

FATE AND TRANSPORT MODELING OF PESTICIDES APPLIED TO TURF

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FATE AND TRANSPORT MODELING OF PESTICIDES APPLIED TO TURF

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This research centers on modeling fate and transport processes affecting pesticides applied to turfgrass systems. Interest in predicting pesticide fate and transport from these systems stems from observations of pesticide residues in urban surface and groundwaters, and the need for information with which to assess human health and ecological risks of using these pesticides, total maximum daily load and other water quality management studies.

The main processes that affect pesticide fate and transport in turf systems are reviewed, and general magnitudes of each process are reported. Dissipation rates for turf systems are compared to half-life values for aerobic decay in soil, photolysis and field dissipation. From this analysis, microbial decay appears to be a major factor in pesticide dissipation. Decay rates specific for turf are developed based on dissipation rates from these systems. The hypothesis that the use of soil-based decay rates leads to overestimation of pesticide runoff, volatilization and leaching losses from turfgrass systems is tested by means of long term simulations involving diverse turf, climatic and management conditions. Results indicate significant differences in estimations based on soil and turf decay rates as a result of differences in estimating the pesticide's persistence in the turf foliage and thatch. However, care should be taken when modeling pesticides that are weakly sorbed to organic matter.

The research also includes the development of a volatilization model that is based on splitting pesticides into surface and retained deposits and allowing

volatilization to occur from the surface deposits only. This model replicated daily volatilization fluxes better than models previously developed for turf, and was incorporated into the Turf Pesticide Model (TPM), which was designed to predict pesticide runoff, leaching, volatilization and decay on a daily basis using relatively few input parameters. Uncalibrated tests of TPM against data from diverse field studies indicated that the model explained 75% of the observed variation in drainage, 63% for pesticide leaching, 65% for runoff volumes, 64% for pesticide loss in runoff, and 62% for pesticide volatilization. TPM can provide information for risk, TMDL, environmental and water quality studies centered on evaluating the impacts of pesticides applied to turf.

BIOGRAPHICAL SKETCH

Antoni Magri was born in Colorado, but shortly thereafter his family moved to South Africa. After living for 15 years in that beautiful country, the family moved back to their origin: Chile. There, Antoni obtained a B.S. in Agricultural Engineering. After working for a few years in an environmental consulting company, he and his wife, Carolina, came to Cornell for advanced training. After obtaining an M.S. with emphasis in Environmental Information Sciences, Antoni enrolled in the Department of Biological and Environmental Engineering to pursue a Ph.D. in the arena of fate and transport modeling of non-point source pollution processes.

Dedico este trabajo a mi familia: Carolina mi esposa, Patricia, Eduardo, Cristian y Suzanne, mis padres y hermanos, quienes siempre están conmigo. Agradezco todo su apoyo y paciencia, sin lo cual terminar no hubiera sido posible.

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CHAPTER 1

INTRODUCTION

The theme of the research presented in this dissertation is the modeling of fate and transport processes affecting pesticides applied to turfgrass systems. As these are complex biological systems, several factors play important roles. Interest in predicting pesticide fate and transport from these systems stems from observations of pesticide residues in urban surface and groundwaters, and the need to assess human health and ecological risks of using these pesticides, along with a need of information on which to base total maximum daily load and other water quality management studies.

Chapter 2 reviews the main processes that affect pesticide fate and transport in turf systems. General magnitudes of each process are reported based on a variety of field studies. Dissipation rates are compared to published half-life values for aerobic decay in soil, photolysis and field dissipation. From the analysis, microbial decay appears to be a major factor in pesticide dissipation, and decay rates specific for turf are developed based on an analysis of dissipation rates from these systems.

In Chapter 3, the hypothesis that the use of soil-based decay rates in fate and transport modeling may lead to overestimation of pesticide runoff, volatilization and leaching losses from turfgrass is formulated. The hypothesis is tested by means of long term simulations involving diverse turf, climatic and management conditions. Simulation results indicate that the use of soil-based decay rates may indeed lead to overestimation of pesticide runoff, leaching and volatilization as a result of overestimating the pesticide's persistence in the turf foliage and thatch.

However, the simulation results also indicate that care should be taken when modeling pesticides that are weakly sorbed to organic matter, as pesticide infiltration

into the soil may predominate over microbial decay in the turf foliage and thatch. For these pesticides, most of the microbial decay will occur in the soil, and soil half-lives are more appropriate than turf half-lives in modeling this process.

An important component of a general fate and transport model for pesticides applied to turf is volatilization. A previously published volatilization model was examined and found to replicate daily volatilization fluxes poorly. This was due to the assumption that all pesticide mass in the turf foliage and thatch is available for volatilization. An alternate model is developed in Chapter 4, based on splitting the pesticide into surface and retained deposits, and allowing volatilization to occur from the surface deposits only. This model replicated daily volatilization fluxes considerably better, and was used in the formulation of a general fate and transport model.

Chapter 5 describes the Turf Pesticide Model (TPM), a general fate and transport model for pesticides applied to turf. The model is designed to predict pesticide runoff, leaching, volatilization and decay on a daily basis using few input parameters. The model is based on TurfPQ (a model designed to predict runoff and infiltration of pesticides applied to turf, Haith 2001), the volatilization model developed in Chapter 4, and a subsurface component that tracks drainage and leaching through the soil. Both TurfPQ and the volatilization model are conceptualized for well established turf. This should be taken into account when modeling pesticides applied to recently seeded turf, as soil erosion (which is not included in the model), may be a significant source of pesticide transport from the system.

Results of testing TPM against data from several field studies representing varied turf, soil, climatic and management scenarios are presented in Chapter 6. The model was tested without performing any calibration, and was found to perform acceptably well. The model explained 75% of the observed variation in drainage, 63%

for pesticide leaching, 65% for runoff volumes, 64% for pesticide loss in runoff, and 62% for pesticide volatilization. These results indicate levels of performance that could be expected in situations where no data is available for calibration.

Chapter 7 reviews the main conclusions of the research. The Appendix contains a Users' Manual for the Turf Pesticide Model software developed based on the equations presented in Chapter 5.

CHAPTER 2

PESTICIDE DECAY IN TURF: I. REVIEW OF PROCESSES AND EXPERIMENTAL DATA

Abstract

Decay rates are central parameters in modeling pesticide fate and transport in the environment. Pesticide decay is usually modeled as a first order process, and variations in half-life can have significant impacts on model predictions. Decay rates for turf are scarce, and most simulation efforts must resort to values based on pesticide behavior in soils. This chapter describes the main dissipation processes affecting pesticides applied to turf, and compares aerobic soil decay rates from the USDA-ARS Pesticide Properties Database (ARS 2006) and from The Pesticide Manual (Tomlin 2003) to dissipation values in turf found in the literature for 18 pesticides currently registered for turf. Median half lives were 39.5 days for the ARS values, 32.4 days for Tomlin's values and 5 days for the turf-specific values. The turf dissipation half-lives are considered to be representative of the microbial decay processes occurring in well established turf, where the majority of the pesticide is retained in the foliage and thatch. The impacts of using soil vs. turf half-lives in simulation studies are evaluated by performing long term (100 year) simulations for several pesticides, turf types and climates, and results are presented in Chapter 3.

INTRODUCTION

Turf is an intensively managed biotic system (Gardner et al. 2000, Wu et al 2002a) and can account for up to 80% of the pervious surfaces in urban areas, of which approximately half may be subjected to high input management (Schueler

2000a). Annual pesticide application rates can be 3 to 8 times higher on golf courses, and 3 times higher on home lawns, than those for agricultural land (Kopell 1994, Schueler 2000b). Pesticide concentrations in water originating from urban areas and golf courses have been found to exceed environmental and drinking water standards (Cohen et al. 1999, US Geological Survey 1999). There is also concern regarding exposure to pesticides upon reentry to treated areas, especially for children using turf at schools yards and parks (Cowell et al. 1993, Hurto and Prinster 1993, Sears et al. 1987).

While monitoring studies provide valuable information, they are costly and it is often hard to extrapolate findings to other locations and conditions. Simulation models are frequently used in their stead to estimate pesticide loads to surface water, groundwater and the atmosphere. Most simulation studies rely on published pesticide property databases to obtain parameter values. In this study, pesticide decay in turf is examined, which is generally modeled as an exponential function, and thus has the potential to significantly affect fate and transport assessments of a chemical in the environment.

This work is divided into two main parts. Chapter 2 examines pesticide dissipation processes in turf. Decay rates are computed for 25 pesticides applied to turf and compared to published half-life values for aerobic decay in soil, photolysis and field dissipation. Based on this analysis, the hypothesis that the use of soil-based decay rates in fate and transport modeling may lead to overestimation of pesticide runoff, volatilization and leaching losses from turfgrass is formulated. In Chapter 3, this hypothesis is tested by performing long-term simulations involving six pesticides, four geographic locations and three distinct turf types to account for variability in pesticide characteristics, climate and turf.

Pesticide dissipation processes in turf

Several processes are involved in the dissipation of pesticides from turf. Physical removal can occur via runoff, volatilization and infiltration into the soil. Portions of the pesticides that infiltrate may leave the system via leaching. Removal of clippings during mowing may also contribute to the physical removal of pesticides. Additionally, pesticides can be degraded on site by photolysis when exposed to sunlight, by hydrolysis and other chemical reactions, or by microbial activity in the turf and soil layers. These processes are represented in Figure 2.1. Systemic pesticides can also be absorbed into plant tissue, where they may be translocated and undergo enzymatic breakdown.

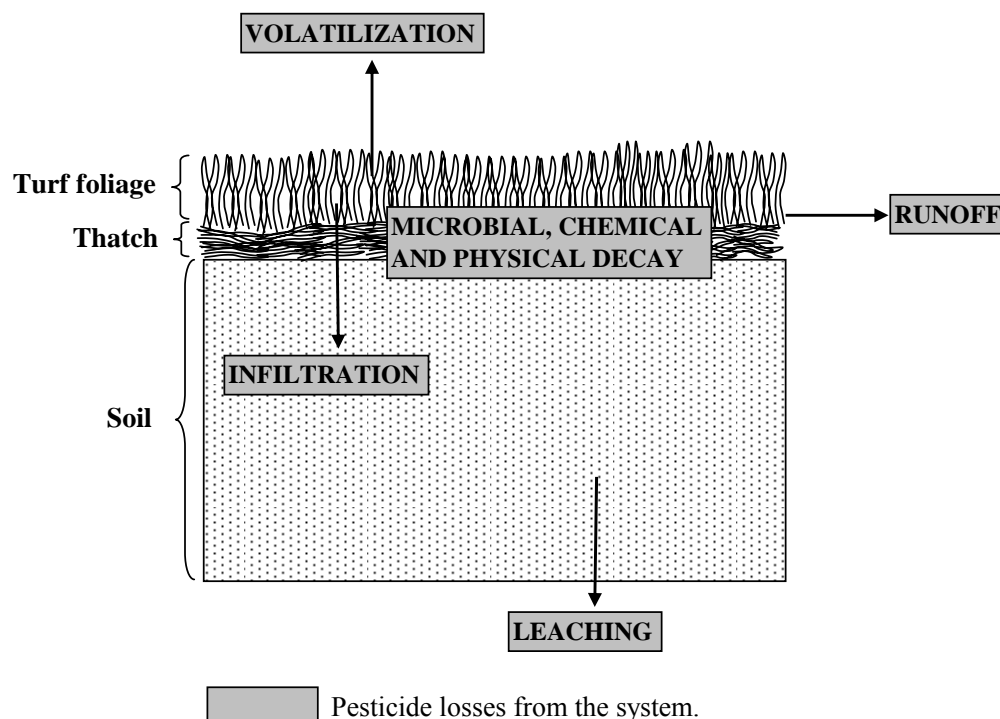


Figure 2.1. Pesticide losses from a turfgrass system.

Pesticides vary significantly in their physical and chemical characteristics, and are not equally susceptible to all dissipation processes. The following sections review magnitudes of the main processes that determine pesticide fate in turf.

Pesticide retention in foliage and thatch

Turf has dense foliage and often forms an underlying layer of thatch, which is comprised of dead and decaying vegetative matter. During application, these layers intercept most of the pesticide, allowing very little to reach the soil directly. In addition, foliage and thatch contain large amounts of organic carbon, which strongly adsorb pesticides and impede further movement to the soil.

Strong retention in foliage and thatch is arguably the most important factor governing pesticide dissipation in turf. It makes the pesticides less susceptible to physical removal by runoff, infiltration and volatilization, and, as described subsequently, exposes them to large and highly active microbial populations that reside in these layers.

Regarding pesticide retention, Niemczyk and Krueger (1987) found 96-99% of applied isazofos in the thatch layer, even after post-application irrigation. Gardner and Branham (2001b) recovered 95% of applied propiconazole from the foliage and thatch layers. Niemczyk and Filary (1988 cited by Liu and Hsiang 1996) found that 96-99% of the residues of nine pesticides remained adsorbed by thatch during 7 days after application, despite immediate irrigation. Niemczyk et al. (1988) found that 97% of ethoprop, isazofos and isofenphos remained in the thatch. Cisar and Snyder (1996) found that that most of the chlorpyrifos, isazofos, isofenphos and ethoprop they applied were retained in the thatch layer, where they degraded over time.

Lab studies further confirm that turfgrass leaves and thatch strongly adsorb organic compounds and should have a significant impact on the fate of pesticides applied to turfgrass (Lickfeldt and Branham 1995, Dell et al. 1994). Horst et al. (1996) found that thatch was highly retentive and contained 7 times more pesticide than the foliage for all the pesticides they examined. Retention to organic matter in thatch was

found to be the main impediment to downward movement into the soil profile by Branham and Wehner (1985), Gardner et al. (2000) and Niemczyk et al. (1977).

Pesticide adsorption in turf has been cited as the cause of reduced pesticide mobility (Smith and Bridges 1996, Stahnke et al. 1991). Tashiro (1980) found that retention of chlorpyrifos and diazinon in thatch had a significant effect on the fate of the insecticides. Liu and Hsiang (1996) indicated that thatch can adsorb significant amounts of applied pesticides, reducing the amount reaching the roots and soil, and affecting plant uptake of systemic pesticides. Niemczyk et al. (1977) found that insecticides adsorb to the organic thatch layer in turfgrass, and that this was the main factor in preventing adequate control of insects in the soil.

Pesticide losses via runoff and leaching

Pesticides that are strongly retained in the foliage and thatch may be less likely to be transported by runoff and leaching as less is available for dissolution in rainfall and irrigation waters. However, some strongly sorbed and persistent pesticides may have higher total runoff and leaching losses as they remain for longer periods of time in the mixing zone (i.e. the turf foliage and thatch layers).

Pesticide transport in runoff has been studied by several investigators. Smith and Bridges (1996) produced high runoff losses (7.3 – 9.9%) by irrigating immediately after applications of 2,4-D, dicamba and mecoprop. Losses decreased rapidly in runoff events over the following days (1.4 – 3.5% for the second event, and <1% for the following events). Similar patterns, with maximum losses of 10% or less, were found by Hong and Smith (1997) for dithiopyr and by Watschke et al. (2000) for mecoprop. Evans et al. (1998) measured diazinon from non-sequential runoff events, and found that losses increased as soil moisture increased (higher soil moisture caused increased runoff volumes), but all losses were 1.2% or less. Cole et al. (1997) also found this

soil moisture effect in trials for 2,4-D, chlorpyrifos, dicamba and mecoprop, with maximum losses of up to 10%.

Wu et al. (2002a,b) found low cumulative leaching of metalaxyl, chlorothalonil, chlorpyrifos and trichlorfon. Gardner and Branham (2001a) found no ethofumesate below the first 10 mm of soil under thatch, and indicated that leaching was greatly reduced by turf. Sears and Chapman (1979) found that even with low amounts of thatch, very little chlordane, chlorpyrifos or diazinon moved through the foliage and thatch into the soil. They also found less than 2% of isazofos and less than 3% of chlorpyrifos in underlying soil and concluded that downward movement through the turf was minimal. Branham et al. (1993) found that cumulative leaching of isazofos was less than 1%. Frederick et al. (1996) found little vinclozolin in the soil, and none beyond 40 mm deep. Sears et al. (1987) found only trace amounts of diazinon in the soil, while Thompson et al. (1984) recovered less than 1% of applied 2,4-D from the soil.

From these experiments it appears that runoff losses may be considerable in the first few days after application, but decrease shortly thereafter. Little pesticide seems to leach from soil under well established turf (dense foliage and a layer of thatch), and appears to be mostly retained and degraded in the thatch or top layers of soil. Petrovic and Larsson-Kovach (1996) provided evidence that soluble pesticides such as mecoprop can leach in large amounts (cumulatively up to 62% over 4 months) under immature stands of turf (recently seeded, no thatch layer), rapidly draining root media (sand) and high irrigation. In a repeated experiment 3 years later, the authors found a 10 fold decrease in mecoprop leaching, and attributed the difference to turf density and surface vegetative biomass. Results from immature turf should be regarded as extreme, with the more general case being high retention in thatch, and

runoff and leaching losses on the order of 10% or less. The extreme case does, however, indicate potential for high losses when the turf is being established.

Pesticide losses via volatilization, photolysis and removal of clippings

Strong adsorption may reduce volatilization (Hornsby et al. 1996), but retention to foliage has the potential to increase photolysis and removal in clippings. Many studies have found the latter two losses to be minimal (<1%), but a few have reported significant losses.

Wu et al. (2002a,b) found minimal volatilization for chlorothalonil, metalaxyl and trichlorfon, but a cumulative loss of 2 - 2.7% for chlorpyrifos. Racke et al. (1993) indicate that volatilization may be important for chlorpyrifos dissipation from foliage. Gardner and Branham (2001b) indicate that volatilization may have been important for the dissipation of mefenoxam, but not for propiconazole in their experiments. Branham et al. (1993) found no volatilization of DCPA, but a cumulative loss of 2-5% for isazofos. Sears et al. (1987) indicated that volatilization was not a major factor for diazinon dissipation. Frederick et al. (1996) estimated that volatilization loss of vinclozolin was about 0.35%. Haith et al. (2002) reported mean volatilization losses (based on several experiments for each pesticide) of 0.28% for carbaryl, 0.81% for trichlorfon, 1.53% for isofenphos, 1.63% for bendiocarb. On the other hand, Cooper et al. (1990) found 13% loss of pendimethalin via volatilization over 5 days, while Murphy et al. (1996 a,b) found 8% volatilization for triadimefon and 12% for trichlorfon and isazofos within 7 d after application. Haith et al. (2002) reported mean volatilization losses 8.25% for chlorpyrifos, 10.3% for isazofos, 10.5 for diazinon, and 15.2% for ethoprop. The highest volatilization loss reported by Haith et al. (2002) for any individual experiment was 22.2% (for ethoprop).

Estimations of loss due to photolysis are scarce. Cooper et al. (1990) attributed a 10% loss of pendimethalin to exposure to unshielded light, and indicated that this may be a primary route for dithiopyr degradation on turf. Stahnke et al. (1991) attributed a 6% loss of pendimethalin in 6h after application to a combination of photodegradation and volatilization. Sigler et al. (2003) indicated that photodegradation may be important for triadimefon, metalaxyl and vinclozolin. On the other hand, Frederick et al. (1996) estimated that vinclozolin loss due to photodegradation was minimal in their experiments. Published photodegradation half-lives for the pesticides examined in detail later in the chapter (which are presented in Table 2.2) indicate that photodegradation may be an important in the dissipation of diazinon, ethofumesate, iprodione, metalaxyl and trichlorfon.

Clippings do not seem to contribute importantly to pesticide removal. For example, Wu et al (2002 a,b) found less than 0.3% removal for chlorothalonil, metalaxyl, chlorpyrifos and trichlorfon. Cisar and Snyder (1996) found less than 1% of chlorpyrifos, isazofos, isofenphos and ethoprop in clippings, but indicate that losses may be higher (up to 8% of chlorpyrifos) when the pesticides are applied in granular rather than liquid form.

Mass balances for pesticides applied to turf

Few studies allow the construction of detailed mass balances in order to determine major dissipation pathways of pesticides applied to turf. Wu et al. (2002 a,b) measured volatilization and leaching losses, as well as turf and soil pesticide concentrations. The plots were flat and runoff was not observed. Volatilization and leaching losses were small, as were the amounts of pesticide recovered from the soil. Metalaxyl, chlorothalonil, trichlorfon and chlorpyrifos all degraded rapidly in the turf layer and in the complete (turf + soil) system. Half-lives based on the mass balances

for the complete turf and soil system were: 3.4 d for metalaxyl, 4.1 d for chlorothalonil, 3.3 to 4.1 d for trichlorfon and 6.5 to 7 d for chlorpyrifos. First order models fit the observed dissipation well in all cases.

With the mass balances accounting for transport from the site (runoff, leaching, volatilization and removal in clippings), the remaining dissipation processes are degradation on site, including photodegradation, hydrolysis and other chemical reactions, and microbial activity in the thatch and soil. Metalaxyl and trichlorfon are metabolized in plants, but chlorothalonil and chlorpyrifos are not (Tomlin 2003), so plant uptake and enzymatic breakdown does not fully explain the rapid dissipation rates. Photolysis half-lives for these pesticides (13.9 d for metalaxyl, 365 d for chlorothalonil, and 11.7 d for trichlorfon, ARS 2006) are not small enough to account for the rapid decay either. The half-lives based on the mass balances are also considerably smaller than those for aerobic decay in soil (40 d for metalaxyl, 48 d for chlorothalonil, 6.4 d for trichlorfon, and 30.5 d for chlorpyrifos, ARS 2006). Since most of the pesticides were recovered from the foliage and thatch layer, it follows that this is where most of the pesticide dissipation occurred, and that it was most likely due to rapid microbial decay in these layers.

Branham et al. (1993) provide mass balance information for isazofos using model ecosystems. Cumulative leaching was 1-2%, and runoff did not occur due to the system's design. Volatilization occurred for 4 days after application and accounted for 3-5% of the initial mass. The dissipation half-lives for the turfed systems were 6 – 8.2d. The aerobic soil half-life for isazofos is 40.5d (ARS 2006). The authors found that isazofos degraded 2-3 times quicker in turf than bare soil treatments. Most of the labeled ¹⁴C isazofos was recovered as a metabolite and as unextractable residues in the soil. This was attributed to more active microbial biomass in the turf treatments, and

indicates that the main dissipation route was microbial decay in the turf and top layer of soil.

Microbial decay of pesticides in turf

From the review above, microbial decay (the aerobic and anaerobic oxidation and reduction of pesticides by microbial populations to produce energy) appears to be an important route of pesticide dissipation from turf. Adding to this evidence, microbial decay of pesticides in turf is expected to be faster than decay in soil for two reasons. First, turf foliage and thatch provide an environment that can sustain highly active microbial populations (Branham et al. 1993, Cole and Turgeon 1978, Gardner and Branham 2001a, Gardner et al. 2000 and Horst et al. 1996,). Raturi et al. (2004) found that total microbial biomass was on average 10 times greater in thatch than in the underlying soil. They also found that basal respiration (a measure of microbial activity) was greater in thatch than soil, and concluded that thatch provides a more suitable environment for microbes. As microbial populations degrade pesticides as a source of energy, larger and more highly active microbial populations would lead to a more rapid decay of the pesticides retained in the turf layer.

Second, turf is frequently subjected to repeated applications of pesticides. Management strategies include several applications per year, and continue for long periods of time as turf areas remain relatively unaltered in the landscape. Repeated applications have resulted in enhanced degradation (whereby a pesticide is degraded more rapidly than usual by microorganisms) in turf and soil for several pesticides (Niemczyk and Chapman 1987, Sigler et al. 2000). Enhanced degradation is especially evident in the experiments of Frederick et al. (1996), where repeated applications caused a significant increase in degradation rates. This phenomenon results from an

increase in number of the fraction of the microbial population that can use the pesticide as a source of energy (Niemczyk and Chapman 1987, Sigler et al. 2000).

With large amounts of the pesticide retained in the foliage and thatch, where large, highly active and adaptable microbial populations reside, one would expect to find faster pesticide decay in turf than in soil.

