### **USGA ANNUAL REPORT**

Evaluation of Turfgrass Management Practices to Minimize Potential Volatile and Dislodgeable Foliar Residues of Turfgrass Pesticides

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## **Executive Summary**

Volatilization and dislodgeable foliar residues of turfgrass pesticides following application are major routes of exposure to golfers via inhalation and dermal penetration. Our past research has determined that pesticides with high vapor pressures and inherent high toxicities result in Inhalation Hazard Quotients IHQs greater than 1.0. From this determination, our research has progressed to examine methods of suppressing volatilization and dislodgeable residues in order to reduce potential golfer exposure. The adjuvant, Silwet L-77, was selected for its superior wetting, thatch penetrating, and volatilization suppressing properties (Policello et al., 1995). Three pesticides with relatively high vapor pressures were applied to small circular turfgrass plots with or without the adjuvant. Volatilization was measured with high volume air samplers and using the Theoretical Profile Shape (TPS) method. Dislodgeable residues samples were collected by wiping treated turf plots with dampened cheese cloth. The potential hazard associated with exposure to the volatile and dislodgeable residues was determined by IHQs and Dermal Hazard Quotient (DHQs) determination using the USEPA Hazard Quotient method (Murphy et al., 1996ab).

# Specific Objective 1: (Year 1)

Evaluation of selective turfgrass management practices to minimize potential volatile and dislodgeable foliar residues of turfgrass pesticides: Determination of volatile and dislodgeable foliar residues of organophosphorous (chlorpyrifos and isofenphos) and carbamate (bendiocarb) insecticides in the presence or absence of an organosilicone adjuvent, Silwet L-77.

## **Work Completed (10/20/98):**

The three pesticides used in the present study were selected using criteria generated by previous work on turf by Clark et al., 1997 (see Tables 1 & 2 below). Chlorpyrifos, a commonly used organophosphorous insecticide on turf, is categorized as a high vapor pressure pesticide with a vapor pressure of  $2.0 \times 10^{-5}$  mmHg. Although, IHQs and DHQs for chlorpyrifos never exceeded 1.0, this insecticide has similar high inherent toxicity and its application resulted in similar levels of volatile and dislodgeable foliar residues compared to other more problematic organophosphorous insecticide such as ethoprop and isazafos. However, the extensive data base on the use, toxicity and bio-availability of chlorpyrifos has allowed the USEPA to assign this insecticide an uncertainty factor of 100, which results in a reference dose of only 0.003 and a subsequent reduction of calculated IHQs and DHQ values. Because of its relative safety as determined by our research, chlorpyrifos was included to examine what the addition of the available Silwet L-77 would do to residues of this highly volatile and inherently toxic insecticide. Less complete toxicity data for a pesticide increases the uncertainty factor, which decreases the RfD value that in turn increases the calculated IHQ and DHQ values. Isofenphos, an organophosphorous insecticide having an intermediate vapor pressure  $(3.3 \times 10^{-6} \text{ mmHg})$ , was selected because it was not detected in our previous work at levels that caused concern. Bendiocarb was selected as a representative carbamate that has an intermediate vapor pressure  $(3.4 \times 10^{-6} \text{ mmHg})$  and its application to turfgrass is also deemed safe by the above criteria.

Table 1: Inhalation hazard quotients (IHQs) for turfgrass pesticides in the high (i.e., vapor pressures > 1.0 x  $10^{-5}$  mm Hg), intermediate (i.e., vapor pressures between  $1.0 \times 10^{-5}$  mm Hg and  $1.0 \times 10^{-7}$  mm Hg) and low (i.e., vapor pressures <  $1.0 \times 10^{-7}$  mmHg) vapor pressure groups.

