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

Douglas A. Haith, Cornell University, Principal Investigator

1998 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

Mathematical models can potentially be used to estimate volatilization of chemicals applied to turf. However, the complexity and limited testing of volatilization models restrict their general applicability. An alternative procedure estimates concentrations using simple *volatilization indicators* which are determined from basic chemical properties and the temperature and wind speed at the application site. Using data from field studies for eight different turf pesticides, three different indicators were evaluated for their ability to predict vapor concentrations. Chemical vapor pressure was the simplest indicator considered, and it was 70% effective in predicting variations in vapor concentrations. The effectiveness increases to 90% when factors related to solubility, adsorption and wind speed are added to produce the G/V indicator.

We further tested the use of volatilization indicators by using them to classify the inhalation hazards associated with 37 different applications of the eight pesticides to grass. Health hazards were determined by comparing inhaled dose to the EPA's reference doses. Inhaled doses were computed using both measured vapor concentrations and concentrations determined from the indicators. As shown in Table 1, the volatilization indicators produced the same rankings of health hazards that were obtained from the measured concentrations. Although further testing is necessary, the research suggests that with a table of chemical properties and a weather forecast, it may be relatively easy to identify whether or not application of a pesticide to turf on a particular day may be hazardous to golfers or lawn users.

| Chemical | HQ from Measured Concentration | HQ from Concentration Regressions on Vapor Pressure | G/V |
|---|---|---|---|
| Bendiocarb | 0.01 | 0.03 | 0.02 |
| Carbaryl | 0.00 | 0.01 | 0.00 |
| Chlorpyrifos | 0.09 | 0.04 | 0.11 |
| Diazinon | 2.80 | 2.70 | 1.50 |
| Ethoprop | 70.20 | 61.90 | 64.40 |
| Isazophos | 5.20 | 13.10 | 11.20 |
| Isofenphos | 0.12 | 0.17 | 0.15 |
| Trichlorfon | 0.04 | 0.04 | 0.03 |

**Table 1. Inhalation Hazard Quotients (HQ) Determined from Measured and Calculated Concentrations.**

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## GOALS

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## 1998 PROGRESS

Hazard quotients (HQ) are fundamental tools for assessment of health risks from inhalation of volatilized chemicals. They are given by the inhaled chemical dose divided by the chronic reference dose, and can be determined given knowledge of the concentrations of pesticide vapors in the air above turfgrass. These concentrations depend on chemical properties, application rates and environmental conditions and our research during the current year was largely an effort to relate these concentrations to basic indices of pesticide volatilization.

The most obvious indicators of pesticide volatilization are vapor pressure ($p_V$, mPa) and Henry constant (h, dimensionless). The first measures the general tendency of a chemical to escape as a vapor from solution and the second is the ratio of gaseous concentration or density to dissolved (solution) concentration at equilibrium. Vapor pressure and Henry constant are sensitive to environmental conditions through their dependence on temperature. However, there are other factors that mediate these influences in a turfgrass setting. Adsorption to organic matter limits volatilization opportunities, air movement removes the vapor from the site and moisture increases the total mass of dissolved chemical. Two more general indices which include these phenomena were derived by considering an equilibrium mass balance of a pesticide in a turfgrass system consisting of foliage and thatch.

The G/V indicator is given by

$$G/V = (h\,P)\,10^{6} / (k_{oc}\,V) \qquad (1)$$

Where h = Henry constant, P = pesticide application (g/ha), $k_{oc}$ = organic carbon partition coefficient ($cm^3/g$) and V = wind velocity (m/s). A related indicator substitutes vapor pressure ($p_v$) for h:

$$G/V^{*} = (p_v\,P)\,10^{-3} / (k_{oc}\,V) \qquad (2)$$

The $10^6$ and $10^{-3}$ terms in Equations 1 and 2 are scaling constants.

Volatilization indices were evaluated using data from on-going 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.* (*1*). 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. All chemicals were applied as sprays. Sampling data included concentrations at 0.7 m height, surface and air temperatures, solar radiation and wind speed for each period. Measured concentrations generally fell to very low levels after the second day following application.

Volatilization indices were compared with the maximum vapor concentrations measured during the two days following pesticide application. Thirty-seven concentrations were available, each corresponding to the maximum vapor concentration measured in the two days following application of a pesticide in a specific week. Henry constants and vapor pressures were determined for the surface temperatures measured during the periods of maximum concentration. Wind speeds from these same periods were used. Indices were compared with concentrations using simple linear regression analyses.

Regressions between concentrations (C, $\mu g/m^3$) and Henry constant were not significant. However, concentrations were strongly related to vapor pressure. The associated regression equation,

$$C = 0.523 + 0.100\, p_v \qquad (3)$$

has a standard error of 1.71 and $R^2 = 0.706$.