Estimation of pesticide half-lives for turf

In this section, pesticide dissipation rates from turf are reviewed, and these values are taken to be representative of microbial decay rates by assuming that turf foliage and thatch retain most of the pesticide, and that microbial decay predominates over other dissipation process in the combined foliage and thatch layer. For modeling purposes, foliage and thatch are treated as one lumped computational layer; only pesticide transfer in and out of the entire layer is accounted for. Additionally, if microbial decay is the dominant dissipation process, it may cause other dissipation processes to appear to follow first order behavior, as noted above for volatilization and runoff.

While some of the studies reviewed reported pesticide dissipation rates or half-lives, others only provided the amounts of pesticide observed in the turf over time. In these cases, dissipation rates were calculated by fitting exponential functions of the form:

$$C_t = C_0 e^{-kt} \quad [2.1]$$

in which C_t is the amount of pesticide at time t after application, C_0 is the amount of pesticide present in the turf fraction immediately after application, and k is the dissipation rate of the pesticide.

Exponential functions generally fit pesticide amounts in the diverse turf fractions (foliage and/or thatch) well ($R^2 > 0.8$). In some cases, the initial dissipation

was too rapid to be adequately fit with Eq. [2.1]. Biphasic exponential models gave better fits to these data (also noted by Frederick et al. 1994). In order to be consistent, however, only half-lives based on rates from Eq. [2.1] were considered in the analysis. Half-lives were derived from dissipation rates as: Half-life (d) = $\ln(2) / k$ (d^{-1}).

In reviewing the studies, it was apparent that diverse methodologies were used to examine pesticide persistence in turf. Some studies sampled turf foliage, thatch and soil and analyzed the total amount of pesticide in each layer, while others only examined the persistence of residues that were physically dislodgeable from the foliage. Dislodgeable residues are of interest in reentry exposure studies, but they do not represent total pesticide residues in the foliage (portions of which can be found adsorbed to or within the leaves), and they are susceptible to washoff by rain and irrigation (Kuhr and Tashiro 1978, Thompson et al. 1984). Thus, they do not provide reliable data on which to base degradation rates, and were not included in the estimation of turf half-lives.

In most cases, several half-lives were reported or calculated for each pesticide. These were summarized by taking an average for each pesticide. For some of the pesticides, the average was heavily affected by one large half-life value arising from experimental conditions encountered in a specific trial. To compensate for this, half-life values for each pesticide were also summarized by taking the median. This process resulted in half-life values for 25 pesticides, of which 18 are currently registered for use on turf (Vance Communication Corporation 2006).

For comparison purposes, half-lives for turf were contrasted with aerobic soil half-lives from the ARS Pesticide Properties Database (ARS 2006) and from The Pesticide Manual (Tomlin 2003). Photolysis rates on soil were converted to half-lives and included in the comparison. Field dissipation half-lives from the ARS PPD (ARS

2006) were also included as they encompass all pathways of pesticide disappearance and provide a comparison to the turf specific dissipation values.

Pesticide dissipation half-lives for turf

Dissipation half-lives for turf are summarized in Table 2.1. The type of study briefly indicates if the analyses were based on the pesticide found on foliage or in thatch, and if dislodgeable residues or the total amount of pesticide remaining was measured.

Of the 25 pesticides presented in Table 2.1, 18 are currently registered for use on turf (Vance Communication Corporation, 2006). Half-life values for these pesticides, as well as aerobic soil, photolysis and field dissipation half-lives are presented in Table 2.2.

As shown in Tables 2.1 and 2.2, half-lives for some pesticides show a wide range of values because one or a few values that are much higher than all others. For this reason, it is suggested that pesticide half-lives for turf be based on the median of the individual half-life values (shown in the third column of Table 2.2).

Based on the values in Table 2.2, photolysis may explain rapid dissipation of some of the pesticides from turf (such as diazinon, ethofumesate and iprodione), but does not provide an explanation for the rapid decay rates of the other pesticides. Additionally, photolysis is likely to affect pesticides on the surface of the leaves, but dense foliage should protect pesticides retained in the thatch from the sunlight necessary for this mechanism of decay.

Table 2.1 Pesticide dissipation half-lives for different turf systems.

Pesticide	Chemical name	Half-life (d)†	Type of study	Reference
2,4-D	2,4-Dichlorophenoxy-acetic acid	2.6 (1 – 24.9) n=9	Foliage, dislodgeable and total residues	Bowhey et al. 1984
2,4-D		1.5 (1 – 39.6) n=8	Foliage and thatch, dislodgeable and total residues	Thompson et al. 1984
Benefin	N-butyl-N-ethyl-a,a,a-trifluoro-2,6-dinitro-p-toluidine	61.6 n=1	Lab incubation of thatch, total residues	Hurto et al. 1979
Carbendazim	1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene idazole-2-ylcarbamate	17.5 n=1	Lab bioassay using thatch, total residues	Liu and Hsiang 1996
Chlordane	1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene	76.2 n=1	Foliage and thatch, total residues	Sears & Chapman 1979
Chloroneb	1,4-dichloro-2,5-dimethoxybenzene	39 (8.7 – 69.3) n=4	Lab incubation of foliage and thatch, total residues	Frederick et al. 1994
Chlorothalonil	2,4,5,6-tetrachloro-1,3-benzenedicarbo-nitrile	4.5 (2.2 – 5.6) n=4	Foliage and thatch total residues, complete system mass balance, and lab incubation of thatch	Wu et al. 2000a
Chlorpyrifos	O,O-diethyl O-3,5,6-trichloro-1-hydroxy-ethylphosphonate	7 (6.4 – 247.6) n=5	Foliage and thatch total residues, complete system mass balance, and lab incubation of thatch	Wu et al. 2000b

Table 2.1 (Continued).

Pesticide	Chemical name	Half-life (d)†	Type of study	Reference
Chlorpyrifos		9.5 (6 – 12) n=4	Foliage, thatch and soil, total residues	Horst et al. 1996
Chlorpyrifos		14.7 n=1	Foliage and thatch, total residues	Sears and Chapman 1979
Chlorpyrifos		7.2 (5.7 – 8.6) n=2	Foliage, thatch and soil, total residues	Racke et al. 1993
Chlorpyrifos		3.6 (3.3 – 3.8) n=2	Foliage, dislodgeable residues	Hurto and Prinster 1993
Chlorpyrifos		9.7 (8.6 – 10.6) n=4	Foliage, total residues	Kuhr and Tashiro 1978
Chlorpyrifos		6.1 (3.2 – 7.1) n=3	Foliage, dislodgeable and total residues	Lemmon and Pylypiw 1992
Chlorpyrifos		6.4 (1 – 11.8) n=2	Thatch, total residues	Sears et al. 1987
Cyproconazole	1,2,4-triazole-1-ethanol	10 n=6	Foliage and thatch, total residues	Gardner et al. 2000
DCPA	Dimethyl 2,3,5,6-Tetrachloro- terephthalate	5.6 (5.1 – 6) n=2	Foliage, dislodgeable residues	Hurto and Prinster 1993

Table 2.1 (Continued).

Pesticide	Chemical name	Half-life (d)†	Type of study	Reference
DCPA		225.7 (61.9 – 577.6) n=6	Foliage, thatch and soil, complete mass balance	Branham et al. 1993
DCPA		37.8 n=1	Lab incubation of thatch	Hurto et al., 1979
Diazinon	O,O-Diethyl O-(2-isopropyl-4- methyl-6-pyrimidinyl) thiophosphoric acid	2.6 n=1	Foliage and thatch, total residues	Sears and Chapman 1979
Diazinon		2.4 (2.3 – 2.5) n=2	Foliage, dislodgeable residues	Hurto and Prinster 1993
Diazinon		6.1 (5.3 – 6.9) n=4	Foliage, total residues	Kuhr and Tashiro 1978
Diazinon		2.6 (2.6 – 4.1) n=3	Foliage, total residues	Lemmon and Pylypiw 1992
Diazinon		1.6 (0.8 – 5.4) n=20	Dislodgeable and residues on various fractions of leaves and thatch	Sears et al. 1987
Dicamba	2,5-Dichloro-6-methoxybenzoic acid	1.6 (1.2 – 2) n=2	Foliage, dislodgeable residues	Bowhey et al. 1987
Dithiopyr	Dimethyl 2-(difluoromethyl)-4-(2- methylpropyl)-6-(trifluoromethyl)- 3,5-pyridinedi-carbothioate	5.8 (3.6 – 9) n=17	Dislodgeable, surface and total residues on foliage	Cowell et al. 1993

Table 2.1 (Continued).

Pesticide	Chemical name	Half-life (d)†	Type of study	Reference
Dithiopyr		5.9 (4.3 – 7.4) n=2	Foliage, total residues	Schleicher et al. 1995
Ethofumesate	(±)-2-ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl methanesulfonate	3 n=1	Foliage, thatch and soil, total residues	Gardner and Branham 2001a
Halofenozide	N-4-chlorobenzoyl-N-benzoyl-N-tert-butylhydrazine	64 n=1	Foliage, thatch and soil, total residues	Gardner and Branham 2001a
Iprodione	3-[3,5-dichlorophenyl]-N-isopropyl-2,4-dioximidizolidine-1-carboximide	3.6 n=1	Foliage, total residues	Sigler et al. 2003
Isazofos	O-(5-chloro-1-(1-methylethyl)-1H-1,2,4-triazol-3-yl) O,O-diethyl phosphorothioate	6.5 (5 – 11) n=4	Foliage, thatch and soil, total residues	Horst et al. 1996
Isazofos		14.7 (12.6 – 26.1) n=5	Thatch, total residues	Niemczyk and Krueger 1987
Isazofos		7.1 (6 – 8.2) n=2	Foliage, thatch and soil, complete mass balance	Branham et al. 1993
Isofenphos	2-[[Ethoxyl[(1-methylethyl)amino]phosphinothioyl]oxy]benzoic acid 1-methylethyl ester	4.1 (3.8 – 4.3) n=2	Foliage, dislodgeable residues	Hurto and Prinster 1993
Isofenphos		3.1 (2.3 – 5) n=3	Foliage, total residues	Lemmon and Pylypiw 1992

Table 2.1 (Continued).

Pesticide	Chemical name	Half-life (d)†	Type of study	Reference
Isofenphos		9.7 (1.1 – 18.2) n=2	Foliage and thatch, dislodgeable and total residues	Sears et al. 1987
Mecoprop	2-(2-Methyl-4-chlorophenoxy) propionic acid	1 (0.8 – 1.2) n=2	Foliage, dislodgeable residues	Bowhey et al. 1987
Mefenoxam	N-(2,6-dimethylphenyl)-N- (methoxyacetyl)-D-alanine methyl ester	5.5 (5 – 6) n=2	Foliage, thatch and soil, total residues	Gardner and Branham 2001b
Metalaxyl	Methyl N-(methoxyacetyl)-N-(2,6- xylyl)-DL-alaninate	3.1 (1.4 – 110) n=4	Foliage and thatch total residues, complete system mass balance, and lab incubation of thatch	Wu et al. 2000a
Metalaxyl		13.5 (10 – 25) n=4	Foliage, thatch and soil, total residues	Horst et al. 1996
Metalaxyl		3.7 n=1	Foliage, total residues	Sigler et al., 2003
Metalaxyl		4.6 n=1	Foliage, total residues	Taylor 1996, cited by Sigler et al. 2003
Pendimethalin	N-(1-Ethylpropyl)-3,4-dimethyl- 2,6-dinitrobenzenamine	15 (6 – 15) n=4	Foliage, thatch and soil, total residues	Horst et al. 1996
Pendimethalin		2.2 (2.1 – 2.3) n=2	Foliage, dislodgeable residues	Hurto and Prinster 1993

Table 2.1 (Continued).

Pesticide	Chemical name	Half-life (d)†	Type of study	Reference
Pendimethalin		5.7 (4.4 – 6.9) n=2	Foliage, total residues	Schleicher et al. 1995
Pendimethalin		8.1 (7 – 9.2) n=2	Foliage, total residues	Stahnke et al. 1991
Pendimethalin		7.6 (5.1 – 10.7) n=10	Foliage, total residues	Gasper et al. 1994
Pendimethalin		5.5 (3.4 – 7.3) n=3	Foliage, total residues	Lemmon and Pylypiw 1992
Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole	13.5 (12 – 15) n=2	Foliage, thatch and soil, total residues	Gardner and Branham 2001b
Triadimefon	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butanone	3.3 n=1	Foliage, total residues	Sigler et al., 2003
Triadimefon		1.6 n=1	Foliage, total residues	Taylor 1996, cited by Sigler et al. 2003
Triadimefon		7.2 (2 – 11.6) n=4	Lab incubation of foliage and thatch	Frederick et al. 1994
Trichlorfon	O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate	3.3 (1 – 6) n=5	Foliage and thatch total residues, complete system mass balance, and lab incubation of thatch	Wu et al. 2000b

Table 2.1 (Continued).

Pesticide	Chemical name	Half-life (d)†	Type of study	Reference
Vinclozolin	3-(3,5-dichloro-phenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione	10.8 (7.7 – 13.9) n=4	Lab incubation of foliage and thatch	Frederick et al. 1994
Vinclozolin		1.9 (1 – 63) n=24	Foliage and thatch, total residues	Frederick et al. 1996

† Half lives are given as the median value, range in parenthesis, and n is the number of half-life values derived from each study for a particular pesticide.

Table 2.2. Comparison of half-lives for pesticides registered for use on turf.

Pesticide	Turf dissipation (d)		Aerobic in soil (d)		Photolysis on soil (d)†	Field dissipation (d)		
	Average	Median	ARS†	Tomlin‡		Min. †	Avg. †	Max. †
2,4-D	27.5	24.9	5.5	7.0	69.3	4.0	14.0	15.0
Benefin	61.6	61.6	51.0	35.8		24.0	80.0	131.0
Chlorothalonil	4.2	4.5		14.2	365.0§	2.0	48.0	90.0
Chlorpyrifos	20.5	8.7	30.5	40.2		4.0	43.0	139.0
Diazinon	3.4	2.6	39.0	16.0	4.6	2.8	7.0	13.0
Dicamba	1.6	1.6	18.0	14.0	198.0	8.0	16.0	25.0
Dithiopyr	6.7	7.0		39.0				
Ethofumesate	3.0	3.0	143.0	155.8	6.9	20.0	80.0	150.0
Halofenozide	64.0	64.0		426.8		42.0‡	154.5‡	267.0‡
Iprodione	3.6	3.6	50.0	70.0	4.2		7.0	
Mecoprop	1.0	1.0		10.0			21.0	
Mefenoxam	5.5	5.5		21.0				
Metalaxyl	18.8	7.3	40.0	29.0	13.9	27.0	77.0	296.0
Pendimethalin	8.6	7.4	1300.0	105.0		8.0	174.0	480.0
Propiconazole	13.5	13.5	53.0	49.5	138.6	109.0	115.0	123.0
Triadimefon	5.5	4.5	6.0	12.0	86.6	6.0	54.0	95.0
Trichlorfon	3.1	3.3	6.4		11.7	1.0	1.5	2.2
Vinclozolin	7.4	2.3				3.0	14.0	75.0
Median	6.1	5.0	39.5	32.4	41.6	7.0	45.5	109.0
Mean	14.4	12.6	145.2	65.3	89.9	18.6	56.6	135.8
Max	64.0	64.0	1300.0	426.8	365.0	109.0	174.0	480.0
Min	1.0	1.0	5.5	7.0	4.2	1.0	1.5	2.2

Sources: Average and median turf half-lives were estimated based on data in Table 2.1.

† ARS PPD (2006). ‡ The Pesticide Manual (Tomlin 2003). § Pesticide reported as stable to photolysis. A half-life of 1 year was assumed. Blank entries denote no available information.

In Table 2.2, the minimum field dissipation rates are similar to the turf half-lives (median values of 7 and 5 d, respectively), indicating that the microbial decay rates found for turf are not unreasonable, considering that microbial decay is a major pathway of pesticide dissipation, especially in systems that can sustain large, active microbial populations over time, such as turf.

No significant linear or non-linear relationships were found between the turf half-lives and the ARS values in Table 2.2. An R^2 of 0.35 was found between Tomlin's values and the turf half-lives, but was not strong enough to use in estimating default turf half-life values as it was driven by the high half-life values of ethofumesate and halofenozide.

It should be noted that the turf half-lives for benefin and halofenozide are much larger than those of the other pesticides. For benefin, the ARS soil half-life is 51 d, while Tomlin (2003) gives values of 19.6 to 52 d. The value of 61.6 d found for turf arose from a lab incubation study (Hurto et al. 1979). Several other lab incubation studies were found to produce half-lives that were considerably longer than those based on field observations, possibly because some factors present in the outdoor environment were missing (Wu et al 2000a, Wu et al 2000b, Branham et al. 1993). However, these values were included in the analysis for lack of other data regarding the pesticide. In the case of halofenozide, Tomlin (2003) gives a half-life of 3 to 77 d for turf. This suggests that the value of 64 d found by Gardner and Branham (2001a) may be close to the upper limit for turf half-life, and may have resulted from particular conditions occurring during the experiment (the authors mention that rainfall occurred shortly after application which moved the pesticide rapidly into the soil).

The turf half-life for 2,4-D (24.9 d) is the only case in which the turf half-life is longer than the published aerobic soil half-life. This turf half-life is at the upper end of turf half-lives of 1 to 3 weeks, cited by Thompson et al. (1984). The turf half-life value

of 24.9 d is based on 2 field studies, and there is no indication that particular circumstances extended 2,4-D persistence.

Changes in pesticide characteristics are evident when the pesticides in Table 2.2 are contrasted with those that were eliminated from the analysis as they are no longer registered for use on turf (carbendazim, chlordane, chloroneb, cyproconazole, DCPA, isazofos and isofenphos). Unregistered pesticides had a median turf half-life of 17.5 d, with a range between 7.2 and 244.9 d, illustrating the shift towards less persistent pesticides in order to reduce environmental and human health risks.

Use of turf dissipation rates in modeling pesticide decay

Pesticide dissipation rates could be used to represent microbial decay rates in turf by assuming that turf foliage and thatch retain most of the pesticide, and that microbial decay predominates over other dissipation process in the foliage and thatch layers. However, this assumption may not be valid for all pesticides and turf conditions. While most of the field studies reviewed found pesticide transport (runoff, leaching and volatilization) to be on the order of 10% or less, some cases indicated much higher losses. Pesticides that are not strongly retained to the organic matter in turf foliage and thatch are more susceptible to transport processes. Additionally, turf conditions can strongly affect pesticide fate. As illustrated by the findings of Petrovic and Larsson-Kovach (1996), immature turf retains little pesticide. In addition to this, recently established turf may not have fully developed microbial populations that have not had time to adapt to using the pesticide as a source of energy, so that the effect of microbial decay may be less than in fully established turf and making enhanced degradation unlikely to occur until later in the turf system's life when repeated applications of the same pesticide have occurred.

In situations where the turf dissipation rates are unlikely to be valid representations of microbial decay rates, it may be best to use the more conservative soil aerobic microbial decay rates to model microbial decay in turf systems.

CONCLUSIONS

From the literature review, there appears to be considerable evidence that microbial decay is the major pathway of pesticide dissipation in turf. Further analysis of dissipation studies from turf produced a set of half-lives that was previously unavailable, and which demonstrates that pesticide dissipation is considerably faster in well established turf than in soil. Use of these turf dissipation half-lives to represent microbial decay in simulation studies seems justified by evidence of large, highly active and adaptable microbial populations residing in the foliage and thatch layers of mature turf. However, care should be taken as these values are not likely to be representative of microbial decay for pesticides that are weakly sorbed to foliage and thatch, or in situations where the turf is not fully established and the microbial populations have not adapted to using the pesticide as a source of energy. It should be noted that immature stands of turf are likely to produce higher pesticide losses to the surrounding environment, and that risks of reentry in the first few days after application may be considerable.

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CHAPTER 3

PESTICIDE DECAY IN TURF: II. IMPLICATIONS FOR FATE AND TRANSPORT MODELING

Abstract

Decay rates are central parameters in modeling pesticide fate and transport in the environment. Pesticide decay is usually modeled as a first order process, and variations in half-life can have significant impacts on model predictions. Decay rates for turf are scarce, and most simulation efforts must resort to values based on pesticide behavior in soils. Aerobic soil decay rates from the USDA-ARS Pesticide Properties Database (ARS 2006) and from The Pesticide Manual (Tomlin 2003) were compared in Chapter 2. Impacts of using soil vs. turf half-lives in modeling are evaluated in this chapter by performing long term (100 year) simulations for six of the pesticides. Effects of climate and turf type were incorporated by simulating applications to three distinct turf types in four locations across the USA. When turf half-lives were used instead soil based values, predicted pesticide losses (pooled across all pesticides, locations and turf types) due to volatilization, runoff and infiltration decreased by 27%, 76%, and 54%, respectively, while the amount of pesticide decayed in the turf layer increased by 45%. Similar results were found when the median turf half life (5 d) was used in the simulations, suggesting that it may be a reasonable default half-life value for pesticides on turf.

INTRODUCTION

Turf is an intensively managed biotic system (Gardner et al. 2000, Wu et al 2002a) and can account for up to 80% of the pervious surfaces in urban areas, of

which approximately half may be subjected to high input management (Schueler 2000a). Annual pesticide application rates can be 3 to 8 times higher on golf courses, and 3 times higher on home lawns, than those for agricultural land (Kopell 1994, Schueler 2000b). Pesticide concentrations in water originating from urban areas and golf courses have been found to exceed environmental and drinking water standards (Cohen et al. 1999, US Geological Survey 1999). There is also concern regarding exposure to pesticides upon reentry to treated areas, especially for children using turf at schools yards and parks (Cowell et al. 1993, Hurto and Prinster 1993, Sears et al. 1987).

While monitoring studies provide valuable information, they are costly and it is often hard to extrapolate findings to other locations and conditions. Simulation models are frequently used in their stead to estimate pesticide loads to surface water, groundwater and the atmosphere. Most simulation studies rely on published pesticide property databases to obtain parameter values. This study examines pesticide decay in turf, which is generally modeled as an exponential function, and thus has the potential to significantly affect fate and transport assessments of a chemical in the environment.

Chapter 2 examined pesticide dissipation processes in turf. Decay rates were computed for 25 pesticides applied to turf and compared to published half-life values for aerobic decay in soil, photolysis and field dissipation. Based on this analysis, the hypothesis that the use of soil-based decay rates in fate and transport modeling may lead to overestimation of pesticide runoff, volatilization and leaching losses from turfgrass is developed. In this chapter, the hypothesis is tested by performing long-term simulations involving six pesticides, four geographic locations and three distinct turf types to account for variability in pesticide characteristics, climate and turf.

METHODS

Simulation model

For the purpose of testing the hypothesis, two models that were developed and tested for pesticides applied to turf were combined. The pesticide runoff model TurfPQ (Haith, 2001) predicts pesticide loss via runoff from turf, infiltration to the underlying soil and the amount of pesticide decayed in the turf layer. TurfPQ was integrated with a pesticide volatilization model formulated by Walden and Haith (2003) based on the Hargreaves-Samani equation for potential evapotranspiration. Both models operate on daily time steps.

Independently, both models have been shown to perform well without calibration. TurfPQ's performance was assessed for 6 pesticides applied at 5 study sites located in four states, and achieved an R^2 of 0.65 (Haith 2001) between the simulated and observed pesticide runoff values. The pesticide volatilization model's performance was tested for 8 pesticides, achieving an R^2 of 0.67 (Walden and Haith 2003). The combined model was re-tested, but very little difference in the performance was found, meaning that losses due to runoff and volatilization can be estimated by combining both models without significant loss in precision.

Parameters required to describe each study site in the combined model are as follows: a CN2 runoff curve number based on turf and soil conditions; organic carbon content of the turf vegetation and thatch layer (kg/ha); dates and amounts of the pesticide applied to the turf (g A.I./ha); site latitude; and a monthly indicator to denote growing and dormant seasons. Parameters needed to characterize the pesticides are: half-life (d); organic carbon partition coefficient (K_{oc} , cm^3/g); molecular weight; vapor pressure (kPa) and the temperature at which it was measured ($^{\circ}\text{C}$); and the state of the pesticide as applied to the turf (solid or liquid). Values for each of these parameters are described in the following sections.