Pesticide	Vapor Pressure (mmHg)	OPP RfD (mg/kg/day)	Day 1 (IHQs)	Day 2 (IHQs)	Day 3 (IHQs)
(High V.P.)					· · · · · · · · · · · · · · · · · · ·
DDVP *	1.6 E-2	0.0005	0.06	0.04	0.02
Ethoprop	3.5 E-4	0.000015	50	26	1.2
Diazinon	9.0 E-5	0.00009	3.3	2.4	1.2
Isazafos	5.6 E-5	0.00002	8.6	6.7	3.4
Chlorpyrifos	2.0 E-5	0.003	0.09	0.1	0.04
(Intermediate V.P.)					
Trichlorfon	3.8 E-6	0.002	0.02	0.004	0.004
Bendiocarb	3.4 E-6	0.005	0.02	0.002	0.002
Isofenphos	3.3 E-6	0.0005	n/d	0.02	n/d
Chlorthalonil	5.7 E-7	0.015	0.001	0.001	0.0003
Propiconizole	4.2 E-7	0.0125	n/d	n/d	n/d
Carbaryl	3.1 E-7	0.014	0.0005	0.0001	0.00004
(Low V.P.)			·		
Thiophanate-Methyl	7.1 E-8	0.08	n/d	n/d	n/d
Ipridione	3.8 E-9	0.061	n/d	n/d	n/d
Cyfluthrin	2.0 E-9	0.025	n/d	n/d	n/d

n/d = non - detected.

note: The IHQs reported in table 1 are the maximum daily IHQs measured on that sampling day.

Table 2: Dermal hazard quotients (DHQs) for turfgrass pesticides listed with increasing RfDs from top to bottom through day 3 post application.

Pesticide	OPP RfD (mg/kg/day)	Day 1 (DHQs)			Day 2 (DHQs)	Day 3 (DHQs)
	(mg/ng/duy)	15 Minutes	5 Hours	8 Hours	12:00 P.M	12:00 P.M
Ethoprop	0.000015	16.0	1.64	1.35	0.23	0.34
Isazafos	0.00002	1.05	1.17	0.97	0.16	0.21
Diazinon	0.00009	3.0	0.28	0.22	0.04	0.05
Isofenphos DDVP <sup>a</sup>	<b>0.0005</b> 0.0005	<b>0.32</b> 0.06	<b>0.05</b> 0.003	<b>0.05</b> 0.003	<b>0.01</b> n/d <sup>a</sup>	<b>0.01</b> n/d <sup>a</sup>
Trichlorfon	0.002	0.64	0.007	0.009	0.008	0.005
Chlorpyrifos	0.003	0.17	0.02	0.016	0.003	0.004
Bendiocarb	0.005	0.31	0.006	0.01	0.006	0.0008
Propiconizole	0.00125	0.0002	0.003	0.0002	0.0005	0.0002
Carbaryl	0.0014	0.003	0.00008	0.0001	0.00006	0.000002
Cyfluthrin	0.0025	b	b	b	ь	b
Ipridione	0.0061	0.0004	0.0003	0.0003	0.0004	0.0003
Thiophanate-	0.008	b	b	b	b	b

<sup>&</sup>lt;sup>a</sup> - DDVP was not applied, but is the breakdown product of trichlorfon.

### **Procedure and Methods:**

Sampling occurred from 7/18/98 through 9/8/98 at the Umass Turf Farm in Deerfield, MA. Each circular plot received pesticide formulations at the maximum recommended rates with or without adjuvant. Formulations consisted of a total of 13.5 gallons of pesticide applied to a 10 m radius plot. Each tank mixture consisted of 18.75 fl. oz. of Dursban (chlorpyrifos), 11.25 fl. oz. of Oftanol (isofenphos) and 0.470 lbs. of Turcam (bendiocarb), per 15 gallons of water. The adjuvent, Silwet L-77, was added to one of the two tank mixtures for each plot at a rate of 0.1 %. There was a total of eight applications (4 with and 4 without adjuvent and alternating between plots), each followed by one week of volatile and dislodgeable residue sample collection (**Table** 3). A total of 310 samples have been collected over the four sampling intervals.

b - Data not available

Volatile and dislodgeable residues from the treated plots were collected using high volume air samplers (Staplex) packed with XAD-4 resin (Rohm and Haas) and dampened analytical grade cheese cloth. Both the resin and cheese cloth were solvent extracted and concentrated using a previous method (Murphy et al., 1996ab), and stored at -15°C until analysis are performed.

