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Development & Testing of Indices & Models of Pesticide Volatilization from Turfgrass

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2000 Executive Summary

Goals

- *Develop and test concise indicators of volatilization hazard that can be used by turf managers to determine the likely degree of health hazard associated with pesticide applications.*
- *Develop and test alternative models of turfgrass pesticide volatilization.*

Progress

The M2CM model proposed by Weed *et al.* (1999) was adapted to estimate volatilization losses from turf. The model assumes that pesticide vaporization is proportional to water vaporization (evapotranspiration, ET) and degradation is first order or exponential. The primary difficulty in using the model is determination of the rate constant. Our approach was to estimate the rate constant from solar radiation and heat of vaporization. We also assume that the proportionality constant (β), is invariant within the chemical volatilization classes proposed by Clark *et al.* (2000).

Model testing was based on data from field turf experiments at the University of Massachusetts, Amherst. Testing data covered 20 week-long experiments during 1995-97. For the high volatilization group, β was estimated by fitting the first week's model results for ethoprop to observations. The first week's data for chlorpyrifos was similarly used to determine β for the intermediate group. Testing results are shown in Table 1. Although individual weeks or experiments are not always well-fitted by the model, mean volatilization losses for each chemical are relatively accurate. More significantly, these means correctly reflect the relative differences in volatilization levels among chemicals.

Chemical	Experi-ments (weeks)	Volatilization (%) Model	Observed
High Vapor Pressure			
Diazinon	4	9.2	10.5
Ethoprop	7	14.2	15.2
Isazofos	4	9.8	10.3
Intermediate Vapor Pressure			
Bendiocarb	4	3.4	1.6
Carbaryl	4	0.1	0.3
Chlorpyrifos	4	10.7	8.3
Trichlorfon	4	0.7	0.8
Isofenphos	6	1.1	1.5

Table 1. Comparison of Measured and Predicted Pesticide Volatilization from Turf Plots.

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GOALS

- *Develop and test concise indicators of volatilization hazard that can be used by turf managers to determine the likely degree of health hazard associated with pesticide applications.*

- *Develop and test alternative models of turfgrass pesticide volatilization.*

2000 PROGRESS

Modified 2-Compartment Model (M2CM)

The M2CM model proposed by Weed *et al.* (1999) was developed for pesticide losses from soil. Dissipation is conceptualized as occurring at different rates in two compartments. Rapid losses from compartment one are due to volatilization and washoff. Compartment two losses are due to biodegradation. Adsorption, runoff and leaching are not considered. Weed *et al.* (1999) applied their model to volatilization of alachlor from soil covered by a corn stubble. However, the model would also appear to be a reasonable approximation to pesticide volatilization from turfgrass, with compartment one consisting of the grass and thatch and compartment two made up of the underlying soil. In this case it would be assumed that volatilization from the soil is negligible.

The model assumes that pesticide vaporization is proportional to water vaporization (evapotranspiration, ET) and degradation is first order or exponential. The equations are

$$C_{t+\Delta t} = (C_t - V_t)\, e^{-\Delta t} \qquad (1)$$

$$V_t = k_v\, Rel_t\, ET_t\, C_t \qquad (2)$$

$$Rel_t = (C_t/C_0)\,(\rho_c / \rho_w) \qquad (3)$$

where, C_t is pesticide mass on foliage at time t (g/ha), V_t is volatilization during time interval Δt (g/ha), ET_t is ET during Δt (mm), C_0 is initial chemical on foliage (g/ha), ρ_c and ρ_w are saturated chemical vapor densities of pesticide and water, respectively (mg/*l*), and k_v is the volatilization rate constant (mm^{-1}).

The primary difficulty in using the model is determination of the rate constant. Calibration is an option, but sufficient data will seldom be available in field situations. Our approach was to assume a relationship between solar radiation and heat of vaporization. Net solar radiation Rn (J/ha) is the energy input for volatilization and ΔHv, heat of vaporization (J/mol), is the required energy for volatilization. If we divide ΔHv by the chemical's molecular weight M, we obtain the energy required to volatilize a gram of the chemical. Comparing this quantity with the net incoming radiation, an upper limit on the mass of chemical that could be volatilized (g/ha) results. Assuming k_v is proportional to this mass, we have

$$k_v = \beta\, (Rn / \Delta Hv)\, M \qquad (4)$$

Finally, we assume that β, he proportionality constant, is invariant within classes of similar chemicals. For example, Clark *et al.* (2000) classify chemicals according to their propensities for volatilization based on vapor pressures: high (>10^{-5} mm Hg), intermediate (10^{-7} - 10^{-5} mm Hg), and low (< 10^{-7} mm Hg). Only the first two are of concern, implying that only two values of β need be determined.