Simulation scenarios

In order to account for the vast differences between pesticides, geographic locations and types of turf, simulations for combinations of six pesticides applied to three turf types located in four cities dispersed across the U.S. were performed.

Pesticides

Six pesticides commonly applied to turf were selected for the simulation analysis. They were chosen in order to have a wide range of key properties in determining losses in runoff, volatilization and infiltration (half-life, Koc and vapor pressure). Chemical characteristics of the six pesticides are presented in Table 3.1.

Table 3.1. Pesticide chemical characteristics.

Pesticide	Type	Median turf half-life (d)†	Soil aerobic half-life (d)	Koc (cm ³ /g)	Vapor Pressure (kPa, 25°C)	Molecular weight
Chlorothalonil	Fungicide	4.5	48	5000	7.60E-08	265.9
Chlorpyrifos	Insecticide	8.7	31	9930	2.50E-06	350.6
Dicamba	Herbicide	1.6	18	10	1.66E-06	221.0
Pendimethalin	Herbicide	7.4	1300	13400	1.20E-06	281.3
Propiconazole	Fungicide	13.5	53	650	5.60E-08	342.2
Trichlorfon	Insecticide	3.3	6	15	5.00E-07	257.4

Source: ARS PPD (2006) unless otherwise noted.

† Calculated median half-lives for turf.

Locations

Four locations were selected: Albany NY, Atlanta GA, Fresno CA and Olympia WA. Albany and Olympia have temperate climates, but their rainfall distribution is significantly different, occurring mostly in the dormant season in Olympia. Atlanta represents humid climate, while Fresno has a dry climate in which turf is heavily

dependent on irrigation during the growing season. Characteristics for each location are summarized in Table 3.2.

Table 3.2. Location characteristics.

Location	Mean Annual Precipitation (mm)	Mean Temperature (°C)	Growing Season
Albany NY	980	8.6	May-Sep
Atlanta GA	1275	16.7	Apr-Oct
Fresno CA	285	17.3	Mar-Nov
Olympia WA	1290	9.8	May-Oct

Source: NOAA (2006).

Turf types

Conditions of the turf can also vary greatly and were incorporated in the analyses by simulating pesticide applications to home lawns, golf course fairways and golf course greens. To parameterize the model, vegetation height and thatch thickness are necessary (in order to estimate the organic carbon content of the turf layer), as is a runoff curve number based on turf and soil characteristics. These are summarized in Table 3.3.

Table 3.3. Turf characteristics.

Turf Type	Vegetation height (mm)	Thatch thickness (mm)	Soil Hydrologic Group	Runoff Curve Number	Organic Carbon (kg/ha)
Home Lawn	58	10	C	64	15,000
Golf Fairway	11	8	C	67	10,200
Golf Green	3.5	5	A	35	6,000

Vegetation heights and thatch depths for golf course turf are taken from Haith and Rossi (2003). For home lawns, vegetation height is an average of recommended values for warm and cool season turf from Provey (2002), and lawn thatch thickness is

the recommended value by Harivandi (1984). Soil hydrologic group C was selected for home lawns and golf course fairways as a mid-range condition of infiltration and runoff, while group A was chosen for greens as they are usually constructed of sand and artificially drained. Runoff curve numbers for the three turf-soil conditions are taken from Haith and Andre (2000). Organic carbon values are based on default organic matter contents developed by Haith (2001).

Pesticide applications

Application rates for each pesticide were derived by selecting mid-range label values and converting them to grams of active ingredient applied per hectare. The pesticides were applied as liquid sprays in all the simulations. The number of applications of each pesticide was determined by Haith and Duffany (2007), based on state recommendations, state use surveys and case studies. Application rates and number of applications for each turf type are summarized in Table 3.4.

Table 3.4. Pesticide application rates and frequencies.

Pesticide	Rate per Application (g A.I./ha)	Number of applications per year		
		Lawns	Fairways	Greens
Chlorothalonil	9350	0	5 – 13	5 – 13
Chlorpyrifos	1120	0	4 – 6	4 – 6
Dicamba	560	2	2	2
Pendimethalin	1940	1	1	1
Propiconazole	550	2	3	3
Trichlorfon	7570	1	0	4 – 6

Weather

Weather is a main driving mechanism for pesticide runoff, infiltration and volatilization. In order to create a representative dataset and allow accurate

comparisons of the effects of variations in half life values, long term (100-year) simulations were based on artificially generated weather sequences for each of the four locations. The USCLIMATE weather generator (Hanson et al. 1994) was used to produce daily rainfall, and maximum and minimum air temperatures.

Irrigation was added during the growing season by comparing potential evapotranspiration (PET) computed using the Hargreaves-Samani equation (as described by Jensen et al. 1990) with rainfall over 3-day periods. If PET exceeded rainfall during the 3-day period, the deficit was added on the third day as irrigation.

RESULTS

Overall Pesticide Fate

Annual losses (expressed as % of the applied amounts to allow for comparisons between pesticides) from the turf layer due to volatilization, runoff, infiltration and decay were pooled over all pesticides, turf types and locations. Overall means for model estimates for all six pesticides generated by using the ARS, turf and median turf half-lives were then compared, and are shown in Table 3.5.

Table 3.5. Overall mean losses for six pesticides.

Location	Half life	Volatilization (%)	Runoff (%)	Infiltrated (%)	Degraded on turf (%)
Albany	ARS	1.9	0.2	41.7	55.6
Albany	Turf	1.3	0.0	20.9	77.8
Albany	Med. Turf	1.3	0.0	24.9	73.8
Atlanta	ARS	2.3	0.5	45.5	51.1
Atlanta	Turf	1.7	0.2	21.7	76.4
Atlanta	Med. Turf	1.6	0.2	25.2	73.0
Fresno	ARS	2.3	0.0	44.0	53.1
Fresno	Turf	1.8	0.0	19.6	78.6
Fresno	Med. Turf	1.6	0.0	23.7	74.8
Olympia	ARS	1.4	0.2	41.6	56.1
Olympia	Turf	1.0	0.0	18.1	80.9
Olympia	Med. Turf	1.0	0.0	22.6	76.4
Mean	ARS	2.0	0.2	43.2	54.0
Mean	Turf	1.5	0.1	20.0	78.4
Mean	Med. Turf	1.3	0.1	24.1	74.5
% Change	ARS to Turf†	-26.8	-75.5	-53.6	45.3
% Change	ARS to Med. Turf	-33.3	-75.6	-44.2	38.0
% Change	Turf to Med. Turf	-8.8	-0.3	20.2	-5.0

† % Change was calculated as: (Mean ARS - Mean Turf) / Mean ARS * 100

Mean losses are similar for all sites, but differences in using ARS, turf and median of the turf half-lives are apparent. Turf and median turf half-lives produce considerably reduced estimates of pesticide loss via volatilization, runoff and infiltration. This is due to the considerable increase in the amount of pesticide decayed in the turf layer. Overall, turf and median turf half-lives produced similar estimates of loss, except for infiltration, where the median of the turf half-lives resulted in 20% more infiltration than the turf half-lives.

Also, it appears from the infiltration percentages that the simulations based on turf half-lives are more in accordance with the low infiltration amounts found in the field studies cited in Chapter 2 (most of which reported leaching losses of 5% or less).

Mean Annual Losses

Mean annual losses are contrasted in Table 3.6. Results for each pesticide are ordered in rows as arising from using: the aerobic soil half-life, the turf half-life and the median of the turf half-lives. Pesticide masses were converted to percentages of the annual application to allow for comparisons between pesticides. Mean annual results were statistically compared using Fisher's protected Least Significant Difference (LSD).

Significant decreases in loss via runoff, volatilization and infiltration exist for all pesticides. The exception is trichlorfon runoff, and is probably due to the three half-lives being similar and runoff losses being minor. While changes in losses via runoff and volatilization for all pesticides are relatively small, large changes in the amount of pesticides infiltrating the soil are evident in the results, and are likely to have significant impacts on the estimates of turf-applied pesticides leaching into groundwaters.

Table 3.6. Mean annual pesticide losses.

Pesticide	Half-life (d)	Volatilization (%)	Runoff (%)	Infiltrated (%)	Degraded on turf (%)
Chlorothalonil	48	0.22 a	0.07 a	8.10 a	91.52 b
Chlorothalonil	4.5	0.14 b	0.01 b	1.07 b	98.79 a
Chlorothalonil	5	0.14 b	0.01 b	1.13 b	98.73 a
<i>LSD (0.05)†</i>		<i>0.00</i>	<i>0.01</i>	<i>0.13</i>	<i>0.13</i>
Chlorpyrifos	31	9.80 a	0.02 a	2.63 a	87.52 c
Chlorpyrifos	8.7	7.74 b	0.00 b	0.81 b	91.44 b
Chlorpyrifos	5	6.45 c	0.00 b	0.53 c	93.03 a
<i>LSD (0.05)</i>		<i>0.23</i>	<i>0.00</i>	<i>0.05</i>	<i>0.25</i>
Dicamba	18	1.07 a	0.19 ab	88.33 a	10.41 c
Dicamba	1.6	0.44 c	0.12 c	47.63 c	51.81 a
Dicamba	5	0.82 b	0.16 bc	70.58 b	28.43 b
<i>LSD (0.05)</i>		<i>0.02</i>	<i>0.05</i>	<i>0.73</i>	<i>0.72</i>
Pendimethalin	1300	1.73 a	0.55 a	37.37 a	57.53 b
Pendimethalin	7.4	1.20 b	0.00 b	0.38 b	98.41 a
Pendimethalin	5	1.02 c	0.00 b	0.26 b	98.72 a
<i>LSD (0.05)</i>		<i>0.04</i>	<i>0.03</i>	<i>0.49</i>	<i>0.52</i>
Propiconazole	53	0.20 a	0.32 a	39.45 a	60.01 c
Propiconazole	13.5	0.17 b	0.09 b	15.69 b	84.05 b
Propiconazole	5	0.12 c	0.04 c	6.78 c	93.05 a
<i>LSD (0.05)</i>		<i>0.00</i>	<i>0.03</i>	<i>0.55</i>	<i>0.54</i>
Trichlorfon	6	0.51 a	0.12 a	65.50 a	33.87 c
Trichlorfon	3.3	0.40 c	0.10 a	52.93 c	46.57 a
Trichlorfon	5	0.48 b	0.12 a	62.73 b	36.67 b
<i>LSD (0.05)</i>		<i>0.02</i>	<i>0.07</i>	<i>1.01</i>	<i>1.00</i>

† Fisher's Least Significant Difference, $\alpha = 0.05$. For each pesticide and loss mechanism, means followed by the same letter are not significantly different at the 0.05 probability level.

Dicamba and trichlorfon show high infiltration rates. As pointed out in Chapter 2, pesticides that are not strongly retained in the turf foliage and that are more susceptible to infiltration into the soil. Organic carbon partition coefficients (K_{oc}) are 10 for dicamba and $15 \text{ cm}^3 \text{ g}^{-1}$ for trichlorfon, both of which are very low. Caution

should be exercised when modeling fate and transport of these pesticides as the microbial decay rates developed in Chapter 2 may not be valid as they are based on the assumption that microbial decay is the major avenue of dissipation, and that all other avenues of dissipation are relatively small. This is of more importance for dicamba, for which there is a large difference between the soil aerobic half-life and the turf half-lives, and of less importance for trichlorfon as all 3 half-lives are similar.

Annual mass balances were verified for each simulation. In cases where the ARS half-life values were used, small amounts of the pesticide carried over from one year to the next. For pendimethalin, however, the ARS half-life value of 1300 d caused significant carry-over, and simulations reached steady-state after 10 years. This was not corrected for as it constituted only 10% of the simulated data for this pesticide, and elimination of the first 10 years of data would have increased average losses via runoff, volatilization and infiltration, exacerbating the already significant differences between ARS and the turf and median turf half-life results.

CONCLUSIONS

Use of these turf half-lives developed in Chapter 2 to represent microbial decay in simulation studies is justified by evidence of large, highly active and adaptable microbial populations residing in the foliage and thatch layers of mature turf, which is where large amounts of the pesticides are retained and degraded. However, caution should be used for pesticides that have low Koc values, as the assumptions used in deriving the turf half-lives may not be met. This is of more importance for pesticides of low Koc that show large relative differences between the soil aerobic and the turf half-lives.

Simulation results for turf and soil-based half-life values were significantly different, and indicate that the use of aerobic soil half-life values may cause

considerable overestimation of pesticide losses via runoff, volatilization and infiltration. This appears to be consistent with many studies that indicate relatively low potential for environmental impacts from turf. It should be noted, however, that pesticides that are weakly sorbed to organic matter or those that are applied to immature stands of turf are likely to produce higher pesticide losses to the surrounding environment, and that risks of reentry in the first few days after application may be considerable.

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CHAPTER 4

A MODEL FOR PESTICIDE VOLATILIZATION FROM SURFACE DEPOSITS ON TURF

Abstract

A previously developed and tested model for pesticide volatilization from turf (WH model, Walden and Haith 2003) was modified by separating pesticide residues into surface and retained fractions. Surface deposits of pesticides are subject to volatilization, microbial decay and transfer to the retained fraction. Pesticides in the retained fraction are sorbed to organic matter in the foliage and thatch, and are assumed to be unavailable for volatilization. Thus, the retained fraction operates as a sink, withdrawing pesticide from the pool available for volatilization. Transfer rates from surface to retained deposits were based on experimental data that show rapid decrease in volatilization and in residues sampled from the surface of the foliage and thatch following an application. The surface deposit model (SD model) was calibrated using the same 2 pesticides as for the calibration of the WH model. Model predictions were then tested against the same dataset of 6 pesticides used in testing the WH model. The SD model overpredicted overall average daily volatilization (2.43% vs. 1.61% of the applied mass in the predictions and field observations, respectively), largely due to the overprediction of one of the test pesticides. However, the SD model did replicate daily volatilization dynamics better than the WH model (R^2 of 0.62 and 0.34, respectively).

INTRODUCTION

Turf is an intensively managed biotic system (Gardner et al. 2000, Wu et al 2002a). Annual pesticide application rates can be 3 to 8 times higher on golf courses, and 3 times higher on home lawns, than those for agricultural land (Kopell 1994, Schueler 2000). Elevated application rates have caused concern regarding exposure to pesticides upon reentry to treated areas, especially for children using turf at schools yards and parks (Cowell et al. 1993, Hurto and Prinster 1993, Sears et al. 1987) and golfers (Murphy et al. 1996 a,b, Clark et al. 2000).

Although field studies have demonstrated that pesticides applied to turf tend to remain adsorbed to the foliage and thatch layers and generally degrade rapidly (Niemczyk and Krueger 1987, Niemczyk et al. 1988, Cisar and Snyder 1996, Frederick et al. 1996), there is nevertheless the potential for these pesticides to pose risks to human health, especially during the first few days after application. One of the major risk pathways of interest is the inhalation of volatilized pesticides (Woodrow and Seiber 1997).

Mathematical models play an important role in estimating health risks as they allow rapid estimation of environmental pesticide concentrations under diverse climatic and management scenarios. A volatilization model for pesticides applied to turf was developed by Haith et al. (2002), and was further refined by Walden and Haith (2003). The model was then used to estimate pesticide inhalation risk to golfers (Murphy and Haith 2007).

This chapter modifies the pesticide volatilization model formulated by Walden and Haith (WH model, 2003) by separating the pesticide into two compartments. The surface deposit volatilization model (SD model) was tested using the same dataset as in Walden and Haith (2003), and was found to better replicate daily pesticide volatilization dynamics.

METHODS

The Haith et al. (2002) and Walden and Haith (2003) volatilization models

Haith et al. (2002) proposed that modeling pesticide volatilization from vegetation rather than from the soil surface was more appropriate for turf due to turf's dense foliage and thatch layers. The volatilization model was based on the similarities between water and pesticide vaporization. Pesticide volatilization was estimated by adjusting potential evapotranspiration (PET) using ratios of water and chemical saturated vapor pressures and latent heats of vaporization. The model also included first order degradation of the pesticides over time. The Penman equation was used to determine PET from turf, based on hourly climatic data.

Walden and Haith (2003) evaluated the impact of using simpler equations which estimate PET on a daily basis and require climatic data that is routinely collected at field sites and weather stations. They found that a model based on the Hargreaves-Samani equation (as described by Jensen et al. 1990) performed as well as the Penman based version, while requiring only daily maximum and minimum air temperature data as climatic inputs.

Both versions of the volatilization model were tested against the same set of field data, which consists of repeated applications of eight pesticides to turf over a span of 3 years. The hourly Penman based model was calibrated using 2 pesticides and tested against field observations of the remaining 6 pesticides. It achieved an R^2 of 0.67 for the 6 test pesticides. The daily Hargreaves-Samani model was not recalibrated, and was tested using all 8 pesticides, achieving an R^2 of 0.65.

It should be noted that model calibration and testing were based on the total pesticide volatilized in each experiment. The ability of the models to replicate daily fluctuations of pesticide volatilization was not tested. Reproduction of daily pesticide

volatilization dynamics is of interest for risk analyses based on acute exposure and maximal daily exposure.

Daily pesticide volatilization dynamics from turf

Field trials have found that pesticide volatilization from turf follows a daily pattern of high initial loss, which decreases rapidly over time (Wu et al. 2002 a,b, Taylor et al. 1977, Taylor and Spencer 1990, Murphy et al. 1996 a,b, Cooper et al. 1990). In order to assess this, experimental evidence from Haith et al. (2002), Wu et al. (2002 a,b), Murphy et al. (1996 a,b) and Taylor et al. (1977) was examined. Pesticide volatilization losses were transformed to percentages of the applied amounts. Exponential functions of the form shown in Eq. [4.1] were then fitted to the data.

$$V_t = V_0 \exp(-kt) \quad [4.1]$$

where V_t = mass of pesticide volatilized during day t (g), k = rate of decline in volatilization (d^{-1}). Microsoft Excel Solver (Microsoft, WA) was used to estimate values for V_0 and rate k which minimized the sum of squared deviations between observed values and equation's estimates. Observations were given the same weight in the optimization. Initial values for V_0 and k_t were set to 0, which gave stable optimization results. Goodness of fit was judged visually and by computing the coefficient of determination (R^2) between the observed and modeled values. Parameter estimation using Solver was preferred over regressions on the log transformed measurements, as the regressions tend to give higher weight to low values (Beulke and Brown 2001, Weisstein 2007), thus underemphasizing volatilization occurring shortly after application (which is when most of the volatilization occurs). Optimization was carried out for each volatilization experiment (49 in total). Results are summarized by source and pesticide in Table 4.1.

Table 4.1. Rate parameter values for pesticide volatilization.

Source	Pesticide	Chemical name	Rate k (d ⁻¹)†	R ²
Haith et al. (2002)	Isazofos	<i>O,O</i> -diethyl <i>O</i> -(5-chloro-1-(1-methylethyl)-1H-1,2,4-triazol-3-yl) phosphorothioate	0.85 (0.31-1.64) n=4	0.56-1.00
	Bendiocarb	2,2-dimethyl-1,3-benzodioxol-4-yl methylcarbamate	0.93 (0.16-1.71) n=4	0.40-1.00
	Diazinon	<i>O,O</i> -diethyl <i>O</i> -(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate	0.87 (0.32-1.38) n=4	0.57-1.00
	Ethoprop	<i>O</i> -ethyl S,S-dipropyl phosphorodithioate	1.24 (0.39-2.23) n=7	0.75-1.00
	Trichlorfon	Dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate	1.22 (0.39-2.22) n=4	0.86-1.00
	Carbaryl	1-naphthyl-N-methylcarbamate	0.86 (0.60-1.24) n=3	0.95-1.00
	Chlorpyrifos	<i>O,O</i> -diethyl <i>O</i> -(3,5,6-trichloro-2-pyridyl) phosphorothioate	0.67 (0.26-0.93) n=4	0.37-1.00
	Isofenphos	1-methylethyl 2-((ethoxy((1-methylethyl) amino)phosphinothioyl) oxy) benzoate	0.81 (0.56-1.13) n=4	0.73-1.00
Wu et al. (2002a)	Metalaxyl	Methyl N-(methoxyacetyl)-N-(2,6-xylyl)-DL-alaninate	0.3 n=1	0.79
	Chlorothalonil	2,4,5,6-tetrachloro-1,3-benzenedicarbo-nitrile	0.07 n=1	0.51
Wu et al. (2002b)	Trichlorfon		1.00 (0.81-1.20) n=2	0.98-1.00
	Chlorpyrifos		0.46 (0.45-0.48) n=2	0.99-0.99

Table 4.1 (Continued).

Source	Pesticide	Chemical name	Rate k (d^{-1}) [†]	R^2
Murphy et al. (1996a)	Trichlorfon		0.19 n=1	0.80
	Isazofos		0.32 n=1	0.96
Murphy et al. (1996b)	Triadimefon	1-(4-chlorophenoxy)- 3,3-dimethyl-1-(1H- 1,2,4-triazol-1-yl) butanone	0.35 n=1	0.99
	Mecoprop	2-(2-Methyl-4- chlorophenoxy) propionic acid	1.10 n=1	1.00
Taylor et al. (1977)	Dieldrin	1,2,3,4,10,10- Hexachloro-6,7-epoxy- 1,4,4a,5,6,7,8,8a- octahydro-1,4-endo- exo-5,8- dimethanonaphthalene	0.49 n=1	0.98
	Heptachlor	1(3a),4,5,6,7,8,8- heptachloro- 3a(1),4,7,7a-tetrahydro- 4,7-methanoindene	1.96 n=1	1.00
Overall Average			0.88	

[†] Rate k is given as the average value, range in parenthesis, and n is the number of experiments. R^2 are given as a range of values for the experiments.

Extremely high rates (8.06 d^{-1} for carbaryl and 7.96 d^{-1} for isofenphos) resulted from one experiment for each pesticide in which volatilization was only detected on the day of application. A second experiment for isazofos only detected volatilization on the day following the application, resulting in a poor fit of Eq. [4.1] to the data ($R^2 = 0.11$). All three experiments were reported by Haith et al. (2002). Results from these experiments were excluded from the data summarized in Table 4.1 and from further analysis.

The only exception to rapid exponential decrease was chlorothalonil (Wu et al. 2002a), which volatilized at an almost constant and relatively low rate (0.07 d^{-1}) over 8 days following application.

Daily dynamics of pesticides surface deposits on turf

Several studies have measured the dynamics of pesticide residues that can be physically dislodged from the surface of the foliage and thatch after an application. This portion of the pesticide is usually referred to as dislodgeable residues. Samples are taken by scuffing the surface of the foliage and thatch with a dampened cotton cloth or polyurethane foam, which is then analyzed for pesticide. Different areas of treated turf are sampled on different dates so that sampling does not interfere with the dissipation of the pesticide. From these experiments, the decline in surface deposits of the pesticide (i.e. the dislodgeable residues) can be determined.

Several studies have gone further, and distinguished between dislodgeable residues and those that have been adsorbed (to the waxy cuticle of the leaves or to the organic carbon present in turf foliage and thatch) or absorbed into the inner structures of the leaves (Bowhey et al. 1987, Sears et al. 1987, Thompson et al. 1984). They have found that dislodgeable residues, like volatilization, decrease exponentially after application. In order to assess this, measurements of dislodgeable residues were

obtained from Bowhey et al. (1987), Cowell et al. (1993), Hurto and Prinster (1993), Sears et al. (1987) and Thompson et al (1984). Exponential functions of the form shown in Eq. [4.2] were fitted to the observations.

$$P_t = P_0 \exp(-kt) \quad [4.2]$$

where P_t = mass of pesticide recovered by sampling for dislodgeable residues on day t (g), k = rate of decline in dislodgeable residues (d^{-1}). The fitting procedure was identical to that described previously in fitting Eq. [4.1] to the volatilization data. Results are summarized by source and pesticide in Table 4.2.

A very low R^2 (0.04) was obtained for an isazofos experiment conducted by Murphy et al. (1996a). Low R^2 was caused by high recovery of dislodgeable residues on the second day of the experiment, whereas recovery was low on the first and third days, and none were recovered after that. An extremely high rate ($26.86 d^{-1}$) was found for one study of 2,4-D by Thompson et al. (1984), and was due to a heavy rainfall shortly after application, which caused the pesticide to be washed off and no dislodgeable residues collected on subsequent days. The rates obtained from these two studies were excluded from Table 4.2 and from further analysis. A high rate ($8.9 d^{-1}$) was found for one experiment of diazinon conducted by Sears et al. (1987). Equation [4.2] fitted the experimental data well ($R^2 = 0.99$), so this rate was deemed accurate and was maintained in the dataset.

