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

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1999 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

Two models were tested for their abilities to predict volatile pesticide fluxes from turf. The Pesticide Root Zone Model (PRZM), version 3 (Carsel *et al.*, 1998), which combines soil and foliage volatilization models with components for pesticide leaching and runoff. The Modified Two-Compartment Model (M2CM) was used by Weed *et al.* (1999) to estimate alachlor dissipation 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 is assumed that volatilization from the soil is negligible.

Model predictions and field measurements of pesticide volatilization losses are compared in Table 1. Field measurements are data from 0.2-ha turf plot experiments at the University of Massachusetts, Amherst, MA. The M2CM obviously performed much better than PRZM. The PRZM deficiencies are particularly serious because the model may also be used to estimate runoff and leaching losses of pesticides. When applied to turf, the very high, and inaccurate volatilization from foliage removes pesticide from the turf system, limiting the chemical available for other loss mechanisms. As a result, PRZM may badly underestimate pesticide runoff and leaching.

Chemical	Volatilization during the Week (%)		
	Measured	PRZM	M2CM
Bendiocarb	1.6	83.7	1.1
Carbaryl	0.3	39.0	0.3
Chlorpyrifos	8.3	82.6	11.6
Diazinon	10.5	67.8	14.6
Ethoprop	15.2	80.4	17.2
Isazofos	10.3	77.5	18.2
Isofenphos	1.5	29.8	0.1
Trichlorfon	0.8	39.5	0.9

Table 1. Comparison of Measured and Predicted Volatilization from Turf Plots for Eight Pesticides.

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.*

1999 PROGRESS

Two models were tested for their abilities to estimate volatile pesticide fluxes from turf. The first of these models is the Pesticide Root Zone Model (PRZM), version 3 (Carsel *et al.*, 1998), which combines the Jury *et al.* (1990) model with a foliage volatilization model as well as components for pesticide leaching and runoff. The second model is the modified two-compartment model (M2CM) proposed by Weed *et al.* (1999).

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 weeks during 1996 and 1997. 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.

Pesticide Root Zone Model (PRZM)

Pesticide volatilization in PRZM consists of vaporization from the soil and a plant canopy. Chemical volatilization from the soil (g/day) is given by

$$J_I = (D_a A / d) (C_{g,1} - C_{g,d}) \qquad (1)$$

where,

D_a = molecular diffusivity of chemical in air (cm^2/day)
A = cross section area of the site (cm^2)
d = thickness of stagnant air boundary layer (cm)
$C_{g,1}$ = vapor-phase concentration in surface soil layer (g/cm^3)
$C_{g,d}$ = vapor-phase concentration above the boundary layer (g/cm^3)

The soil concentration $C_{g,1}$ is determined from an equilibrium mass balance of dissolved, adsorbed, and vaporized pesticide in the soil surface layer. Above ground concentration $C_{g,d}$ is generally considered negligible, and a boundary layer thickness of 5 cm is assumed.

Volatilization from the plant canopy (g/cm^2-day) is

$$J_{pl} = K_f M \qquad (2)$$

where,

M = current pesticide mass on foliage (g/cm^2)
K_f = volatilization rate (1/day)

In addition to gaseous losses, M is depleted by washoff from precipitation and a first order decay term which presumably corresponds to biochemical and/or photochemical degradation.

As applied to turfgrass, all pesticide is applied to foliage, and the only mechanism for addition of chemical to the soil is washoff from precipitation. Hence, in the absence of significant storm events, most volatilization will be from the plant canopy, i.e., the turfgrass. The volatilization rates K_f are specified by the user, and are not related to environmental variables (temperature, wind speed, etc.). The rates suggested in the PRZM manual are relatively large (0.05 - 0.30 for organophosphates and 0.09 - 0.63 for carbamates), generally indicating volatilization losses of at least 10% per day.

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. The chemical mass balances for the two compartments are:

$$C1_t = C1_{t-1} - WS_t - C1Vol_t \quad (3)$$

$$C2_t = C2_{t-1} + WS_t - C2Bio_t \quad (4)$$

where,

$C1_t$, $C2_t$ = chemical mass in compartments 1, 2, respectively at the beginning of day t (kg/ha)
$C1Vol_t$ = volatilization of chemical from compartment 1 on day t (kg/ha)
WS_t = washoff of chemical from compartment 1 to compartment 2 on day t (kg/ha)
$C2Bio_t$ = chemical decay from biodegradation on day t kg/ha)

Washoff is determined by

$$WS_t = k_w R_t C1_t \quad (5)$$

where,

R_t = rain on day t (mm)
k_w = washoff coefficient (1/mm)

Volatilization is assumed proportional to evaporation:

$$C1Vol_t = k_v \ relVol_t EV_t C1_t \quad (6)$$

with,

k_v = volatilization rate (1/mm)
EV_t = evaporation on day t (mm/day)

and the relative volatilization of the chemical compared to water is

$$relVol_t = (C1_t / C1_0)(\rho_{ct} / \rho_{wt}) \quad (7)$$

where,

$C1_0$ = original chemical application (kg/ha)
ρ_{ct} = saturated vapor density of chemical on day t (mg/l)
ρ_{wt} = saturated vapor density of water on day t (mg/l)

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.