Chlorpyrifos and isofenphos will be analyzed using a Hewlett Packard 5890 gas chromatogram (GC) in the flame photometric detector (FPD) mode. Bendiocarb will be analyzed using a Kratos High Pressure Liquid Chromatography (HPLC) with a post column reaction system (Roy et al., M.S. thesis, UMASS - Amherst, in progress).

Determined volatile and dislodgeable concentrations will used to calculate IHQ and DHQ values (Murphy et al. 1996 ab). A statistical comparison of IHQ and DHQ values for adjuvant / no adjuvant will be used to determine the efficacy when adding Silwet L-77 at a rate 0.1% to turfgrass pesticide tank mixtures.

Table 3. Sampling Schedule of Applications From 7/98 - 9/98

Volatile Residue Samples								
Day 1	Day 2 & 3	Day 5	Day 7					
0700-0800 Application	0700-1100	1100-1500	1100-1500					
0800-0900 First Air Sample	1100-1500							
0900-1100 #2	1500-1900							
1100-1500 #3								
1500-1900 #4								
<u>Dermal Samples</u>								
Day 1	Day 2 & 3	Day 5	Day 7					
0700-0800 Application	1200	1200	1200					
0815 First Dermal Wipe								
1000 2 Hrs. Post Application								
1300 5 Hrs. Post Application								

### **Current Status:**

Samples are currently being analyzed and will be completed by February of 1999. Possible future objectives for the summer of 1999 are determination of volatile and dislodgeable foliar residues following chlorpyrifos, isofenphos, and bendiocarb applications to turfgrass in areas adjacent to the golf course where the dosimetry study is being conducted.

### References

- 1. Wilson, J.D. et al. 1982. Estimation of the rate of gaseous mass transfer from a surface plot to the atmosphere. Atmosph. Environ. 16:1861-1867
- 2. U.S. Environmental Protection Agency. 1995 Office of Pesticide Programs reference dose tracking report. Washingtion, D.C.
- 3. Murphy, K.C. 1994. The determination of volatile and dislodgeable residues from pesticide-treated turfgrass and an assessment of human exposure. Ph.D. dissertation, Dept. of Chemistry, Univ. of Massachusetts, Amherst. pp 135.
- 4. Clark, J.M. 1996. Evaluation of management factors affecting volatile and dislodgeable foliar residues. USGA. 1996 Turfgrass and Environmental Research Summary. USGA, Far Hills, NJ. pp 60-63.
- 5. Clark, J.M. 1997. Development and evaluation of best management systems for screening turfgrass pesticides for potential volatility and dislodgeable residues. 1997 Turfgrass Field Book. CFNR, UMASS-Amherst pp. 45-51.
- 6. Dong, M.W. et al. 1990. Practical considerations for rugged N-Methylcarbamate analysis using an HPLC postcolumn-derivitization system. LC-GC. 10(6):442-446
- 7. Knoche, M., Tamura, H. and Bukovac, M. J., 1991, Performance and stability of the organosilicone surfactant L-77: effect of pH, concentration and temperature. J. Agric. Food Chem. Vol. 39 202-206.
- 8. Policello, G.A., et al., The influence of pH on the performance of organosilicone surfactants. Pesticide Formulations and Application Systems: 14th Volume, ASTM STP 1234, Franklin R. Hall, Paul D. Berger, and Herbert M. Collins, Eds., American Society for Testing and Materials, Philadelphia, 1995.