Close correspondence of the overall average values of rates k in Tables 4.1 ($0.88d^{-1}$) and 4.2 ($1.09d^{-1}$) suggests that both the volatilization process and the collection of dislodgeable residues occur from the same pool of pesticide: i.e. residues that are located on the surface of the foliage.

Table 4.2. Rate parameter values for pesticide dislodgeable residues.

Source	Pesticide	Chemical name	Rate k (d ⁻¹)†	R ²
Bowhey et al. (1987)	2,4-D	2,4-Dichlorophenoxy-acetic acid	0.29 (0.20-0.63) n=7	0.46-0.97
	Mecoprop		0.69 (0.37-1.01) n=2	0.56-0.99
	Dicamba	2,5-Dichloro-6-methoxybenzoic acid	0.57 (0.34-0.79) n=2	0.40-0.99
Cowell et al. (1993)	Dithiopyr	Dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-trifluoromethyl)-3,5-pyridinedi-carbothioate	0.77 (0.08-1.70) n=8	0.91-1.00
Hurto and Prinster (1993) ‡	Chlorpyrifos		0.17 (0.16-0.18) n=2	0.98-0.99
	DCPA	Dimethyl 2,3,5,6-Tetrachloro-terephthalate	0.13 (0.12-0.14) n=2	0.91-0.94
	Diazinon		0.29 (0.28-0.30) n=2	0.96-0.99
	Isofenphos		0.20 (0.18-0.21) n=2	0.95-0.96
	Pendimethalin	N-(1-Ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine	0.31 (0.30-0.32) n=2	0.95-0.95
Murphy et al. (1996a)	Trichlorfon		0.55 n=1	0.92
Murphy et al. (1996b)	Triadimefon		0.64 n=1	0.95
	Mecoprop		0.74 n=1	0.99

Table 4.2 (Continued).

Source	Pesticide	Chemical name	Rate k (d ⁻¹)†	R ²
Sears et al. (1987)	Diazinon		3.58 (0.43-8.90) n=8	0.66-1.00
	Chlorpyrifos		3.08 n=1	1.00
	Isofenphos		2.14 n=1	1.00
Thompson et al (1984)	2,4-D		0.50 (0.03-0.73) n=5	0.36-0.98
Overall Average			1.09	

† Rate k is given as the average value, range in parenthesis, and n is the number of experiments. R² are given as a range of values for the experiments.

‡ Data for experiments by Hurto and Prinster (1993) were derived from equations fitted by the authors. R² values are those reported by the authors.

It seems unlikely that sorbed portions of the pesticide contribute largely to pesticide volatilization. Wolters et al. (2004) indicated that persistence of pesticide deposits on the leaves is one of the main factors in determining volatilization from plants, and developed a model in which volatilization decreased in proportion to the decrease in mass of these deposits. Their results indicated that pesticide penetration into the leaves reduced volatilization, and occurred at rates between 0.5 and 2 d⁻¹. These values are comparable to those in Tables 4.1 and 4.2.

Modification of the WH pesticide volatilization model

The WH model was formulated under the assumption that all the pesticide mass in the turf was available for volatilization, and no distinction was made between surface and sorbed fractions. Pesticide mass declined due to volatilization and microbial decay only, and thus the pesticide available for volatilization persisted for many days after application. This resulted in the model predicting relatively constant volatilization losses in the days following an application, rather than the exponential decline observed in the field data.

To account for this decline, the WH model was modified so that pesticide volatilization occurs only from surface residues. At application, all of the pesticide is assumed to be placed on the surface of the foliage and thatch. Surface residues decrease over time due to microbial decay, volatilization and sorption to plant organic matter, which acts as a sink by reducing the pesticide mass available for volatilization. The model is shown in Figure 4.1.

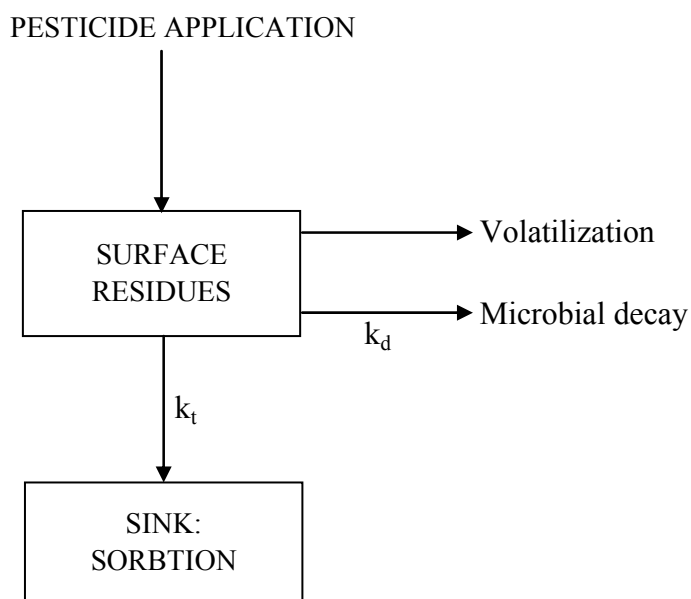


Figure 4.1. A surface deposit model for pesticide volatilization from turf.

Surface residues are susceptible to removal from the system via volatilization, reduced by microbial decay at rate k_d (d^{-1}), and transferred to the sink at rate k_t (d^{-1}). The sink contains residues that have been adsorbed to organic matter or absorbed into plant tissue, and is assumed to be empty at the time of the first pesticide application.

Both microbial decay and transfer affecting the surface residues are assumed to be first order, and the corresponding mass balance is described by:

$$C_{t+1} = (C_t - V_t) \exp(-(k_d + k_t)) \quad [4.3]$$

where C_t is the mass of pesticide on the surface of turf foliage and thatch ($g\ ha^{-1}$) at the beginning of day t , and V_t is the amount of pesticide volatilized from the surface deposits on day t ($g\ ha^{-1}$). Pesticide volatilization is estimated using the model described by Walden and Haith (2003):

$$V_t = a R_t C_t \quad [4.4]$$

where a is a volatilization constant (mm^{-1}), R_t is the relative volatility of the pesticide and water during period t (mm), and C_t is the mass of pesticide available for volatilization (i.e. surface deposits) at the beginning of day t (g ha^{-1}). Relative volatility is given by:

$$R_t = \text{PET}_t (p_{\text{sct}} / p_{\text{swt}}) (\lambda_{\text{wt}} / \lambda_{\text{ct}}) \quad [4.5]$$

in which PET_t is the potential evapotranspiration during day t (mm); p_{sct} and p_{swt} are the saturated vapor pressures of the pesticide and water, respectively, during day t (kPa); and λ_{ct} and λ_{wt} are the latent heats of vaporization of the pesticide and water, respectively, during day t (J g^{-1}). Equation [4.5] adjusts potential evapotranspiration to account for differences in pesticide and water saturated vapor pressures and the energy required for vaporization.

Methods for computing vapor pressures and heats of vaporization as functions of temperature are:

$$\lambda_{\text{wt}} = 2501 - 2.361 T_t \quad [4.6]$$

$$p_{\text{swt}} = 3.38639 [(0.00738 T_t + 0.8072)^8 - 0.000019 | 1.8 T_t + 48 | + 0.001316] \quad [4.7]$$

where T_t = average air temperature during day t ($^{\circ}\text{C}$). Pesticide vapor pressures and heats of vaporization are determined from Grain (1982), as described by Haith et al. (2002):

$$\ln(p_{\text{sct}} / p_{\text{sc0}}) = [M \lambda_{\text{c0}} / \Delta Z_b R T_{\text{a0}}] \{ 1 - [3 - 2(T_{\text{at}} / T_{\text{a0}})]^m (T_{\text{a0}} / T_{\text{at}}) - 2m[3 - 2 (T_{\text{at}}/T_{\text{a0}})]^{m-1} \ln(T_{\text{at}}/T_{\text{a0}}) \} \quad [4.8]$$

$$M \lambda_{\text{c0}} / R T_{\text{a0}} = K_f [9.03 + \ln(T_{\text{a0}}/p_{\text{sc0}})] \quad [4.9]$$

In these equations, p_{sc0} is the vapor pressure (kPa) at absolute temperature T_{a0} (K), λ_{c0} is the latent heat of vaporization (J g^{-1}) at T_{a0} , M is the molecular weight of the pesticide, R is the gas constant ($8.32 \text{ J mol}^{-1} \text{ K}^{-1}$), ΔZ_b is the compressibility factor at boiling point (dimensionless), T_{at} is the absolute mean air temperature during day t

(K), and m is equal to 0.19 for liquid and 0.8 for solid pesticide formulations. Based on examples given by Grain (1982), $\Delta Z_b = 0.97$ and $K_f =$ is a constant with a mean value 1.06 for a range of organic compounds. The pesticide's latent heat of vaporization is also calculated from Eq. [4.9] by substituting T_{at} for T_{a0} .

Potential evapotranspiration is calculated using the Hargreaves-Samani equation, as described by Jensen et al. (1990):

$$PET_t = 0.0023 R_{At} T_{Dt}^{1/2} (T_t + 17.8) / \lambda_{wt} \quad [4.10]$$

where T_{Dt} is the difference between the maximum and minimum temperature ($^{\circ}\text{C}$) on day t, and R_{At} is the extraterrestrial radiation on day t (kJ m^{-2}) as determined by:

$$R_{At} = [24(60)/\pi] G_{sc} d_r [(\omega_s) \sin(\phi) \sin(\delta) + \cos(\phi) \cos(\delta) \sin(\omega_s)] \quad [4.11]$$

$$d_r = 1 + 0.033 \cos(2\pi\text{DOY}/365) \quad [4.12]$$

where G_{sc} is the solar constant ($82 \text{ kJ m}^{-2} \text{ min}^{-1}$), d_r is the relative distance between the earth and the sun. ω_s is the sunset hour angle (radians), calculated from:

$$\omega_s = \arcsin[-\tan(\phi)\tan(\delta)] \quad [4.13]$$

in which ϕ is the latitude of the site (radians), and δ is the solar declination angle (radians), given by:

$$\delta = 0.4093 \sin[2\pi(284 + \text{DOY})/365] \quad [4.14]$$

where DOY is the day of the year (1 to 365, starting on Jan 1) (Jensen et al. 1990).

Model Testing

Data for model calibration and testing was taken from the same dataset used in the evaluation of the models developed by Haith et al. (2002) and Walden and Haith (2003). Experimental design and sampling methods were as described by Murphy et al. (1996a,b). The testing sites were 0.2 ha plots with Hadley silt loam (coarse-silty, mixed, superactive, nonacidic, mesic Typic Udifluent) at the University of Massachusetts Turfgrass Research Center in South Deerfield, MA. The turf was a well

established creeping bentgrass (*Agrostis palustris* L.), maintained at 13 mm with thatch thickness varying between 10 and 15 mm. Concentrations of volatile residues of eight pesticides were collected using a high volume air sampler and the theoretical profile shape method was used to estimate volatilization mass fluxes (Murphy et al. 1996a,b, Wilson et al. 1982). Eight pesticides were applied in 11 experiments that were conducted during the 1995, 1996 and 1997 growing seasons. Ethoprop was applied in seven of the experiments, isofenphos in six, and bendiocarb, carbaryl, chlorpyrifos, diazinon, isazofos, and trichlorfon were each applied in four of the experiments. The sampling program is described in more detail in Haith et al. (2002).

Physical properties of the pesticides were taken from Haith et al. (2002). However, the SD and WH models were tested using degradation half-lives specific to pesticides on turf developed in Chapter 2 instead of using soil aerobic degradation half-lives, which were used in tests of the previous volatilization models (Haith et al. 2002, Walden and Haith 2003).

Estimation of Transfer Rates

Rates summarized in Tables 4.1 and 4.2 include all dissipation processes affecting surface residues, including washoff, volatilization and microbial decay. In order to produce accurate estimates of the transfer rate k_t to use with the model, dissipation rates for pesticides that had $K_{oc} > 200$ ($\text{cm}^3 \text{g}^{-1}$) and vapor pressure $< 4 \times 10^{-6}$ (kPa at 25°C) were selected. This was done to ensure that the k_t rates were based on pesticides that were not highly susceptible to leaching and volatilization losses. Rates derived from Haith et al. (2002) were excluded from the selection, as this dataset was used later to independently test the model.

The selected rates were then corrected for decay, which is accounted for as a separate process in the model (Eq. [4.3]). The correction used was:

$$k_t = k - k_d \quad [4.15]$$

where k = the dissipation rate of the selected pesticides (from volatilization studies excluding Haith et al. 2002 and from the dislodgeable residue studies).

Resulting transfer rates are shown in Table 4.3. Transfer rates based on two experiments (one for chlorothalonil and one for dithiopyr) resulted in negative values, and were excluded from Table 4.3 and from further analysis.

Table 4.3. Transfer rates by pesticide.

Pesticide	Number of experiments	Transfer rate k_t (d^{-1})
Chlorpyrifos	5	0.79
DCPA	2	0.09
Dieldrin	1	0.45
Dithiopyr	7	0.77
Isofenphos	3	0.80
Pendimethalin	2	0.22
Triadimefon	2	0.34
Overall Average		0.61

For pesticides not included in Table 4.3, the average transfer rate of $0.61 d^{-1}$ may be used as a default value. Values in Table 4.3 generally correspond well with rates of pesticide penetration into plant material found by Wolters et al. (2004), which varied between 0.5 and $2 d^{-1}$.

Data used to calibrate and test the model

Properties of the eight pesticides used in calibrating and testing the volatilization model are given in Table 4.4. All data in Table 4.4 are from Haith et al. (2002), except for the degradation rates in turf, which are taken from Chapter 2.

Table 4.4. Pesticide properties.

Pesticide	Molecular weight	Vapor pressure at 25°C (kPa)	K _{oc} (cm ³ g ⁻¹)	Degradation rate k_d in turf (d ⁻¹)	Transfer rate k_t (d ⁻¹)
<u>Group 1: high vapor pressure (VP ≥ 4E-06 kPa at 25°C)</u>					
Bendiocarb	223.2	4.6×10^{-6}	385	0.04	0.61
Diazinon	304.3	1.2×10^{-5}	1520	0.27	0.61
Ethoprop	242.3	4.3×10^{-5}	104	0.04	0.61
Isazofos	313.7	1.2×10^{-5}	155	0.04	0.61
<u>Group 2: low vapor pressure (VP < 4E-06 kPa at 25°C)</u>					
Carbaryl	201.2	4.9×10^{-8}	288	0.14	0.61
Chlorpyrifos	350.6	2.7×10^{-6}	9930	0.08	0.79
Isofenphos	345.4	4.4×10^{-7}	777	0.04	0.80
Trichlorfon	257.4	5.0×10^{-7}	15	0.21	0.61

Daily maximum and minimum air temperatures for 1995, 1996 and 1997 were obtained for Amherst, MA (Northeast Regional Climate Center, 2006). Latitude (ϕ) of the site is 0.74 radians (42.39 degrees N).

Model calibration was performed in a similar manner as in Walden and Haith (2003): pesticides were split into those of high vapor pressure ($\geq 4 \times 10^{-6}$ kPa at 25°C) and those of low vapor pressure ($< 4 \times 10^{-6}$ kPa at 25°C). Isazofos was selected as the calibration pesticide for the high vapor pressure group, and trichlorfon was used to calibrate the model for the low vapor pressure group.

The volatilization constant a scales volatilization, and can be used to calibrate the total loss of pesticide over an experiment (as done by Haith et al. 2002 and Walden and Haith 2003), or to calibrate pesticide volatilization occurring during the first day of an experiment (0 DAT), which is the starting point of the exponential decline in volatilization over time. The second method of calibration was used here, so that the observed and predicted volatilization for the first day of measurement for isazofos and trichlorfon would correspond as closely as possible. Both isazofos and trichlorfon

were applied in 4 experiments each, so the volatilization at 0 DAT was averaged over 4 experiments for each pesticide and used to calibrate the SD model.

Model performance was evaluated by comparing average daily volatilization for the 6 test pesticides. Coefficients of determination (R^2) were calculated for measured and modeled daily volatilization for each pesticide. Additionally, measured and modeled volatilization was averaged across experiments for each sample day (0, 1, 2, 4, and 6 days after treatment). Although conditions were not identical in each experiment, averaging across experiments in this manner provided a general idea of the decline in volatilization over time for each of the pesticides, and allowed an assessment of how well this behavior was replicated by the model.

RESULTS AND DISCUSSION

Model Calibration

Calibration resulted in values of $a = 295 \text{ mm}^{-1}$ for the high vapor pressure group, and of 1080 mm^{-1} for the low vapor pressure group. These values are considerably higher than those found by Haith et al. (2002), which were 130 mm^{-1} for the high vapor pressure group and 405 mm^{-1} for low vapor pressure group. The increase in values is due to the rapid dissipation of the pesticide mass available for volatilization in the surface deposit model. Results of the calibration of the SD model are shown in Table 4.5. Volatilization losses are expressed as percentage of the applied rates of each pesticide.

Table 4.5. Comparison of observed and predicted pesticide volatilization – calibrations.

Pesticide	Volatilization (%)	
	Observed	SD Model
Isazofos (Group 1, $a = 295 \text{ mm}^{-1}$)		
Average daily volatilization at 0 DAT†	4.68	4.69
R^2 for daily volatilization (n=19)‡		0.26
Trichlorfon (Group 2, $a = 1080 \text{ mm}^{-1}$)		
Average daily volatilization at 0 DAT	0.53	0.53
R^2 for daily volatilization (n=17)		0.59

† Observed and modeled volatilization values are the means of volatilization measured during the first day of 4 experiments for each pesticide.

‡ R^2 was calculated using daily volatilization from all 4 experiments for each pesticide.

Volatilization at 0, 1, 2, 4 and 6 DAT (averaged over 4 experiments for each pesticide) are shown for both calibration pesticides in Figure 4.2. Average daily volatilization of both pesticides, as predicted by the WH model, has been included in the graphs for comparison purposes. In Figure 4.2, R^2 values indicate the correspondence between the observed and modeled volatilization for each sample day, averaged across all experiment in which the pesticide was applied. As such, these R^2 values are limited (based on only 5 values), but help to illustrate differences in the prediction of the SD and WH models.

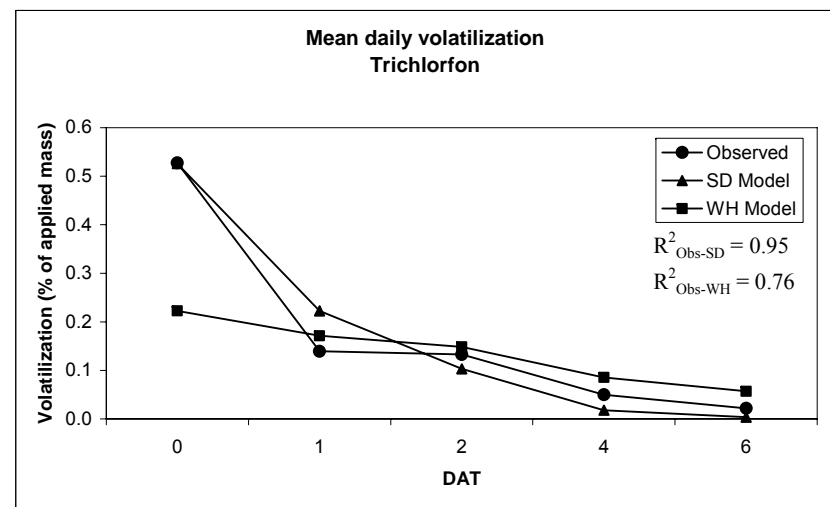
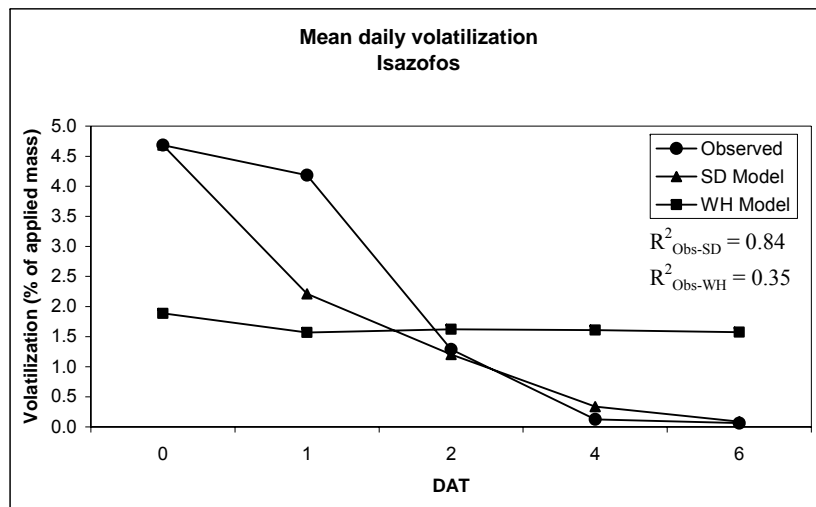


Figure 4.2. Average daily volatilization for the calibration pesticides.

Model Testing

Observed and modeled (SD Model) volatilization losses for the remaining 6 pesticides are summarized in Table 4.6. For comparison purposes, predictions using the WH model as developed and calibrated by Walden and Haith (2003) have also been included. Simulations using the WH model were run using $a = 130 \text{ mm}^{-1}$ for group 1 and 405 mm^{-1} for group 2. Decay rates were specific for turf (Table 4.4).

Table 4.6. Comparison of observed and predicted pesticide volatilization – model tests.

Pesticide	Volatilization† (%)		
	Observed	SD Model	WH Model
<u>Group 1</u>			
Bendiocarb			
Average daily volatilization	0.38	0.59	0.45
R ² (n=17)		0.47	0.35
Diazinon			
Average daily volatilization	2.20	2.43	1.22
R ² (n=19)		0.44	0.26
Ethoprop			
Average daily volatilization	3.79	7.65	4.67
R ² (n=28)		0.58	0.17
<u>Group 2</u>			
Carbaryl			
Average daily volatilization	0.06	0.06	0.01
R ² (n=17)		0.82	0.54
Chlorpyrifos			
Average daily volatilization	1.74	1.26	1.42
R ² (n=19)		0.34	0.00
Isofenphos			
Average daily volatilization	0.40	0.17	0.18
R ² (n=23)		0.29	0.04
Overall Mean	1.61	2.43	1.57
Overall R ² (n=123)		0.62	0.34

† Observed and modeled volatilization values are means of daily volatilization measured in 4 experiments for bendiocarb and diazinon, 7 experiments for ethoprop, 4 experiments for carbaryl and chlorpyrifos, and in 6 experiments for isofenphos.

Coefficients of determination (R^2) of the daily pesticide volatilization vary between 0.29 and 0.82 for the SD model, whereas the WH model produces values between 0.00 and 0.54. The overall R^2 for the 6 test pesticides is greater for the SD model (0.62) than for the WH model (0.34), indicating that the SD model performed better in terms of replicating daily pesticide volatilization dynamics.

Based on the overall results, the SD model appears to overpredict volatilization (overall average volatilization of 2.43% of the applied mass versus 1.61% of the applied mass for the observed data). The main reason for this was the overprediction of ethoprop (7.65% for the SD model vs. 3.79% for the observed data), and may be due to the use of the default transfer rate of 0.61 d^{-1} for this pesticide. This transfer rate, combined with a degradation rate of 0.14 d^{-1} , gives a total dissipation rate of 0.75 d^{-1} for ethoprop, whereas the observed decline in ethoprop volatilization in the field occurred at a mean rate of 1.24 d^{-1} (data from Haith et al. 2002). Closer correspondence between average observed and modeled volatilization could be achieved by calibrating the volatilization constant a for each pesticide, but this would limit the model's applicability to situations where data is available for calibration.

Average daily volatilization dynamics of each pesticide were determined by taking the mean of the pesticide volatilization measured at 0, 1, 2, 4 and 6 DAT across all experiments in which the pesticide was applied. Correspondence of observed and predicted behavior for each of the 6 test pesticides is shown in Figure 4.3.

