESEARCH PROGRAM BY UNIVERSITY PERSONNEL*

Dr. J.M. Clark, P.I. Percent effort - 20%

Dr. R.J. Cooper, CO-PI. Percent effort - 5%

G.R. Roy, M.S. Candidate, Percent effort - 75%

J.J. Doherty, M.S., Research technician, Percent effort - 100%

A. Curtis, B.S., Analytical Chemist - 10%

G. , B.S. Candidate, Percent effort - 25%

VI. *EXPENDITURES*

- Research Assistance -	11,809.72
- Temporary Employees-	9,318.75
- Fringe Benefits -	181.25
- Grad Student Health -	1190.28
- Operational Expenses -	12085.35
- Equipment	1,500.00
- Equipment maintainance	1,000.00
TOC	27,085.35
TIC (16%)	5,693.65
TC	42,797.00

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