Figure 1 shows the relationship between concentrations and the G/V index given by Equation 1. This index, which measures the equilibrium volatilized mass in the turf divided by air velocity, provides a better predictor of concentrations, with the regression

$$C = 0.384 + 0.019\, G/V \qquad (4)$$

having $R^2 = 0.875$ and standard error of 1.11. The regression on G/V*,

$$C = 0.754 + 0.020\, G^*/V \qquad (5)$$

performed nearly as well, with $R^2 = 0.854$ and standard error = 1.20.

Although the regression equations can explain nearly 90% the observed variance in observed vapor concentrations, the scatter shown in Figure 1 indicates that individual concentration predictions may have substantial errors. Nevertheless, the regressions produce robust indicators of health hazards. Based on hazard quotients, concern is not with the exact value of HQ, but rather with chemicals and conditions that are likely to produce values of HQ which approach one. Computed HQs based on measured concentrations and concentrations calculated by the regression equations are compared in Table 1. Although the regressions on volatilization indices often result in HQ values which are different than measured values, the differences are not large enough to produce misleading conclusions regarding hazards. Even the least accurate regression (Equation 3, based solely on vapor pressure) clearly identifies the same hazardous chemicals (HQ > 1) as would be flagged by the measured concentrations.

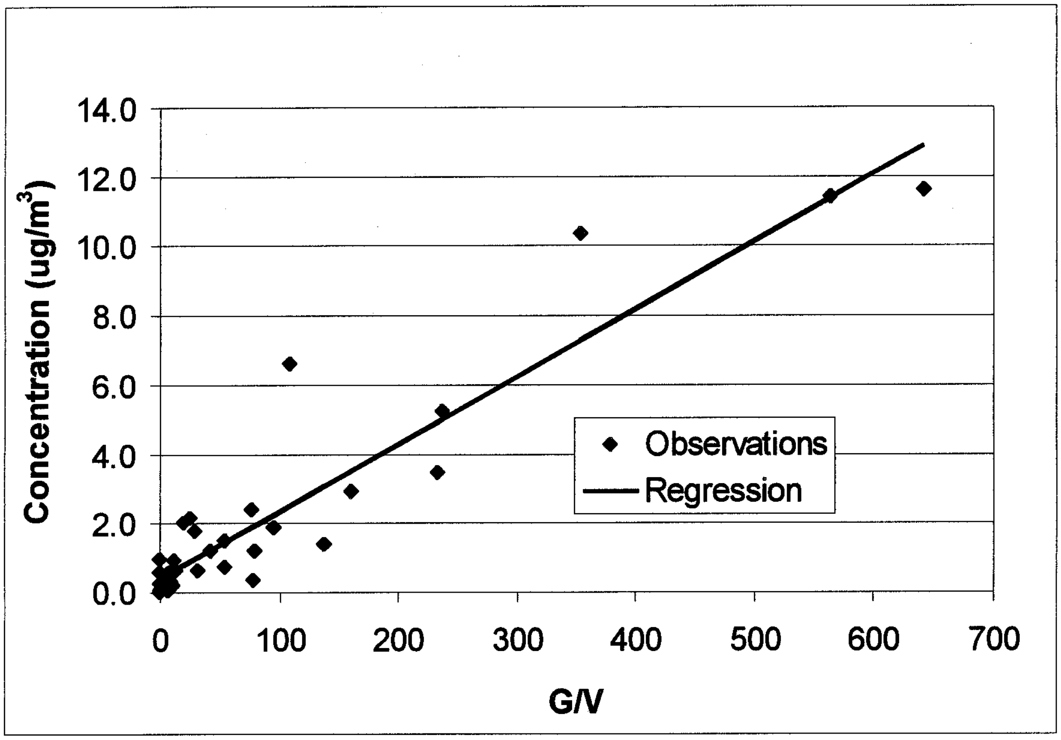


**Figure 1. Maximum Vapor Concentration *vs.* G/V.**

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|---|---|---|---|
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## RESEARCH PLANS FOR 1999

During the next year we expect to continue to refine and test the volatilization indices with additional field data from Massachusetts and possibly other locations. At this point, the regressions given by Equations 3-5 have not truly been tested; i.e., they have only been compared with the measured concentrations which were used to derive them. Also, we will also see if the indices can provide reasonable predictions of volatilized pesticide mass. If so, they may be useful in the second project component – development of mathematical models of pesticide volatilization.

We will be exploring alternative approaches to the modeling of volatilization. One approach will be to apply the PRZM model (Pesticide Root Zone Model) to the Massachusetts plots to see if the model's volatilization predictions are reasonable. We will also construct a simple mass balance model which assumes equilibrium between dissolved, adsorbed and vaporized pesticide in the grass/thatch layer. This model will build on the analyses used in constructing the G/V index (Equation 1).