Figure 4.3. Average daily volatilization for the test pesticides.

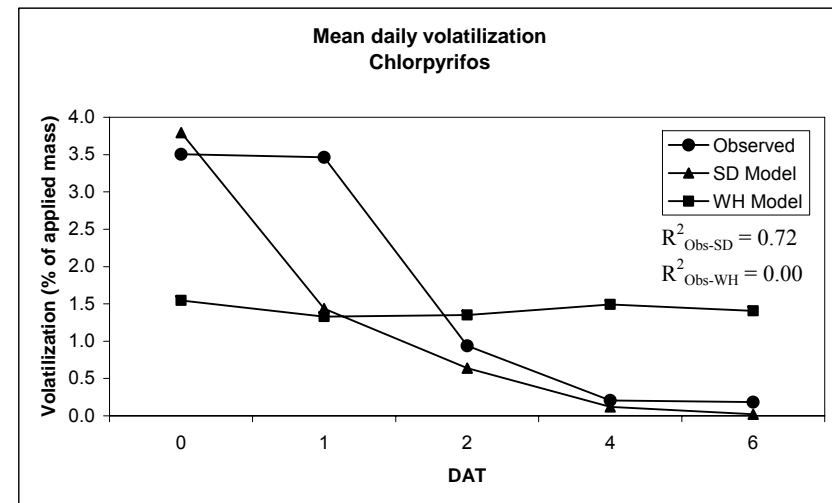
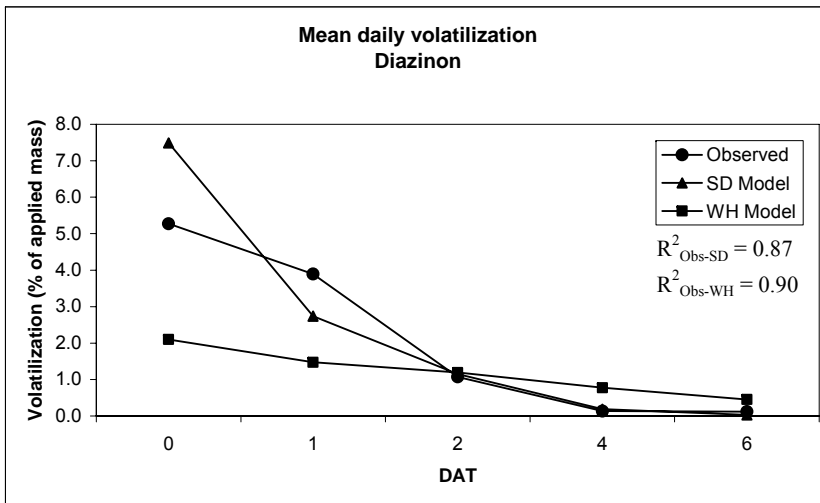
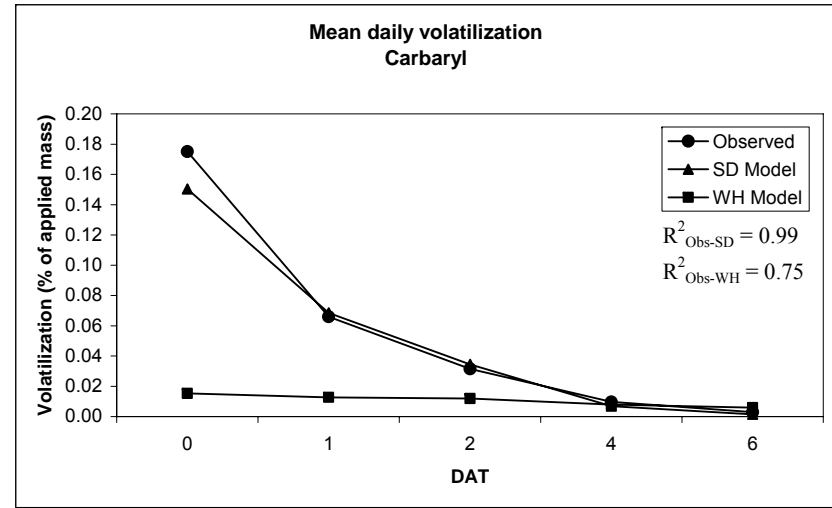
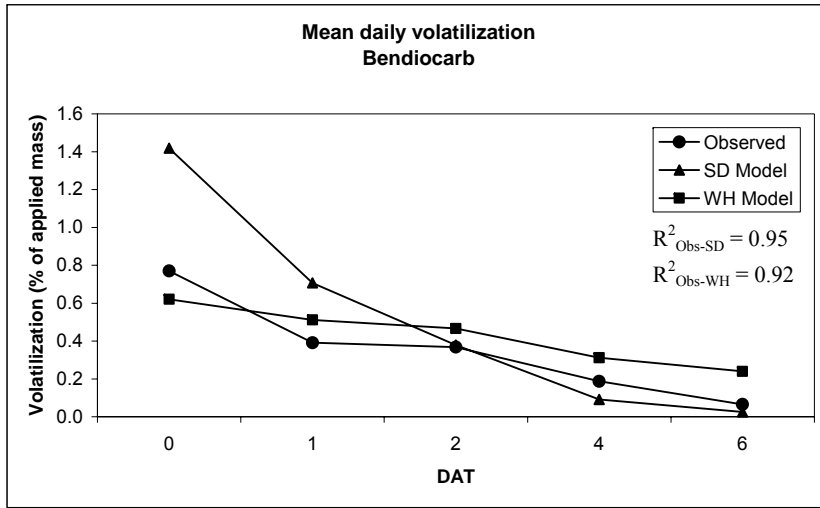
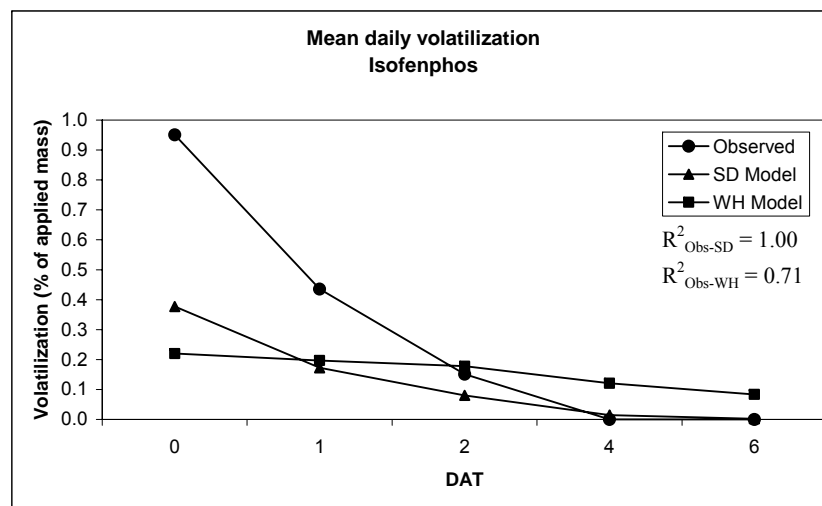
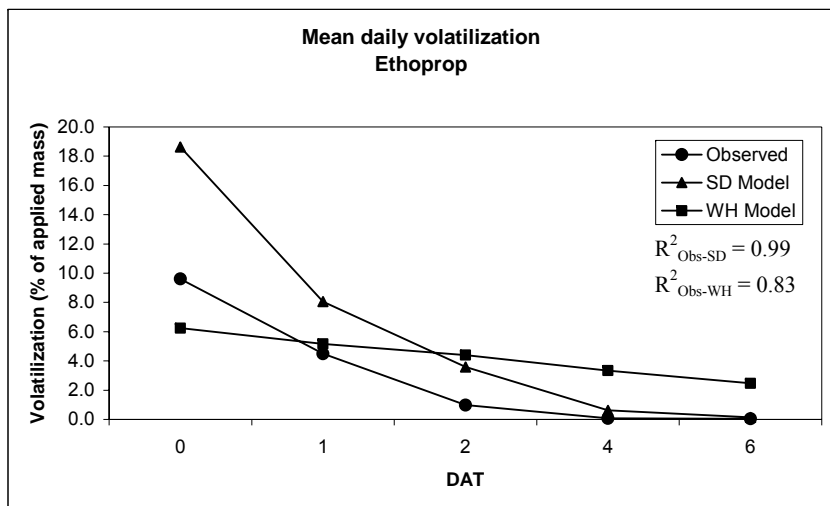


Figure 4.3 (continued).



In Figures 4.2 and 4.3, R^2 values indicate the correspondence between the observed and modeled volatilization for each sample day, averaged across all experiment in which the pesticide was applied. As such, R^2 's are based on only 5 values for each pesticide, but they help to illustrate differences between predictions of the SD and WH models. In general, the SD model reproduced daily volatilization dynamics better than the WH model (R^2 values of 0.72 to 1.00 versus R^2 values of 0.00 to 0.92, respectively).

As shown in Figures 4.2 and 4.3, the WH model predicts almost constant daily volatilization for all of the pesticides. These results arise from the assumption that the entire pesticide mass in the turf foliage and thatch is available for volatilization. Pesticide dissipation is only due to microbial decay and volatilization, which leads to fairly constant volatilization for several days after application.

In contrast, the SD model produces an exponential decline in volatilization for all the pesticides. This is driven mainly by the rapid transfer of pesticides from surface deposits to the sorbed fraction, which removes pesticide mass from the pool available for volatilization.

CONCLUSIONS

A surface deposit model for pesticide volatilization from turf was developed by adopting a model previously developed and tested by Walden and Haith (2003) and modifying the model by splitting the pesticide into surface and retained fractions. In the new model, volatilization was constrained to occur from surface deposits only. This approach was justified by several studies that distinguish between deposited and retained fractions of pesticide, which on turf appear to adhere closely to a fraction deposited on the surface of the foliage and a second fraction retained via sorption to organic matter or absorption into plant tissue. Dissipation rates of dislodgeable

residues (sampled from the surface of the foliage) were similar to those of daily reduction in volatilization. Selected dissipation rates (for pesticides with high K_{oc} and low vapor pressure) were corrected for decay, and used to model the decrease of the surface deposits over time.

The surface deposit model was calibrated in a similar manner to the WH model in Walden and Haith (2003). Testing was done based on daily volatilization for 6 pesticides. While the SD model overpredicted volatilization (largely due to overpredictions for ethoprop), it did replicate the decline in volatilization in days following application better than the WH model.

Limiting volatilization to surface residues allowed improved accuracy of the model's predictions of daily pesticide volatilization, without increasing difficulties in model parameterization.

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CHAPTER 5

TURF PESTICIDE MODEL (TPM), A GENERAL FATE AND TRANSPORT MODEL FOR PESTICIDES APPLIED TO TURF: I. MODEL DESCRIPTION

Abstract

High annual application rates of pesticides to turf have caused concern regarding human health and ecological risks of golf courses, playing fields and home lawns. The Turf Pesticide Model (TPM) is an engineering tool that estimates pesticide losses via runoff, leaching and volatilization from turf systems. The TPM integrates a previously tested runoff model (TurfPQ), a volatilization model based on surface deposits of pesticides in turf, and a leaching component. As such, the model may be useful in risk assessment, total maximum daily load, and other nonpoint source pollution studies that require estimates of pesticide losses through major pathways to environmental media. Simulations require turf, soil and pesticide data that are available in published databases. Default values and parameter estimation methods are included for cases in which data is limited. Model testing datasets, procedures and results are presented in Chapter 6

INTRODUCTION

Turf is frequently recognized as one of the most intensively managed biotic systems (Gardner et al. 2000, Wu et al. 2002), and can account for 80% of the pervious surfaces in urban areas, of which approximately half may be subjected to high input management (Schueler 2000a). Pesticide application rates may be 3 to 8 times higher on golf courses, and 3 times higher on home lawns, than those for agricultural land (Koppell 1994, Schueler 2000b). Pesticide concentrations in water

from urban areas and golf courses have exceeded environmental and drinking water standards (U.S. Geological Survey 1999, Cohen et al. 1999). High application rates have also caused concern regarding exposure to pesticides upon reentry to treated areas, especially for children using turf at schools yards and parks (Cowell et al. 1993, Hurto and Prinster 1993, Sears et al. 1987) and golfers (Murphy et al. 1996 a,b, Clark et al. 2000).

Monitoring and field studies provide valuable data, but they are time consuming and expensive to implement, and their results are not easily extrapolated to different climatic, turf, soil and management conditions. An alternative approach is to use mathematical models to predict the fate and transport of pesticides. Models which have been applied to turf systems include EPIC (Rosenthal and Hipp 1993), GLEAMS (Duborow, et al. 2000, Ma et al. 1999a, Wauchope, et al. 1990), PRZM (Duborow, et al. 2000, Ma et al. 1999a, Smith, et al. 1991), LEACHM (Roy, et al. 2001), OPUS (Ma, et al. 1999b) and SWAT (King and Balogh 2001). These models are fundamentally soil chemistry models developed for agricultural sites. Turf, however, differs from agricultural crops due to its dense near-ground foliage and layer of thatch (which is comprised of dead and decaying vegetative matter). The large amount of organic matter in these layers retains pesticides and has an important effect on their fate and transport.

Use of these models to simulate pesticide runoff and leaching from turf have had varied results. Even after calibration, simulated values differ between 2 and several orders of magnitude from values observed in the field (Duborow et al. 2000, Ma et al. 1999, Roy et al. 2001, Smith, et al. 1991 and Wauchope, et al. 1990). The only evaluations of model performance for pesticide volatilization from turf are those by Haith et al. (2002) and Walden and Haith (2003). These models performed well,

but daily dynamics were not evaluated. A modified model was developed in Chapter 4 to address this.

There is a need for models that can be easily applied to turf scenarios without requiring extensive parameterization and calibration, as a basis for risk assessment, total maximum daily load and turf management studies. This chapter describes a model designed to predict runoff, volatilization, leaching and microbial decay of pesticides in turf and the underlying soil. Default parameter values or estimation methods are provided in order to facilitate the model's use in simulating pesticide fate and transport in turf systems.

MODEL DEVELOPMENT

Pesticide dissipation from turf systems was reviewed in Chapter 2. While many processes affect dissipation, the most important are: volatilization, runoff, infiltration into the soil, leaching from the soil profile, adsorption to turf and soil organic carbon, and microbial decay. These processes, and the associated water gains and losses which drive pesticide transport through the system, are represented in Figure 5.1, and are the basic components of TPM.

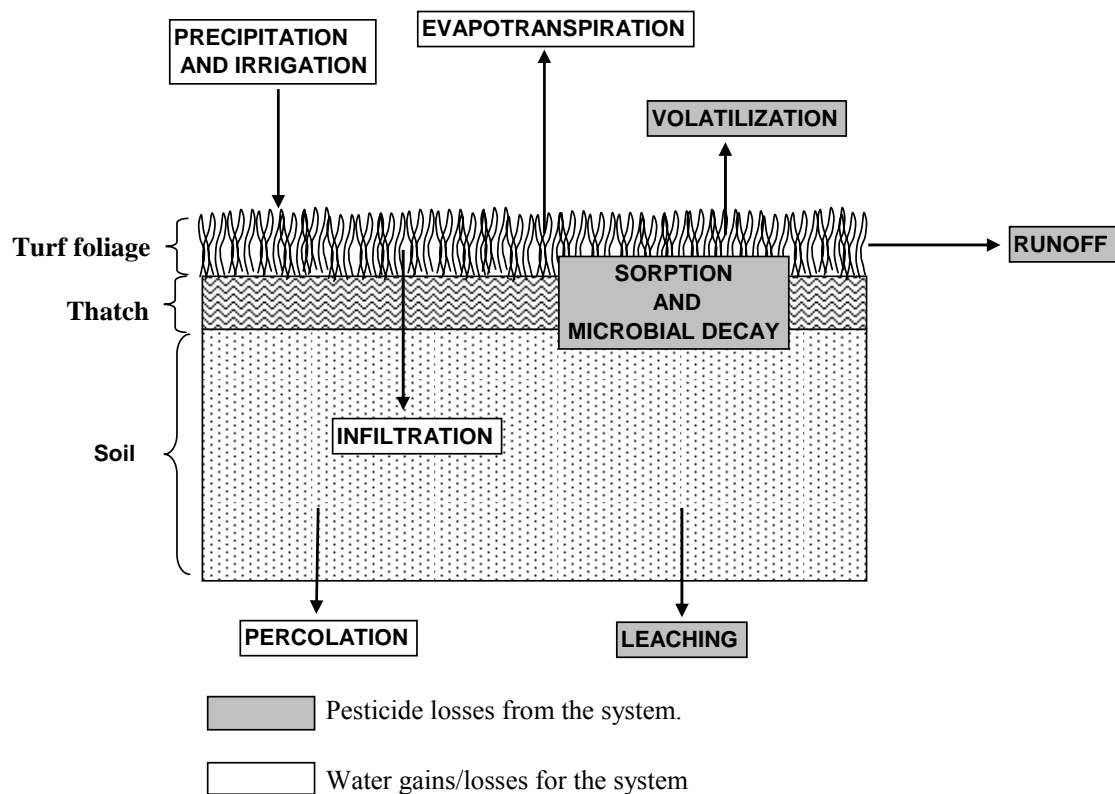


Figure 5.1. Turf system for pesticide fate and transport modeling.

For the purposes of TPM, the turf system is divided into surface and subsurface modules. Surface processes are those occurring in the turf foliage and thatch, and subsurface processes occur in the underlying soil. Movement of water and pesticides from the turf into the soil provides the link between surface and subsurface modules.

Surface (turf) processes

Partitioning and persistence of pesticides applied to turf

Turf is fundamentally different from many other types of vegetation in that it has a near-surface layer of dense foliage and, in most cases, forms an underlying layer of thatch. When a pesticide is applied, these layers intercept the pesticide, preventing it from reaching the soil. In addition, foliage and thatch contain large amounts of organic matter, which strongly adsorb pesticides and impede further movement to the soil.

A two compartment approach is used in TPM to model the fate and transport of pesticides in turf foliage and thatch, as shown in Figure 5.2.

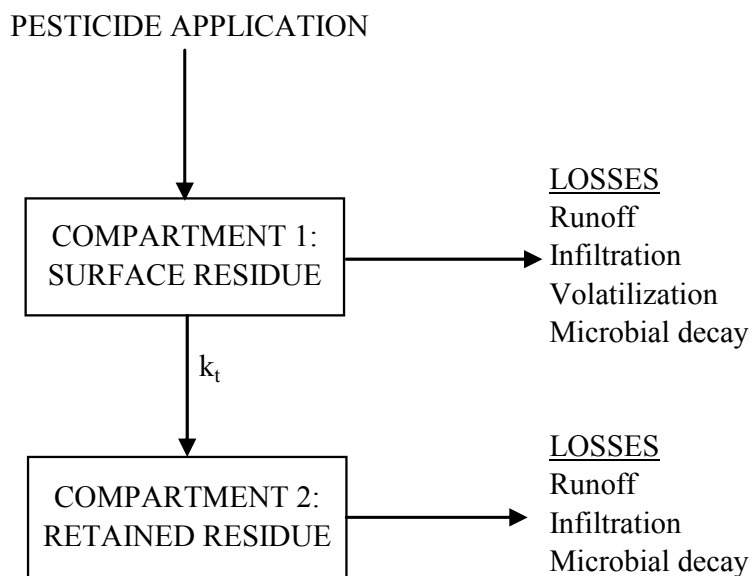


Figure 5.2. Compartmentalization of pesticide residues in turf foliage and thatch.

The first compartment is comprised of residues on the surface of the foliage and thatch, which is where the pesticide is initially placed on the day of application. The second compartment contains residues that have been sorbed to organic matter in

the foliage and thatch. Pesticides in compartment 1 are susceptible to removal from the turf by infiltration, runoff and volatilization. They are also reduced by microbial decay at rate k_d (d^{-1}), and transferred to compartment 2 at rate k_t (d^{-1}). Pesticides in compartment 2 can be removed from the turf via infiltration and runoff, and are also subject to microbial decay at rate k_d . Pesticide volatilization does not occur from compartment 2, as discussed in Chapter 4.

Mass balance equations for the pesticide in compartments 1 and 2 are as follows:

$$P_{1,t+1} = (P_{1,t} + \Delta P_t - PI_{1,t} - PQ_{1,t} - PV_t - PT_t) \exp(-k_d) \quad [5.1]$$

$$P_{2,t+1} = (P_{2,t} - PI_{2,t} - PQ_{2,t} + PT_t) \exp(-k_d) \quad [5.2]$$

where $P_{1,t}$ and $P_{2,t}$ are the masses of pesticide in compartments 1 and 2 at the beginning of day t , respectively, and ΔP_t are applications of pesticide on day t ($g\ ha^{-1}$). Pesticide runoff from compartments 1 and 2 ($g\ ha^{-1}$) during day t are $PQ_{1,t}$ and $PQ_{2,t}$, respectively. Terms $PI_{1,t}$ and $PI_{2,t}$ are the pesticide masses infiltrating the soil from compartments 1 and 2 ($g\ ha^{-1}$) during day t , respectively. Pesticide volatilized during day t is PV_t ($g\ ha^{-1}$). Transfer from compartment 1 to 2 is assumed to be first order, and is given by PT_t ($g\ ha^{-1}$):

$$PT_t = (P_{1,t} + \Delta P_t - PI_{1,t} - PQ_{1,t} - PV_t) (1 - \exp(-k_t)) \quad [5.3]$$

Total pesticide mass in the turf foliage and thatch is given by the sum of Eq. [5.1] and [5.2], resulting in:

$$P_{t+1} = (P_t + \Delta P_t - PI_t - PQ_t - PV_t) \exp(-k_d) \quad [5.4]$$

An example of the change in pesticide mass in compartments 1 and 2, and the total mass in the foliage and thatch is shown in Figure 5.3. In this example, the application rate is $1\ kg\ ha^{-1}$, $k_d = 0.21\ d^{-1}$ and $k_t = 0.29\ d^{-1}$. Losses due to infiltration, runoff and volatilization are not included.

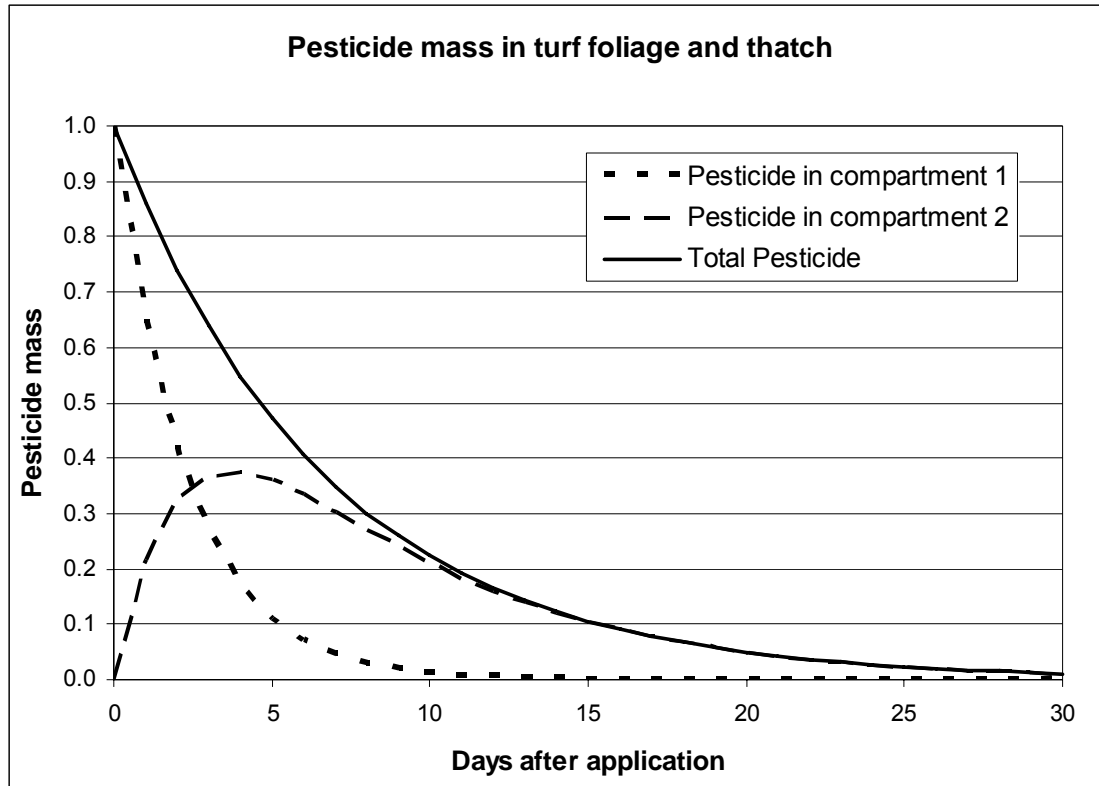


Figure 5.3. Change of pesticide masses in compartments 1 and 2 over time.