Chemical	Application Week	Volatilization during the Week (%) Measured	PRZM	M2CM	Calibrated k_v (mm^{-1})
Bendiocarb	3	1.5	88.9	1.4	40
	6	3.0	88.9	1.9	
	9	0.5	88.9	0.2	
	13	1.4	68.1	1.1	
	Mean	**1.6**	**83.7**	**1.1**	
Carbaryl	3	0.3	39.6	0.4	800
	6	0.4	39.5	0.5	
	9	0.1	39.5	<0.1	
	13	0.3	37.4	0.2	
	Mean	**0.3**	**39.0**	**0.3**	
Chlorpyrifos	1	13.7	83.0	13.5	450
	4	6.9	83.1	17.4	
	7	6.5	83.1	11.1	
	12	6.0	81.0	4.5	
	Mean	**8.3**	**82.6**	**11.6**	
Diazinon	1	17.0	67.9	16.9	150
	4	8.7	67.9	21.5	
	7	6.9	67.9	13.9	
	12	9.2	67.3	5.9	
	Mean	**10.5**	**67.8**	**14.6**	

Table 1. Comparison of Measured and Predicted Pesticide Volatilization from Turf Plots - Bendiocarb, Carbaryl, Chlorpyrifos and Diazinon.

Chemical	Application Week	Volatilization during the Week (%) Measured	PRZM	M2CM	Calibrated k_v (mm^{-1})
Ethoprop	1	22.2	80.6	23.0	80
	4	14.3	80.6	28.5	
	7	10.0	80.6	22.3	
	12	19.1	79.5	8.7	
	16	16.8	80.5	10.2	
	18	11.6	80.5	11.5	
	20	12.1	80.3	16.4	
	Mean	**15.2**	**80.4**	**17.2**	
Isazofos	1	20.6	77.7	20.4	180
	4	5.5	77.7	25.6	
	7	6.6	77.7	19.7	
	12	8.6	76.7	7.2	
	Mean	**10.3**	**77.5**	**18.2**	
Isofenphos	4	0.2	30.9	0.2	30
	7	0.8	27.7	0.1	
	12	1.2	28.0	<0.1	
	16	2.7	30.8	0.1	
	18	2.2	30.8	0.1	
	20	2.0	30.6	0.1	
	Mean	**1.5**	**29.8**	**0.1**	
Trichlorfon	3	1.2	39.5	1.2	250
	6	1.1	39.5	1.6	
	9	0.4	39.5	0.1	
	13	0.6	39.5	0.8	
	Mean	**0.8**	**39.5**	**0.9**	

Table 2. Comparison of Measured and Predicted Pesticide Volatilization from Turf Plots - Ethoprop, Isazofos, Isofenphos, and Trichlorfon.

In our preliminary testing of this model for turfgrass, we assumed that EV_t is equal to potential evapotranspiration, as given by the equation from Hamon (1961). Weed *et al.* determined a value for the volatilization rate (k_v) for alachlor from soil (k_v = 50,000 mm^{-1}), but no values were available for the eight pesticides in our study. According, we determined the rate by calibration for the first week's pesticide application, and then used this rate for the remaining weeks.

Testing Results

Model predictions and field measurements of pesticide volatilization losses are compared in Tables 1 and 2. The most dramatic result is the tendency of PRZM to severely overestimate pesticide volatilization. This is due to the simple nature of the foliage volatilization model (Equation 2) and the large default values for the volatilization rate (K_f). Also, since these rates do not depend on environmental conditions, volatilization losses are virtually identical from week to week.

The PRZM deficiencies are particularly serious because the model may also be used to estimate runoff and leaching losses of pesticides. When applied to turf, the very high, and inaccurate volatilization from foliage removes pesticide from the turf system, limiting the chemical available for other loss mechanisms. As a result, PRZM may badly underestimate pesticide runoff and leaching.

The second model (M2CM) performed much better, although the accuracy was only achieved by calibration of the initial week's volatilization rate for each pesticide. As shown in Tables 1 and 2, these calibrated rates ranged from 30 to 800 mm^{-1}, substantially less than the 50,000 mm^{-1} value obtained by Weed *et al.* for alachlor.

RESEARCH PLANS FOR 2000

The M2CM appears to be a very promising model for estimating volatilization from turfgrass. We will further evaluate this model in the coming year. Among the issues to be investigated are incorporation of adsortion, development of general procedures for estimating the rate parameter k_v, and selection of the most appropriate procedure for calculating evapotranspiration.

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