Calibration and Field Testing

Model testing was based on data from field turf experiments at the University of Massachusetts, Amherst. The 0.2-ha plots had well-established creeping bentgrass maintained at 1.3 cm height. Experimental design and sampling methods are described in Murphy *et al.* (1996a,b). Testing data covered 20 week-long experiments during 1995-97. Chlorpyrifos, diazinon, ethoprop, isazofos, and isofenphos were applied in weeks 1, 4, 7 and 12, and bendiocarb, carbaryl, and trichlorfon were applied in weeks 3, 6, 9 and 13. Ethoprop and isofenphos were also applied in weeks 16, 18 and 20. In each of these cases, the pesticide was applied as a spray at the beginning of the week, and volatilization measurements were made for the next 7 days.

Chemical	Application Week	Volatilization (%) Measured	Model	
Diazinon	1	17.0	11.9	
	4	8.7	9.9	
	7	6.9	10.1	
	12	9.2	4.7	
	Mean	**10.5**	**9.2**	
Ethoprop	1	22.2	22.4	← **Calibration**
	4	14.3	19.8	
	7	10.0	20.0	
	12	19.1	10.5	
	16	16.8	12.2	
	18	11.6	8.0	
	20	12.1	6.7	
	Mean	**15.2**	**14.2**	
Isazofos	1	20.6	12.8	
	4	5.5	10.6	
	7	6.6	10.9	
	12	8.6	5.1	
	Mean	**10.3**	**9.8**	

Table 1. Comparison of Measured and Predicted Pesticide Volatilization from Turf Plots - High Volatilization Potential (β = 3.3 10^{-7}).

Three of the pesticides (diazinon, ethoprop, and isazofos) are in the high volatilization class and the remainder are in the intermediate class. Samples were generally taken several times for 1 to 4 hour periods during the first two or 3 days following application. Single samples were obtained 5 and 7 days after application. The model was applied to each of these periods, and total volatilization was summed for the seven days. Solar radiation, temperature and wind speed data were available for each sampling period. Evapotranspiration was estimated using the modified Penman Equation as described by Jensen *et al.* (1990). For the high volatilization group, β was estimated by fitting the first week's model results for ethoprop to observations. The first week's data for chlorpyrifos was similarly used to determine β for the intermediate group. These values are $\beta = 3.3\ 10^{-7}$ and $14.2\ 10^{-7}$ for the high and intermediate groups, respectively.

Chemical	Application Week	Volatilization (%) Measured	Model	
Bendiocarb	3	1.5	2.7	
	6	3.0	4.6	
	9	0.6	0.3	
	13	1.4	6.1	
	Mean	**1.6**	**3.4**	
Carbaryl	3	0.3	0.1	
	6	0.4	0.1	
	9	0.1	0.0	
	13	0.3	0.1	
	Mean	**0.3**	**0.1**	
Chlorpyrifos	1	13.7	13.7	← **Calibration**
	4	6.9	11.7	
	7	6.5	11.8	
	12	6.0	5.5	
	Mean	**8.3**	**10.5**	
Isofenphos	4	0.2	2.0	
	7	0.8	1.9	
	12	1.2	0.8	
	16	2.7	0.9	
	18	2.2	0.6	
	20	2.0	0.6	
	Mean	**1.5**	**1.1**	
Trichlorfon	3	1.2	0.6	
	6	1.1	1.0	
	9	0.4	0.1	
	13	0.6	1.2	
	Mean	**0.8**	**0.7**	

Table 2. Comparison of Measured and Predicted Pesticide Volatilization from Turf Plots - Intermediate Volatilization Potential ($14.2\ 10^{-7}$).

Results of the testing are summarized in Tables 1 and 2. The hypothesized approximation for k_v given by Equation 4 is clearly demonstrated. Even though the constant term (β) was calibrated from only one chemical and one experiment (week 1), it provides good results for all other chemicals within the classification. Although individual weeks or experiments are not well-fitted by the model, mean volatilization losses for each chemical are relatively accurate. More significantly, these means correctly reflect the relative differences in volatilization levels among chemicals.

REMAINING RESEARCH

Research on this project is essentially complete. A journal article describing the testing of the M2CM model is now being prepared.

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