This behavior corresponds with dynamics observed by Schleicher et al. (1995) and Stahnke et al. (1991), where surface residues (compartment 1) declined progressively, but retained residues (compartment 2) initially increased due to transfer from the surface deposits.

Surface water balance

A surface water balance model partitions water flow into infiltration and runoff. First, water entering the system is determined to be snow or liquid water based on the average air temperature of the day. The mass balance equation for snow is:

$$SN_{t+1} = SN_t + \Delta SN_t - M_t \quad [5.5]$$

$$\Delta SN_t = Pr_t \quad \text{for } T_t \leq 0 \quad [5.6]$$

where SN_t = water content of the snow present at the beginning of day t (mm), and ΔSN_t = snowfall during day t (mm). Precipitation occurring during day t (Pr_t , mm) adds to the snow pack if the average daily air temperature (T_t , °C) is below freezing. Snowmelt (M_t , mm) occurs at a rate of $4.5 \text{ mm } ^\circ\text{C}^{-1}$ (Haith 1985), until the snow pack has been depleted:

$$M_t = \min [4.5T_t, SN_t] \quad \text{for } T_t > 0^\circ\text{C} \quad [5.7]$$

Liquid water entering the turf is partitioned between runoff and infiltration using a modified version of the U.S. Soil Conservation Service curve number equation, as described by Haith and Andre (2000):

$$Q_t = \frac{(R_t + IR_t + M_t - 0.2S_t)^2}{R_t + IR_t + M_t + 0.8S_t} \quad \text{for } R_t + IR_t + M_t \geq 0.2 S_t$$

$$0 \text{ otherwise.} \quad [5.8]$$

where Q_t is runoff (mm), R_t = rainfall (i.e. precipitation occurring when $T_t > 0^\circ\text{C}$, mm), IR_t = irrigation (mm), and S_t is water detention on day t (mm). S_t is related to a curve number, CN_t , by:

$$S_t = \frac{25400}{CN_t} - 254 \quad [5.9]$$

Curve numbers are selected as linear functions of 5-day antecedent accumulated moisture, A_t (mm):

$$CN_t = CN1 + (A_t/AMC1) (CN2 - CN1) \quad \text{for } A_t \leq AMC1 \quad [5.10]$$

$$CN_t = CN2 + [(A_t - AMC1)/(AMC2 - AMC1)](CN3 - CN2)$$

$$\text{for } AMC1 < A_t < AMC2 \quad [5.11]$$

$$CN_t = CN3 \quad \text{for } A_t \geq AMC2 \quad [5.12]$$

Antecedent moisture (A_t) is calculated as the amount of liquid water (rainfall, irrigation or snowmelt) entering the turfgrass system over 5 days preceding day t . Antecedent moisture limits vary for growing and dormant conditions of the turf.

Values for these limits were calibrated by Haith and Andre (2000) to reflect runoff from turf, and are AMC1 = 13 and 22 mm for dormant and growing seasons, respectively, and AMC2 = 28 and 53 mm for dormant and growing seasons, respectively.

CN1 (the curve number for very dry conditions) and CN3 (the curve number for very wet conditions) are related to CN2 (the curve number for average conditions) through equations from Hawkins (1978):

$$CN1 = \frac{CN2}{2.334 - 0.01334CN2} \quad [5.13]$$

$$CN3 = \frac{CN2}{0.4036 + 0.0059CN2} \quad [5.14]$$

If snowmelt occurs on day t , the upper layers of soil are assumed to be saturated, and CN_t is set to CN3 in order to reflect this in the estimation of runoff.

Using these equations, a single parameter (CN2) is required for the runoff model. Values suggested by Haith and Andre (2000), based on turf and soil conditions, are shown in Table 5.1.

Table 5.1. Curve numbers for turfgrass at average antecedent moisture (CN2).

Cover condition	Soil hydrologic group			
	A	B	C	D
Short grass (lawns < 50mm, fairways, tees, greens)				
Poor condition (cover < 50%)	68	79	86	89
Fair condition (cover 50 – 75%)	49	69	79	84
Good condition (cover > 75%)	39	61	74	80
Tall, dense grass (lawns ≥ 50mm, roughs)	30	58	71	78
Thatched short grass	35	55	67	72
Thatched tall grass	27	52	64	70

Haith and Andre (2000)

Pesticide infiltration and runoff from turf

Dissolved pesticide can be lost in runoff and infiltration (from the turf into the soil). These losses are determined by equations similar to those developed by Haith (2001), which are repeated for compartments 1 and 2 as both are affected by infiltration and runoff processes.

Dissolved pesticide is determined by assuming a linear instantaneous equilibrium between adsorbed and dissolved concentrations of the pesticide:

$$a_t = K d_t \quad [5.15]$$

where a_t is the concentration of the pesticide adsorbed to foliage and thatch dry matter on day t ($\mu\text{g g}^{-1}$), d_t is the concentration of the pesticide dissolved in water on day t ($\mu\text{g cm}^{-3}$), and K is the partition coefficient between the solid and dissolved phases of the pesticide ($\text{cm}^3 \text{g}^{-1}$).

Pesticide mass in compartment 1 can be divided into adsorbed ($A_{1,t}$, g ha^{-1}) and dissolved ($D_{1,t}$, g ha^{-1}) fractions as:

$$P_{1,t} + \Delta P_t = A_{1,t} + D_{1,t} \quad [5.16]$$

Equations [5.15] and [5.16] can be combined as:

$$P_{1,t} + \Delta P_t = a_{1,t} S \times 10^{-3} + d_{1,t} W_t \times 10 \quad [5.17]$$

$$P_{1,t} + \Delta P_t = K d_{1,t} S \times 10^{-3} + d_{1,t} W_t \times 10 \quad [5.18]$$

where W_t is the amount of water in the turf on day t (mm), and S is the mass of solids in the turf, estimated as the foliage and thatch dry matter (kg ha^{-1}). Solving Eq. [5.18] for $d_{1,t}$, and using it in Eq. [5.16] to determine an expression for $D_{1,t}$ gives:

$$D_{1,t} = \frac{(P_{1,t} + \Delta P_t) W_t}{K S \times 10^{-4} + W_t} \quad [5.19]$$

Dissolved pesticide is split between infiltration and runoff by assuming a 2-stage process in which infiltration precedes runoff. The amount of water for pesticide infiltration is $R_t + IR_t + M_t - Q_t$, and water for runoff is Q_t (all in mm). Replacing

these amounts for W_t in Eq. [5.19], and by writing K as K_{oc} (the pesticide's organic carbon partition coefficient, $\text{cm}^3 \text{g}^{-1}$) and expressing S as the organic carbon content (OC, kg ha^{-1}) of the foliage and thatch, the mass of pesticide infiltrated can be expressed as:

$$PI_{1,t} = \frac{(P_{1,t} + \Delta P_{1,t})(R_t + IR_t + M_t - Q_t)}{0.0001 K_{oc} OC + (R_t + IR_t + M_t - Q_t)} \quad [5.20]$$

When infiltration has occurred, the mass of dissolved pesticide is reduced by $PI_{1,t}$, and the following equation can be written for pesticide loss in runoff:

$$PQ_{1,t} = \frac{(P_{1,t} + \Delta P_{1,t} - PI_{1,t}) Q_t}{0.0001 K_{oc} OC + Q_t} \quad [5.21]$$

Equations for compartment 2 are identical, with subscripts 1,t replaced by 2,t.

Organic carbon partition coefficients are available in publications of pesticide chemical properties (ARS 2006, Tomlin 2003), and OC can be estimated based on the height of the foliage and thickness of the thatch using the default approximations proposed by Haith (2001), as shown in Table 5.2.

Table 5.2. Default approximations to organic carbon contents of foliage and thatch.

Vegetative matter	Height (mm)	Organic carbon ($\text{kg ha}^{-1} \text{mm}^{-1}$)
Foliage	6-13	109
	14-26	85
	>26	65
Thatch		1120

Haith (2001)

Pesticide volatilization

Pesticide volatilization is estimated using the model described in Chapter 4, which is a modification of the models developed by Haith et al. (2002) and Walden

and Haith (2003). Chapter 4 developed the model for surface deposits and a sink which withdrew pesticide from the pool available for volatilization. To incorporate this model into TPM, the surface and sink deposits are redefined as compartments 1 and 2, respectively.

The model is based on relating pesticide volatilization to potential evapotranspiration (PET) using ratios of water and chemical saturated vapor pressures and latent heats of vaporization. Pesticide volatilization (PV_t , $g\ ha^{-1}$) is estimated as:

$$PV_t = a R_{Vt} (P_{1,t} + \Delta P_t - PI_{1,t} - PQ_{1,t}) \quad [5.22]$$

where a is a volatilization constant (mm^{-1}), R_{Vt} is the relative volatility of the pesticide and water during period t (mm), which is given by:

$$R_{Vt} = PET_t (p_{sct} / p_{swt}) (\lambda_{wt} / \lambda_{ct}) \quad [5.23]$$

in which PET_t is the potential evapotranspiration during day t (mm); p_{sct} and p_{swt} are the saturated vapor pressures of the pesticide and water, respectively, during day t (kPa); and λ_{ct} and λ_{wt} are the latent heats of vaporization of the pesticide and water, respectively, during day t ($J\ g^{-1}$). Equation [5.23] adjusts potential evapotranspiration to account for differences in pesticide and water saturated vapor pressures and the energy required for vaporization.

Methods for computing vapor pressures and heats of vaporization as functions of temperature are given in Chapter 4. Potential evapotranspiration is calculated using the Hargreaves-Samani equation, as described by Jensen et al. (1990):

$$PET_t = 0.0023 R_{At} T_{Dt}^{1/2} (T_t + 17.8) / \lambda_{wt} \quad [5.24]$$

where T_{Dt} is the difference between the maximum and minimum temperature ($^{\circ}C$) on day t , and R_{At} is the extraterrestrial radiation on day t ($kJ\ m^{-2}$). Equations necessary to calculate R_{At} are given in Chapter 4.

Subsurface (soil) processes.

The soil process model is based on two coupled components: a soil water balance module and a soil pesticide balance module.

Soil water balance

Water movement is simulated as 1 dimensional, vertical flow using a capacity based approach. Soils are split into 10-mm thick computational layers for all calculations related to water and pesticide movement in the soil. Soil layers are assumed to be uniform; preferential flow is not included in the model. Water balance in a soil layer is:

$$SW_{i,t+1} = SW_{i,t} + DR_{i-1,t} - ET_{i,t} - DR_{i,t} \quad [5.25]$$

where $SW_{i,t}$ is the water content (mm) in soil layer i at the beginning of day t , $DR_{i,t}$ is the water (mm) draining from layer i during day t , and $ET_{i,t}$ is evapotranspiration (mm) from layer i on day t .

Evapotranspiration

Evapotranspiration varies according to the type of turf (cool versus warm season grasses). In general, warm season turfgrasses evapotranspire 20% less than cool season grasses, because they have greater photosynthetic efficiency and can continue to fix carbon when their stomata are closed, thus losing less water (Fry and Huang 2004). Cool season turf includes bentgrass, bluegrass, fescue and ryegrass. Warm season turf includes bermudagrass, zoysiagrass, buffalograss and St. Augustine grass. Differences in evapotranspiration are incorporated in the model by multiplying daily potential evapotranspiration by a cover coefficient (CV).

Cover coefficients vary by the type of cover, time of year, and location in the world (Hanks 1992). While generally applicable values are difficult to determine, suggestions are shown in Table 5.3.

Table 5.3. General cover coefficients for warm and cool season turfgrasses.

Turf type	Dormant season	Growing season
Warm-season	0.25	0.70
Cool-season	0.25	0.85

Values in Table 5.3 were derived from cover coefficient data reported by Allen et al. (1998), Aronson et al. (1987), Brown and Albrecht (2004), Brown and Kopec (2000), Brown et al. (1998), Brown et al. (2001), Carrow (1995), Devitt et al. (1992), Ervin and Koski (1998), Howell et al. (1998), Kopec et al. (1991), Meyer and Gibault (1987), Silva (1998), Smeal et al. (2000), Smeal et al. (2005), Snyder (1986), Walker and Kah (1987), and the Northern Colorado Water Conservancy District (2007). The data were classified according to dormant or growing season, and median values were used for the growing season. Dormant season values assume that the turfgrass is fully dormant in the winter, and that water loss to the atmosphere is due to direct evaporation from the soil. As foliage and thatch cover the soil, evaporation is usually low, which is reflected in the dormant season CV values. However, in areas where cool season turfgrass continues to grow during the winter (as in the south western U.S.), the cover coefficient for cool season turfgrass should increase to 0.65 to account for plant transpiration.

A second limitation to evapotranspiration is that water extraction from small soil pores requires more energy than extraction from large soil pores. To approximate this, TPM uses a soil moisture factor (SM_i). The soil moisture factor varies linearly between the wilting point and 50% of the available water capacity of the layer of soil,

as proposed by Hanks (1974). The approach is similar to the soil moisture effects used in other water balance models (Haith and Loehr, 1979, Carsel et al. 2003).

$$\begin{aligned}
 SM_{i,t} &= (SW_{i,t} + DR_{i-1,t} - 10 \theta_{WPi}) [2/(10 \theta_{FCi} + 10 \theta_{WPi})] & [5.26] \\
 &\text{for } 10 \theta_{WPi} < SW_{i,t} + DR_{i-1,t} < (10 \theta_{FCi} + 10 \theta_{WPi})/2 \\
 &= 1 & \text{for } SW_{i,t} + DR_{i-1,t} \geq (10 \theta_{FCi} + 10 \theta_{WPi})/2 \\
 &= 0 & \text{otherwise.}
 \end{aligned}$$

where θ_{FCi} and θ_{WPi} are the volumetric field capacity and wilting points for layer i (mm mm^{-1}). Both are multiplied by 10 as soil layers are 10 mm thick. The soil moisture factor is shown in Figure 5.4.

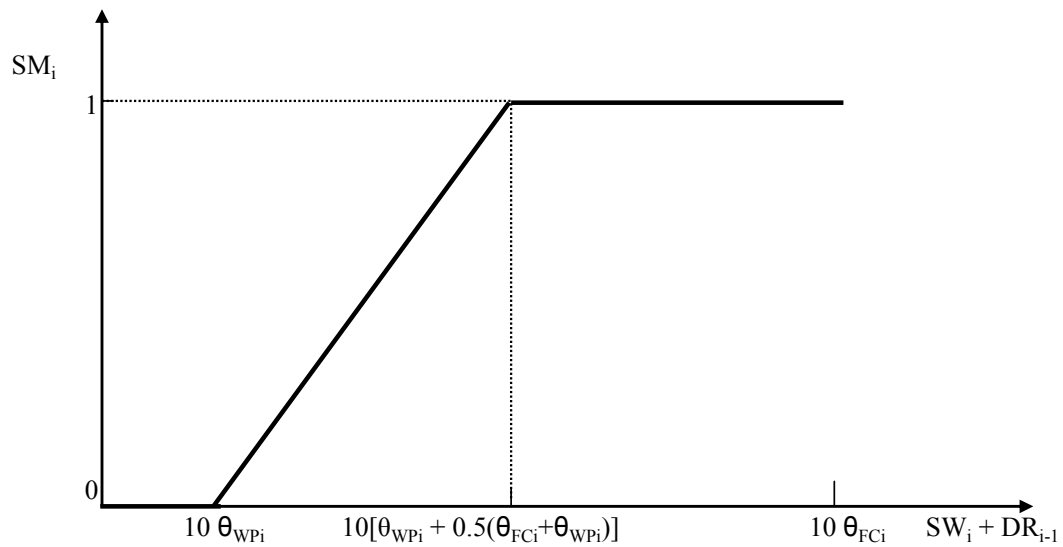


Figure 5.4. Soil moisture factor.

Evapotranspiration is also dependent on the presence of roots in a soil layer. The effect of the root distribution is approximated by assuming a decrease in water uptake by roots with depth, based on an exponential model of the root density in the soil described by Gerwitz and Page (1974):

$$P_i = 100 (1 - \exp(-b Z_i)) \quad [5.27]$$

where P_i is the percentage of root mass occurring between the soil surface and depth Z_i (mm), and b is a constant such that $1/b$ is the depth of soil which contains 63% of the total root mass. Experimental observations (Carroll 1989, R. Green pers. comm., Jordan et al. 2003, Roy et al. 2000, Silva 1988, Suarez-Rey et al. 2000) suggest a default value for b of 80 mm for turf.

An expression for the fraction of the total root mass within any 10-mm thick layer of soil may be derived from Eq. [5.27]:

$$RF_i = \exp(-b 10(i - 1)) - \exp(-b 10i) \quad [5.28]$$

where RF_i is the fraction of the total root mass for soil layer i , which starts at depth $10(i - 1)$ and ends at depth $10i$, with depths in mm and i as an integer denoting each soil layer, starting with $i = 1$ as the topmost layer.

The amount of water uptake from each layer of soil is proportional to the fraction of roots present in each 10-mm thick layer of soil, based on a model by Feddes et al. (2001):

$$S_{i,t} = RF_i CV_t PET_t \quad [5.29]$$

where $S_{i,t}$ is the maximum amount of water uptake that can occur from layer i on day t (mm), which depends on the fraction of root mass occurring in layer i (RF_i) and the evapotranspirative demand on day t ($CV_t PET_t$). Similar approaches to water uptake based on root density have been used by Timlin et al. (2001) and in the GAPS soil-plant-atmosphere model (Rossiter and Rhia 1999).

The final limitation to evapotranspiration from a layer of soil is that water content can not fall below the volumetric wilting point for the layer.

Combining the above constraints to water extraction from the soil, evapotranspiration from each soil layer is determined as:

$$ET_{i,t} = \min[(SW_{i,t} + DR_{i-1,t} - 10 \theta_{WPi}) SM_{i,t}, S_{i,t}] \quad [5.30]$$

This equation states that evapotranspiration from a soil layer is the minimum of the available water that can be extracted from a layer (after the soil moisture factor has been applied) and the amount of water that can be extracted by the roots from that layer in order to satisfy daily evapotranspiration demand.

Water flow in the soil

Water flow through the soil is modeled using a capacity based approach, in which water that exceeds the volumetric field capacity of the layer after evapotranspiration has occurred drains into the layer below:

$$\begin{aligned} DR_{i,t} &= SW_{i,t} + DR_{i-1,t} - ET_{i,t} - 10 \theta_{FCi} \quad \text{for } SW_{i,t} + DR_{i-1,t} - ET_{i,t} > 10 \theta_{FCi} \\ &= 0 \quad \text{otherwise} \end{aligned} \quad [5.31]$$

Drainage Eq. [5.31] is solved by setting $DR_{1,t}$ equal to the water entering the top layer of soil, determined as the difference between liquid water entering the turf system (i.e. rainfall, irrigation and snowmelt) and runoff:

$$DR_{1,t} = R_t + IR_t + M_t - Q_t \quad [5.32]$$

Drainage is assumed to occur within the model's daily timestep. This is adequate for shallow and well drained soil profiles, but is likely to overestimate drainage and pesticide leaching from deep or poorly drained soils.

Pesticide leaching through the soil

Infiltration moves pesticides from the turf into the top layer of soil. Portions of the pesticide travel through the soil layers, coupled with water drainage, and may leach from the bottom of the soil profile into groundwater. Within the soil, pesticides are subject to microbial decay and retention in the soil via adsorption to organic matter. The mass balance equation for pesticide in a layer of soil is:

$$PS_{i,t+1} = (PS_{i,t} + PL_{i-1,t} - PL_{i,t}) \exp(-\alpha_i) \quad [5.33]$$

where $PS_{i,t}$ is the pesticide mass in soil layer i (g ha^{-1}) at the beginning of day t , $PL_{i,t}$ is the pesticide leached from layer i (g ha^{-1}) during day t and α_i is the decay rate for layer i . In Eq. [5.33], pesticide leaching occurs first, and then microbial decay affects the pesticide remaining in the layer. Pesticide entering the top layer of soil is:

$$PL_{1,t} = PI_{1,t} + PI_{2,t} \quad [5.34]$$

with $PI_{1,t}$ and $PI_{2,t}$ (the amount of pesticide infiltrated from compartments 1 and 2 in the turf to the soil, g ha^{-1}), as determined by Eq. [5.20].

If the amount of water in layer i exceeds the volumetric field capacity of that layer, excess water drains to the layer below (Eq. [5.31]), transporting a fraction of the dissolved pesticide with it:

$$PL_{i,t} = \frac{DR_{i,t}}{SW_{i,t} + DR_{i-1,t}} Ds_{i,t} \quad \text{for } SW_{i,t} + DR_{i-1,t} > \theta_{FCi} \quad [5.35]$$

$$= 0 \quad \text{otherwise}$$

where $Ds_{i,t}$ is the mass of pesticide dissolved in the water contained in layer i on day t (g ha^{-1}), and is determined following the derivation presented in equations [5.15] to [5.19] to obtain:

$$Ds_{i,t} = \frac{W_{i,t} (PS_{i,t} + PL_{i-1,t})}{K_i \rho_i + W_{i,t}} \quad [5.36]$$

where $W_{i,t}$ is the water available for pesticide partitioning into dissolved and adsorbed fractions in layer i on day t (mm), and ρ_i is the bulk density of the soil in layer i (g cm^{-3}). The amount of water available for pesticide partitioning into dissolved and adsorbed fractions is the amount of water in the layer after drainage from the layer above has entered it, but before evapotranspiration or drainage to the layer below have occurred. This allows water and pesticide entering layer i during day t to mix completely with the pesticide and water present in the layer at the beginning of day t .

Evapotranspiration is assumed to remove pure water from the soil. Thus, the amount of water available for pesticide mixing and distribution is:

$$W_{i,t} = SW_{i,t} + DR_{i-1,t} \quad [5.37]$$

The pesticide partition coefficient K_i ($\text{cm}^3 \text{g}^{-1}$) in Eq. [5.36] can be estimated from the pesticide's organic carbon partition coefficient (K_{oc}) and the organic carbon content of the soil layer (OC_i , % by mass):

$$K_i = K_{oc} OC_i / 100 \quad [5.38]$$

K_{oc} values are reported for many pesticides in databases such as the ARS Pesticide Properties Database (ARS 2006) and The Pesticide Manual (Tomlin 2006). The organic carbon content of a layer can be estimated from its organic matter content by assuming that 59% of it is organic carbon (Brady 1974, Weber et al. 2000).

Maximum soil depth simulated by TPM is 1000 mm. Pesticides leaching from the bottom layer of soil are assumed to enter shallow groundwater, or, as is more common in golf courses, a drainage system which returns the percolate to surface waters.

Pesticide decay in soil

Pesticide decay in soil is modeled as a first order process, but the rate α_i (from Eq. [5.33] varies according to the depth of the layer. This is an approximation to the effects of diminishing microbial population with depth and its effect on pesticide decay (Wauchope et al. 2004).

The depth effect is a modified version of the function used in the ARS RZWQM model (Wauchope et al. 2004). In RZWQM, the aerobic soil half life is used for the top 250 mm of soil. Between 250 and 1000 mm depth, half life increases linearly to 10 times the soil aerobic half life. The RZWQM model was developed for agricultural systems, in which the soil is regularly tilled, mixing and aerating the top

250 mm of soil. In turf systems, however, soil is not tilled and it seems likely that half lives will decline linearly over the entire 1000 mm depth.

An example of the effect of depth on the pesticide's half-life, as modeled in RZWQM and TPM is shown in Figure 5.5, for a soil aerobic half-life = 25 d.

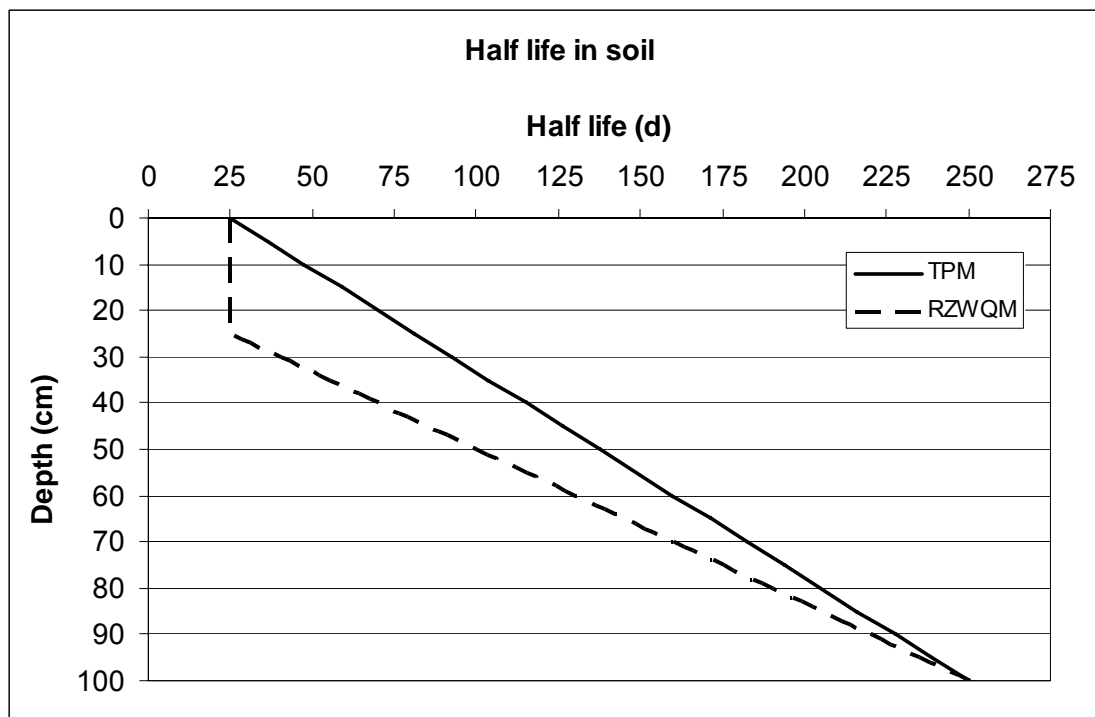


Figure 5.5. An example of the effect of depth on the half-life of a pesticide.

Resulting half-life values are transformed to decay rates for each layer of soil as $\alpha_i = \ln(2)/HL_i$, where HL_i is the half-life resulting from the linear adjustments described previously. Values for α_i are then used in Eq. [5.33] to reduce the pesticide mass in each soil layer from one daily timestep to the next.

Aerobic soil half-lives can be found for many pesticides in publications, such as the ARS Pesticide Properties Database (ARS 2006) and The Pesticide Manual (Tomlin 2006).

Data requirements

A list of input parameters required by the model is provided in Table 5.4.

Table 5.4. Model parameters.

Parameter name	Symbol	Units
Pesticide properties:		
Decay rate on turf	k_d	d^{-1}
Transfer rate from compartment 1 to 2	k_t	d^{-1}
Aerobic half-life in soil	hl_s	d
Organic carbon partition coefficient	K_{oc}	$cm^3 g^{-1}$
Volatilization constant	a	mm^{-1}
Vapor pressure	VP	kPa
Molecular weight	M	dimensionless
Vapor pressure parameter	m	dimensionless
Site conditions:		
Curve number for average moisture condition	CN2	dimensionless
Antecedent moisture limit 1	AMC1	mm
Antecedent moisture limit 2	AMC2	mm
Site latitude	ϕ	radians
Soil volumetric field capacity	θ_{fc}	$mm^3 mm^{-3}$
Soil volumetric wilting point	θ_{wp}	$mm^3 mm^{-3}$
Soil organic carbon content	OC	% by weight
Soil bulk density	ρ	$g cm^{-3}$
Turf conditions:		
Cover coefficients	CV	dimensionless
Organic carbon content of foliage and thatch	OC	$kg ha^{-1}$
Root factor	b	mm^{-1}

Weather data requirements consist of daily maximum and minimum air temperatures and daily water inputs (i.e. precipitation + irrigation). Finally, an indication of growing and dormant seasons must be provided on a monthly basis, and can be determined by the median dates of the first freeze and last frost for the site (Haith and Duffany 2007).

The model has been designed to require relatively few input parameters. Pesticide physical and chemical properties can be obtained from published pesticide property databases. Values for parameters specific to turf and soil conditions may be measured at the site or estimated based on default methods.

SUMMARY

The turf pesticide model was designed to predict pesticide losses from turf systems due to volatilization, runoff, leaching and microbial decay. Pesticides applied to turf are split into 2 compartments: surface and retained residues. Volatilization occurs from surface residues only, while infiltration and runoff occur from both compartments. Infiltration transports pesticides through the underlying soil.

Several simplifying assumptions are made: partitioning is modeled as an instantaneous, linear and reversible process, which affects pesticides in the turf and underlying soil. Soil layers are assumed to be homogeneous, preferential flow is not accounted for, and drainage through the entire soil profile is assumed to occur within 24 hours. Pesticides are assumed to mix completely in each layer before runoff, infiltration and leaching occur. These assumptions may not be equally representative of all turfgrass systems, and care should be taken when applying the model to deep soil profiles, or to soils in which preferential flow may be the predominant transport mechanism.

The model has been tested using several datasets which represent diverse turf, soil, management and climatic conditions. Results are reported in Chapter 6. The model provides an engineering tool that may be useful in water quality, turfgrass management, total maximum daily load and other nonpoint source pollution studies concerned with human health and environmental impacts of pesticides applied to turf.

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CHAPTER 6

TURF PESTICIDE MODEL (TPM), A GENERAL FATE AND TRANSPORT MODEL FOR PESTICIDES APPLIED TO TURF: II. MODEL TESTING

Abstract

The Turf Pesticide Model (TPM) is an engineering model capable of predicting pesticide runoff, volatilization and leaching from turfgrass systems. TPM simulations may be used as a basis for risk assessment and water quality management studies. The model is described in Chapter 5. This chapter presents the datasets, procedures and results of model testing. Tests were performed for 5 pesticides and 4 soil types for leaching, 6 pesticides applied at 4 sites for runoff, and for 8 pesticides applied at 1 site for volatilization. Tests were conducted without calibrating the model, and provide a measure of performance for scenarios in which field data are unavailable for calibration. Coefficients of determination (R^2) between observed and modeled pesticide losses from the turf systems were 0.63 for pesticide leaching, 0.64 for pesticide runoff, and 0.62 for pesticide volatilization. The model requires relatively few input data, most of which are available from a variety of published sources. Default parameter values and estimation procedures are provided for site specific data relating to turf and soil conditions.

INTRODUCTION

The Turf Pesticide Model (TPM) estimates losses of pesticides applied to turf for key risk pathways. These pathways include volatilization into the atmosphere, loss in surface runoff waters, and leaching into shallow aquifers or into drainage systems which return the leachate to surface waters. Pesticide losses through these pathways

pose risks for human health via inhalation of vapors or consumption of contaminated drinking water. They also pose risks to wildlife inhabiting areas close to intensely maintained turfgrass, and to ecosystems that are affected by the quality of surface waters originating from these areas (Racke 2000).

Additional requirements for a widely applicable model are that input parameters be kept to the minimum required to adequately describe the processes involved, and that values for these parameters be available, or default values suggested in their place. The model is described in detail in Chapter 5.

Model credibility resides in the use of logical methods and assumptions in its construction, and also in the model's ability to reproduce diverse experimental data. In this chapter, the data, procedures and results of uncalibrated tests of the model are presented. Efforts were made to test the model using a wide variety of pesticides, turf, soil, climatic and management conditions. The uncalibrated tests provide a measure of the model's performance in situations where field data are unavailable for calibration, but processes in the model may be calibrated to specific situations if data is available.

METHODS

The Turf Pesticide Model was encoded in C++ to run on a daily timestep. Model inputs consist of parameters describing pesticide, turf and soil conditions. Daily weather data are the maximum and minimum air temperatures, and a daily entry for precipitation + irrigation. Model output includes the daily mass of pesticide lost in runoff, volatilized, degraded on the turf, infiltrated into the top layer of soil and leached from the bottom of the soil profile.

No datasets provided simultaneous measurements of runoff, volatilization and leaching of pesticides applied to turf. Due to this limitation, TPM was evaluated using multiple datasets, each of which provided information to test one of the loss pathways.

Field studies for drainage and pesticide leaching

Drainage volumes, pesticide leaching data and information necessary to parameterize TPM were available for two plot-scale studies. The following provides a brief description of each.

In Ithaca, NY (42.45° N), Petrovic and Larsson-Kovach (1996) studied leaching of the herbicide mecoprop (2-(4-chloro-2-methyl-phenoxy) propionic acid) using 37-cm deep lysimeters containing three distinct types of soil: sand, Arkport sandy loam (coarse-loamy, mixed, active, mesic Lamellic Hapludalf) and Hudson silt loam (fine illitic, mesic Glossaquic Hapludalf). These soils belong to soil hydrologic groups A, B and C, respectively.

Creeping bentgrass (*Agrostis palustris* Huds.) turf had been seeded 5 months prior to the application date, and was maintained at a fairway height of 12 mm throughout the experiments. Thatch was nonexistent during the trials (A. M. Petrovic, personal communication 2005). Turf organic carbon content was estimated to be 1308 kg ha⁻¹, based on the default procedure developed by Haith (2001), as given in Chapter 5. Turf was classified as fair condition for sand, and good condition for Arkport and Hudson soils (A. M. Petrovic, personal communication 2005), giving curve numbers (CN2) values of 49, 61 and 74, respectively.

Mecoprop was sprayed at a rate of 3107 g A.I. ha⁻¹ on the 24th of September 1991. An automatic rainout shelter was used to exclude natural rainfall, and irrigation schemes simulated moderate and high precipitation patterns for each soil type. Based on the median freeze/frost dates (Koss et al. 1988), the growing season for this location is from May through September. Cover coefficients of 0.25 and 0.85 were used in the dormant and growing seasons, respectively, as described in Chapter 5. Treatments were replicated four times.

Soil physical properties are given in Table 6.1. Organic matter, sand and clay percentages were taken from Petrovic and Larsson-Kovach (1996), and were used as inputs to the Soil Water Characteristics software (Saxton 2007) to determine bulk density, field capacity and wilting point.

Table 6.1. Soil physical properties for the New York leaching studies.

Soil	Bulk density (g cm ⁻³)†	Organic matter (%)	Field capacity (mm ³ mm ⁻³)†	Wilting point (mm ³ mm ⁻³)†
Sand	1.48	0.8	0.046	0.011
Arkport	1.33	4.4	0.214	0.103
Hudson	1.14	5.8	0.330	0.145

† Values estimated using Soil Water Characteristics software, based on data from Petrovic and Larsson-Kovach (1996).

As the turf had been seeded only 5 months prior to the pesticide application, the stand was described as immature: foliage density had not reached full potential and no thatch had developed. In cases such as this, the decay rate for mecoprop applied to turf developed for Chapter 2 may not be an appropriate parameter value for modeling microbial decay. Reasons for this are that the low quantities of organic matter in immature turf and mecoprop's low Koc value (18.5 cm³ g⁻¹) translate to low retention in the foliage and thatch, and high pesticide infiltration into the soil. Furthermore, enhanced degradation (which results from the microbial population adapting to use the pesticide as a source of energy after repeated pesticide applications) would not have occurred in this case as there was only one application. Due to this, the soil aerobic decay rate (0.07 d⁻¹) was used to model decay in turf and soil, instead of using the turf decay rate of 0.69 d⁻¹ (as suggested in Chapter 2).

The effect of maturing turf on pesticide leaching is evident in the results of Petrovic and Larsson-Kovach (1996), who applied mecoprop to the same turf lysimeters 3 years later in 1994. Total pesticide leached from the sand lysimeters was

10 to 100 times lower than in 1991, and was attributed to the development of dense foliage and thatch.

The second set of experiments was conducted in Riverside, CA (33.97 °N), by Wu et al. (2002 a,b). They studied leaching of the fungicides metalaxyl (methyl N-(methoxyacetyl)-N-(2,6-xylyl)-DL-alaninate) and chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) in 1995, and of the insecticides trichlorfon (dimethyl-2,2,2-trichloro-1-hydroxy-ethylphosphonate) and chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridylphosphorothioate) in 1996 and 1997. The pesticides were sprayed onto creeping bentgrass greens that were maintained at 5 mm height. Turf was well established, with 2 cm of thatch and a 3 cm matt layer. Organic carbon contents measured at the site were 6.1, 3.08 and 0.08% by mass in 1995, and 6.6, 3.4 and 0.3% in 1996, for the thatch, matt and soil layers, respectively (Wu et al. 2002 a,b).

Considering that the rooting media was a well mixed combination of sand and peat, it is somewhat surprising that its organic carbon content increased from 0.08 to 0.3% from 1995 to 1996 (an increase of 275%), especially since organic carbon in the thatch and matt layers increased by only 10% for the same time period. Assuming a bulk density of 0.1 g cm^{-3} , and organic matter content of 95% for peat, a 9:1 sand-peat mix (as used in the experiments) should have approximately 0.4% OC, suggesting that the 0.08% OC value may have resulted from sampling or lab error. Simulations for all three years were run using 0.3% OC.

Organic carbon in the turf was estimated to be 11403 kg ha^{-1} in 1995, and 12293 kg ha^{-1} in 1996 and 1997, based on the OC values measured for thatch and the default estimation procedure described in Chapter 5 for foliage. Rooting media in the lysimeters consisted of 45 cm of the 9:1 sand-peat mixture (by volume), 43 cm of pea gravel and 7 cm of gravel. Properties of the matt and soil layers are given in Table 6.2.

Table 6.2. Soil physical properties for the California leaching studies.

Soil layer	Bulk density (g cm ⁻³) [†]	Organic matter (%) [‡]	Field capacity (mm ³ mm ⁻³) [†]	Wilting point (mm ³ mm ⁻³) [†]
Matt §	1.5	5.30 / 5.85	0.114 / 0.125	0.065 / 0.073
Sand peat mix §	1.5	0.33 / 0.52	0.038 / 0.043	0.004 / 0.008
Gravel	1.6	0.00	0.003	0.003

[†] Values estimated using Soil Water Characteristics. Gravel was assumed to have 0% OM and no soil water holding capacity.

[‡] Organic matter was estimated as 1.72 times the organic carbon content (Weber et al. 2000) reported by Wu et al. (2002 a,b).

[§] First values are for 1995, the second values are for 1996 and 1997.

Turf was well established and had developed a layer of thatch, leading to a CN₂ value of 35 for all three years. Metalaxyl and chlorothalonil were applied to the same plots at rates of 1531 g A.I./ha and 12740 g A.I./ha, respectively, on Sept. 27 1995. Trichlorfon and chlorpyrifos were applied to the same plots at rates of 7650 g A.I./ha and 1530 g A.I./ha, respectively, on June 4 1996 and July 9 1997. Four replications of the experiment were performed in 1995 and 1996, and three in 1997. The growing season for this location extends from March to November (based on median freeze/frost dates from Koss et al. 1988), and cover coefficients of 0.65 and 0.85 were used for the dormant and growing seasons, respectively, as described in Chapter 5.

Experimental records were provided by A.M. Petrovic (personal communication, 2005) and by L. Wu and R. Green (personal communication, 2005) regarding irrigation dates and volumes, drainage sample dates and volumes, and pesticide concentrations in the drainage. Daily weather data (maximum and minimum air temperatures and precipitation) were obtained from the NRCC Climod database (NRCC 2006) for the weather station closest to the Ithaca site and from CIMIS (CIMIS 2006) for the station closest to the Riverside site. Irrigation information was

added to natural precipitation in constructing the weather data input files. Drainage data were converted to depths of water, and pesticide concentrations were converted to percentages of the mass applied in each experiment. Data from the replications of each experiment were averaged.

During these studies, drainage was frequently accumulated over several days before the volumes were measured and samples taken for pesticide analysis. To compare field values with model predictions, the modeled daily values of drainage and leached pesticide mass were summed to match the field sample dates. This resulted in 381 drainage events and 449 pesticide leaching events with which to test the model (2 pesticides were measured for every leachate sample taken in the Wu et al. 2002 a,b studies).

Field studies for water and pesticide runoff

Pesticide runoff data were available for 5 plot studies. The following provides a brief description of each. Soil data are not included because the CN2 value based on the soil's hydrologic class is the only soil parameter necessary for runoff estimation in TPM.

Smith and Bridges (1996) studied runoff of 2,4-D (2,4-dichlorophenoxy-acetic acid), dicamba (2,5-dichloro-6-methoxybenzoic acid) and mecoprop applied to bermudagrass (*Cynodon dactylon* (L.) Pers.) fairways in Griffin, Georgia. Plots were irrigated at 1, 2, 4 and 8 days after treatment. Similar experiments were conducted by Hong and Smith (1997) using granular and emulsifiable concentrate formulations of dithiopyr (Dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-trifluoromethyl)-3,5-pyridinedi-carbothioate). Foliage height was 15 mm for the Smith and Bridges (1996) experiments, and 40 mm for the Hong and Smith (1997) experiments. Thatch was just beginning to form on the plots and a thatch thickness of 1 mm was assumed (Haith,

2001). Turf organic carbon was estimated to be 2395 kg ha⁻¹ for the Smith and Bridges experiments, and 3720 kg ha⁻¹ for the Hong and Smith experiments. Underlying soil was a Cecil sandy clay loam (fine, kaolinitic, thermic Typic Kanhapludult), classified as Hydrologic Soil Group B, However, class C was used in the simulations due to a flow restricting layer causing poor drainage (Haith 2001). Turf and soil conditions gave a CN2 value of 74 for all the experiments. The growing season for this location extends from April to October.

Evans et al. (1998) measured diazinon (*O,O*-diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate) runoff from tall fescue (*Festuca arundinacea* Schreb.) in Lexington, KY. Grass height was between 76 and 102 mm, and no thatch existed on the plots. Turf organic carbon was estimated to be 5785 kg ha⁻¹. Underlying soil was a Maury silt loam (fine, mixed, semiactive, mesic Typic Paleudalf), classified as soil group B, giving a CN2 value of 58. The growing season for this location lasts from May to October. Plots were irrigated at 3 rates prior to pesticide application (0 mm, 6.4 mm, and 12.4 mm). Immediately after application, the plots were irrigated with 96 mm water and the runoff was captured.

Cole et al. (1997) studied chlorpyrifos (*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate), 2,4-D, dicamba and mecoprop runoff from bermudagrass in Stillwater, OK. Turf was 13 mm high with no thatch (Haith 2001). Turf OC was estimated to be 1417 kg ha⁻¹. The underlying soil was a Kirkland silt loam (fine, mixed, superactive, thermic Udertic Paleustoll), classified as soil group D, giving a CN2 value of 80. Conditions for the July experiments were very dry, whereas 165 mm rainfall occurred prior to the August experiments. All experiments were conducted during the growing season (May to October).

Studies conducted at State University, PA were reported by Linde et al. (1995) and Watschke et al. (2000). Runoff data for mecoprop were captured for 2 irrigation

events (10 and 24 June 1992). Two turfs were used: a creeping bentgrass (*Agrostis stolonifera* L.) with dense foliage and 2 mm of thatch, and ryegrass (*Lolium perenne* L.) with no thatch. Both were maintained at 19 mm height. Turf OC was estimated to be 3855 kg ha⁻¹ for the bentgrass and 1615 kg ha⁻¹ for the ryegrass experiments. Underlying soil was a Hagerstown clay (fine, mixed, semiactive, mesic Typic Hapludulf), classified as soil group C. The CN2 values used were 67 for the bentgrass and 74 for the ryegrass experiments.

These datasets provided 55 runoff events, of which 52 events were analyzed for pesticides in the runoff. Runoff volumes were converted to heights of water, and pesticide concentrations were converted to percentages of the applied rates of each pesticide. Weather data were obtained from the nearest weather station to each location from the NRCC Climod database (NRCC 2006). Water applications given in Haith and Andre (2000) were used to construct weather input files for each experiment.

Field studies for pesticide volatilization

Volatilization studies reported by Haith et al. (2002) were conducted at South Deerfield, MA. Experimental design and sampling methods are as described in Murphy et al. (1996 a,b). Turf was a well established creeping bentgrass maintained at 13 mm high. Thatch thickness varied between 10 and 15 mm. Turf organic carbon was estimated to be 15417 kg ha⁻¹ (assuming an average thatch thickness of 12.5 mm). Underlying soil was a Hadley silt loam (coarse-silty, mixed, superactive, nonacidic, mesic Typic Udifluvents), classified as soil hydrologic group B. The CN2 value used for all experiments was 55. Irrigation was applied as necessary to avoid drought, but specific data were not available, and only natural precipitation was included in the simulations. Concentrations of volatile residues of eight pesticides were collected

using a high volume air sampler and the theoretical profile shape method was used to estimate volatilization mass fluxes (Murphy et al. 1996a,b, Wilson et al. 1982). Eight pesticides were applied in 11 experiments that were conducted during the 1995, 1996 and 1997 growing seasons. Ethoprop was applied in seven of the experiments, isofenphos in six, and bendiocarb, carbaryl, chlorpyrifos, diazinon, isazofos, and trichlorfon were each applied in four of the experiments.

Volatilization losses were converted to percentages of the mass applied in each experiment. These datasets provided 123 daily volatilization values (isazofos and trichlorfon were used in Chapter 4 to calibrate the volatilization model, and are excluded from the results presented here).

Pesticide parameter values used for model testing

Parameter values for the pesticides used to test the model are given in Table 6.3. Most of the pesticides were applied as sprays, but granular formulations were used in the following experiments: chlorpyrifos in 1 runoff experiment in Oklahoma, diazinon in 3 runoff experiments in Kentucky, and dithiopyr in 1 runoff experiment in Georgia. Knowledge of solid or liquid formulation of the pesticide was used to determine the vapor pressure parameter m , which has values of 0.19 for liquids and 0.8 for solids, and was used in estimating volatilization.

All model simulations were run using the default value of 80 mm for parameter b used in the root fraction in each layer to estimate evapotranspiration from the soil.

Table 6.3. Pesticide parameter values.

Pesticide	Decay rate on turf (d ⁻¹)	Transfer rate (d ⁻¹)	Soil aerobic half life (d)	Koc (cm ³ g ⁻¹)	Molecular weight	Vapor pressure (kPa)	VP reference temp (°C)
2,4-D acid	0.03	0.61	7.0	48	221.04	1.90×10 ⁻⁸	25
Bendiocarb	0.04	0.61	3.5	385	223.23	4.60×10 ⁻⁶	25
Carbaryl	0.14	0.61	17.0	288	201.23	1.56×10 ⁻⁷	24
Chlorothalonil	0.15	0.61	14.2†	5000	265.92	7.60×10 ⁻⁸	25
Chlorpyrifos	0.08	0.79	30.5	9930	350.62	2.50×10 ⁻⁶	25
Diazinon	0.27	0.61	39.0	1520	304.35	1.41×10 ⁻⁵	22
Dicamba	0.43	0.61	18.0	13	221.04	1.66×10 ⁻⁶	25†
Dithiopyr	0.10	0.61	39.0†	1638‡	401.4†	5.30×10 ⁻⁷ †	25†
Ethoprop	0.04	0.61	24.0	104	242.33	5.10×10 ⁻⁵	24
Isazofos	0.04	0.61	40.5	155	313.70	1.16×10 ⁻⁵	25
Isofenphos	0.04	0.80	93.0	777	345.40	2.93×10 ⁻⁷	25
Mecoprop	0.69§	0.61	10.0†	18.5†	214.65	3.10×10 ⁻⁷	20
Metalaxyl	0.09	0.61	40.0	171	279.34	7.50×10 ⁻⁷	25
Trichlorfon	0.21	0.61	6.4	15	257.44	2.67×10 ⁻⁷	20

ARS (2006).

† Tomlin (2003).

‡ Ahrens (1994).

§ A decay rate of 0.07 d⁻¹ was used for mecoprop in the Petrovic and Larsson-Kovach (1996) studies due to the immaturity of the turf.

Model performance criteria

Model performance was evaluated by comparing measured and modeled values for each leaching, runoff and volatilization event. As drainage and runoff volumes affect pesticide transport, the model's performance in these arenas was also evaluated. Performance was judged based on mean pesticide leaching, runoff, volatilization, and on mean drainage and runoff water heights for each experiment. Coefficients of determination for the measured and modeled event values were also used in the assessment.

RESULTS

Drainage

Mean drainage for the experiments conducted in New York and California are given in Table 6.4.

Table 6.4. Mean drainage results.

Experiment	Drainage (mm per event)	
	Measured	Modeled
CA 1995	0.77	0.58
CA 1996	0.60	0.35
CA 1997	0.48	0.28
NY Sand – Moderate year	0.27	0.27
NY Sand – Wet year	0.40	0.34
NY Hudson – Moderate year	1.30	1.25
NY Hudson – Wet year	1.30	1.29
NY Arkport – Moderate year	1.11	1.29
NY Arkport – Wet year	1.35	1.35
Overall mean	0.61	0.52
Overall R ² (n=381)		0.75

The sampling intervals were larger for the experiments involving Arkport and Hudson soils in New York than for the other experiments, which is the reason why

mean drainage values for those experiments are considerably larger than for any of the other experiments.

Overall, TPM underpredicted drainage by 16.1%. Considering that conditions in CA and NY were very different in terms of climate, turf, soil and season of the year in which the experiments were conducted, this result is promising.

Drainage underprediction in CA was 34%, while in NY underprediction was only 2%. This difference may be due to soil parameter estimation (CA experiments used a sand-peat mix, whereas in NY sand or native soils were used). The difference may also be due to spatially related errors in the estimation of PET using the Hargreaves-Samani equation (Allen et al. 2005), or in the accuracy of the methods used to record irrigation and weather data.

Drainage data for each event is presented in Figure 6.1.

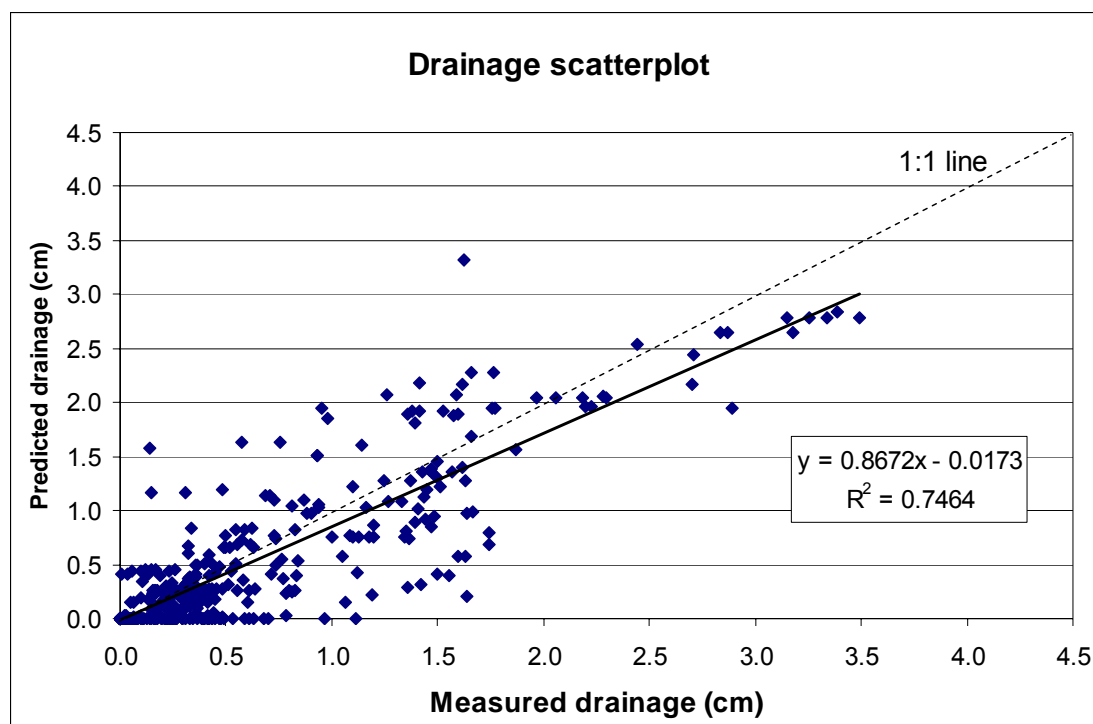


Figure 6.1. Drainage event comparison.

The model explains 75% of the variation observed in the field data, and the regression line in Figure 6.1 falls close to the 1:1 correspondence line (line of perfect fit), indicating acceptable model performance.

Pesticide leaching

Pesticide leaching results are summarized in Table 6.5.

Table 6.5. Mean pesticide leaching results.

Experiment	Pesticide leached (% per event)	
	Measured	Modeled
CA Metalaxyl 1995	0.01	0.01
CA Chlorothalonil 1995	0.00	0.00
CA Trichlorfon 1996	0.00	0.28
CA Chlorpyrifos 1996	0.00	0.00
CA Trichlorfon 1997	0.00	0.29
CA Chlorpyrifos 1997	0.00	0.00
NY Mecoprop, Sand – Moderate year	3.54	2.97
NY Mecoprop, Sand – Wet year	3.41	2.59
NY Mecoprop, Hudson – Moderate year	0.04	0.01
NY Mecoprop, Hudson – Wet year	0.07	0.02
NY Mecoprop, Arkport – Moderate year	0.06	0.04
NY Mecoprop, Arkport – Wet year	0.02	0.14
Overall mean	0.25	0.29
Overall R ² (n=449)		0.63

Overall means for measured and modeled pesticide leaching (0.25 and 0.29%, respectively) indicate that the model overpredicted overall leaching losses by 12%. The model explains 63% of the observed variation. Correspondence is good for metalaxyl, chlorothalonil and chlorpyrifos in CA. Koc values for these three pesticides range between 171 and 9930 cm³ g⁻¹. Trichlorfon experiments in CA detected essentially no leaching, whereas average model predictions were 0.28 and 0.29% of the applied amounts. These averages correspond to total pesticide losses of 12.9 and

23% of the applied mass in 1996 and 1997, respectively. In comparison to the previous three pesticides, trichlorfon has a K_{oc} of only $15 \text{ cm}^3 \text{ g}^{-1}$, indicating that it is not strongly retained to turf or soil organic carbon. A low K_{oc} value, and the model's assumption of complete mixing in each soil layer (as opposed to a retained fraction of the pesticide that does not participate in the sorbed – dissolved redistribution), may explain the model's overprediction.

The ARS Pesticide Properties Database (ARS 2006) gives a range of K_{oc} values between 2 and 38 for trichlorfon. Using 38, mean pesticide leaching decreased to 0.06 and 0.08% for 1996 and 1997, respectively, demonstrating large sensitivity of the predictions to K_{oc} in this case.

Mecoprop is similar to trichlorfon in that it also has a low K_{oc} value (18.5 d). In this case, however, the model generally underpredicted the measured values, except for the experiment involving Arkport soil under the wet year irrigation scheme. Most of the model's underprediction occurred for the sand lysimeters. They represent an extreme case, where turf was recently established from seed, no thatch had formed, and the sand had low organic carbon content. Total pesticide loss was 61.4 and 49.5% of the applied mass for the wet and moderate irrigation treatments, respectively. The model predicted total losses of 46.6 and 41.6% of the applied mass, respectively. For a pesticide as labile as mecoprop, small variations in K_{oc} or the soil organic carbon content could account for these discrepancies.

Although detailed data was not available for the 1994 studies conducted by Petrovic and Larsson-Kovach (1996), TPM simulations results based on assuming 1 mm thatch and using a turf decay rate of 0.69 d^{-1} for mecoprop were similar to the observed values (0.5% vs. 0.9% for the modeled and observed total leaching from sand lysimeters under wet year conditions, respectively, and 0.03% vs. 7.7% for the modeled and observed total leaching from sand lysimeters under moderate year

conditions, respectively). These results serve to illustrate the effect of turf organic matter and decay rates on pesticide leaching.

Pesticide leaching data for each event is presented in Figure 6.2.

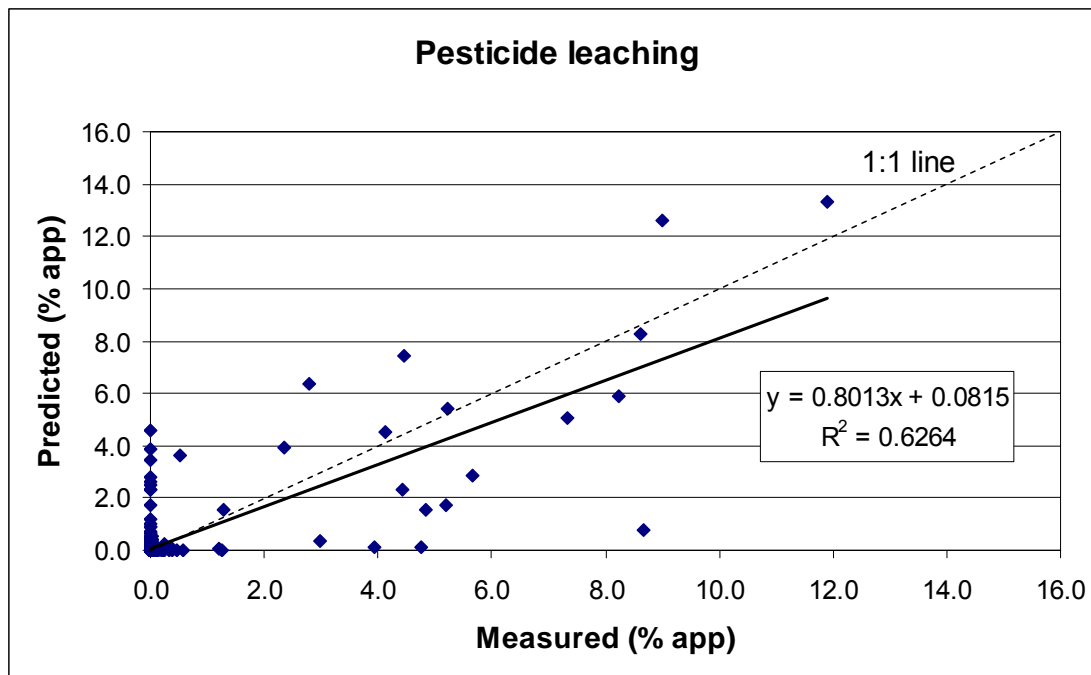


Figure 6.2. Pesticide leaching event comparison.

The regression line falls close to the 1:1 line, indicating acceptable model performance.

Runoff

Mean runoff for the experiments conducted in Georgia, Oklahoma, Kentucky and Pennsylvania are shown in Table 6.6.

Table 6.6. Mean runoff results.

Experiment	Runoff (mm per event)	
	Measured	Modeled
GA Dithiopyr G† August	9.9	10.1
GA Dithiopyr EC‡ August	11.4	10.1
GA Dithiopyr G October	4.3	11.2
GA Dithiopyr EC October	11.4	11.2
GA Avg. for 2,4-D, mecoprop, dicamba	20.2	14.6
OK July Plot C	7.2	14.1
OK August Plot C	56.0	56.1
OK August Plot I	63.0	56.1
KY 0 mm pre-irrigation	2.1	0.2
KY 6.4 mm pre-irrigation	11.2	2.4
KY 12.7 mm pre-irrigation	12.9	6.2
PA bentgrass	2.7	8.6
PA ryegrass	4.9	5.3
Overall mean	9.4	10.2
Overall R ² (n=55)		0.65

† G indicates a granular formulation of the pesticide.

‡ EC indicates an emulsifiable concentrate formulation.

Overall, the model overpredicts runoff by 9.2%, and explains 65% of the observed variation. Results are somewhat different than those of Haith and Andre (2000), although the methodology used to runoff estimation is the same. Discrepancies in the results are due to the way in which simulations of each model were run. Haith and Andre (2000) estimated runoff for discrete events by using weather data for the day of the event, and estimating antecedent moisture based on data described for each experiment. In contrast, TPM simulations were run using continuous weather data obtained from the station closest to the field site. This gave rise to some differences in antecedent moisture, which affected runoff estimation. Continuous weather data were used in the TPM simulations as it is likely that most applications of the model will be performed using weather data obtained for the weather station closest to the study site.

Measured and modeled runoff for each event is shown in Figure 6.3.

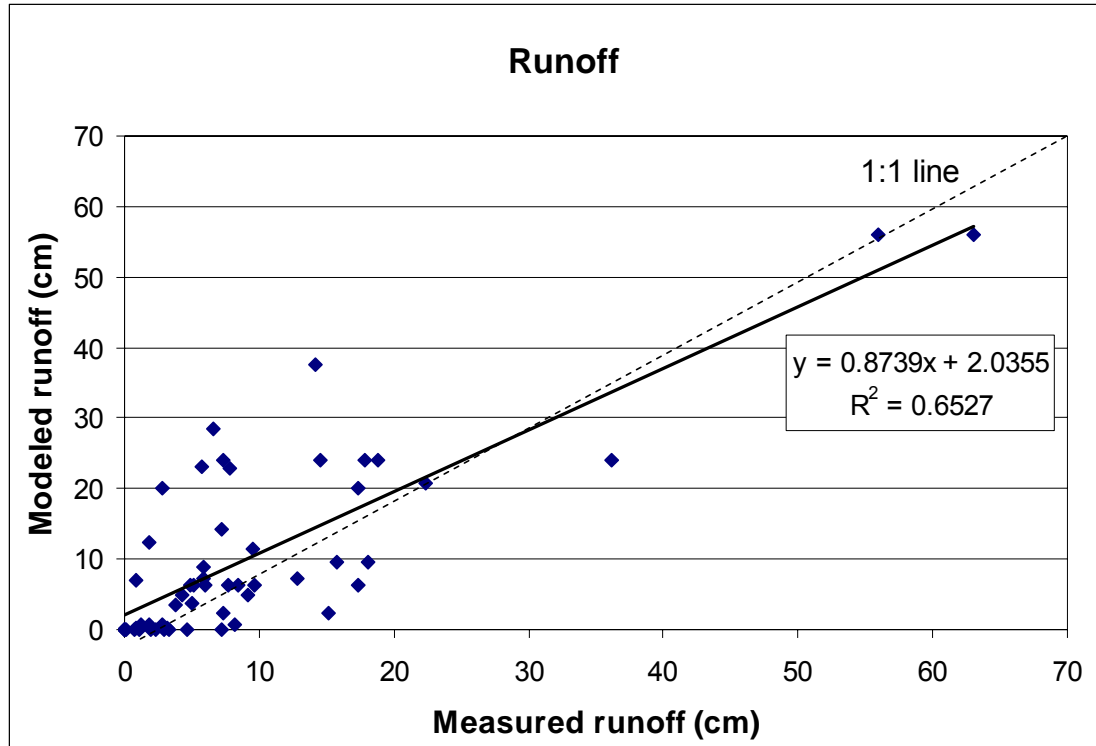


Figure 6.3. Runoff event comparison.

Pesticide runoff

Mean pesticide runoff results are compared by experiment in Table 6.7. Overall, the model overpredicted pesticide loss in runoff by 41%, and explained 64% of the variation observed in the field experiments. These results are practically identical to test results for TurfPQ, on which TPM pesticide runoff is based. The similarity between model predictions indicates that the inclusion of volatilization and the use of turf specific decay rates used in the TPM simulations, in addition to the differences in the weather files did not have a large impact on the estimation of pesticide runoff for these experiments ($R^2 = 0.92$ between TurfPQ and TPM pesticide runoff results).

Table 6.7. Mean pesticide in runoff.

Experiment	Pesticide in runoff (% applied)	
	Measured	Modeled
GA Dithiopyr G (Aug.)	0.27	1.10
GA Dithiopyr EC (Aug.)	0.49	1.10
GA Dithiopyr G (Oct.)	0.14	0.94
GA Dithiopyr EC (Oct.)	0.40	0.94
GA Avg. 2,4-D	2.23	4.96
GA Avg. Dicamba	3.50	1.37
GA Avg. Mecoprop	3.20	1.41
OK July – Plot C 2,4-D	3.10	6.07
OK July – Plot C Chlorpyrifos	0.14	0.95
OK July – Plot C Dicamba	1.40	2.30
OK July – Plot C Mecoprop	3.00	3.09
OK August – Plot C 2,4-D	9.80	20.40
OK August – Plot C Chlorpyrifos	0.94	4.22
OK August – Plot C Dicamba	5.60	7.20
OK August – Plot C Mecoprop	10.00	9.80
OK August – Plot I 2,4-D	8.60	20.40
OK August – Plot I Chlorpyrifos	0.52	4.22
OK August – Plot I Dicamba	4.50	7.20
OK August – Plot I Mecoprop	8.50	9.80
KY 0mm pre-irrig. Diazinon G	0.17	0.02
KY 6.4mm pre-irrig. Diazinon G	0.96	0.24
KY 12.7mm pre-irrig. Diazinon G	1.14	0.64
KY 0mm pre-irrig. Diazinon EC	0.13	0.02
KY 6.4mm pre-irrig. Diazinon EC	0.99	0.24
KY 12.7mm pre-irrig. Diazinon EC	0.69	0.64
PA bentgrass Mecoprop	0.67	1.93
PA ryegrass Mecoprop	2.67	1.18
Overall mean	2.08	2.94
Overall R ² (n=52)		0.64

Measured and modeled pesticide in each runoff event is shown in Figure 6.4.

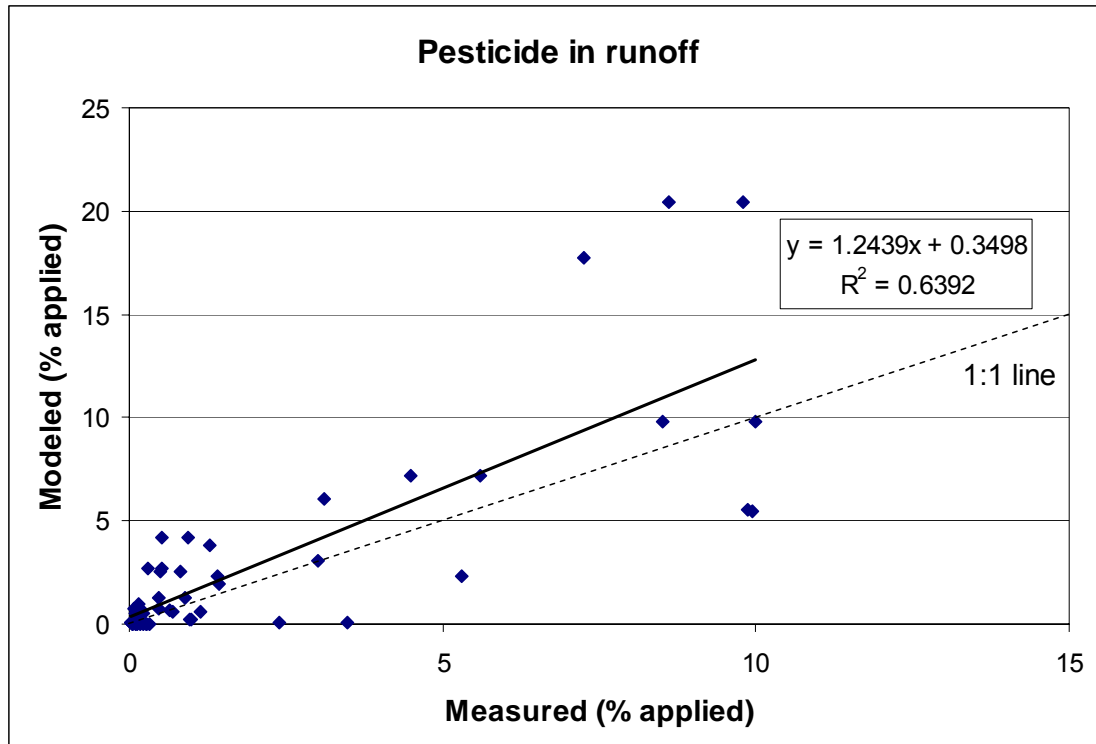


Figure 6.4. Pesticide in runoff.

The scatterplot in Figure 6.4 is very similar to that shown in Haith (2001), with the exception of some points which changed due to the differences in simulations of both models (as explained previously).

Model predictions exceeding 20% of the applied amount are for 2,4-D in the OK studies. Chlorpyrifos runoff was also overestimated in these studies, while dicamba and mecoprop were not. Runoff volume was overestimated for the OK July experiment on plot C, correctly predicted for the August experiment on plot C, and underpredicted for the August experiment on plot I (Table 6.6). Given these results, a possible explanation for the overprediction of 2,4-D and chlorpyrifos in all 3 experiments relates to the pesticides' Koc values ($48 \text{ cm}^3 \text{ g}^{-1}$ for 2,4-D, 9930 for chlorpyrifos, 13 for dicamba and 18.5 for mecoprop). Chlorpyrifos was the most severely overpredicted (by factors of 4.5 and 8), followed by mecoprop (by factors of 2 to 2.4). This seems to indicate that overprediction errors may be related to the

assumption of complete mixing in turf before infiltration or runoff occur, which may not be true for pesticides as strongly retained as chlorpyrifos (high K_{oc} value).

Overpredictions of other pesticides were not as high, with the exception of dithiopyr in the GA experiments. Overprediction was higher for the granular formulation, but the model did overpredict pesticide runoff for the emulsifiable formulation as well. This may be due to parameterization of the pesticide's chemical properties, and also to the assumption that granular formulations are completely available for mixing when water enters the system.

Pesticide volatilization

Average pesticide volatilization losses are compared for each experiment conducted in Massachusetts in Table 6.8. Overall volatilization is overpredicted by 33.7%, and is largely due to overpredictions for ethoprop, as shown in Figure 6.5.

In Figure 6.5, points inside the dashed rectangle are from ethoprop volatilization occurring on the first day during 5 of the 7 experiments in which ethoprop was applied. These points are largely responsible for the model's general overprediction of pesticide volatilization. As discussed in Chapter 4, better results may be achieved by calibrating the model for each pesticide. The goal of the tests presented here, however, was to provide an assessment of the model's uncalibrated performance, as it is likely that simulations conducted for risk, total maximum daily load and water quality studies will not have data available for model calibration.

Table 6.8. Mean pesticide volatilization.

Experiment	Volatilization (% applied)	
	Measured	Modeled
Bendiocarb 95-2	0.31	0.62
Bendiocarb 95-4	0.60	0.59
Bendiocarb 95-6	0.30	0.50
Bendiocarb 96-2	0.28	0.58
Diazinon 95-1	3.40	2.11
Diazinon 95-3	1.74	3.12
Diazinon 95-5	1.38	2.91
Diazinon 96-1	2.30	1.37
Ethoprop 95-1	4.43	5.77
Ethoprop 95-3	2.85	7.99
Ethoprop 95-5	2.00	7.49
Ethoprop 96-1	4.77	4.16
Ethoprop 97-1	5.59	9.00
Ethoprop 97-2	3.88	11.53
Ethoprop 97-3	4.04	9.53
Carbaryl 95-2	0.07	0.06
Carbaryl 95-4	0.08	0.06
Carbaryl 95-6	0.05	0.05
Carbaryl 96-2	0.05	0.06
Chlorpyrifos 95-1	2.73	1.07
Chlorpyrifos 95-3	1.38	1.69
Chlorpyrifos 95-5	1.29	1.52
Chlorpyrifos 96-1	1.49	0.63
Isofenphos 95-3	0.05	0.19
Isofenphos 95-5	0.16	0.16
Isofenphos 96-1	0.31	0.06
Isofenphos 97-1	0.90	0.16
Isofenphos 97-2	0.74	0.25
Isofenphos 97-3	0.68	0.19
Overall mean	1.61	2.42
Overall R ² (n=159)		0.62

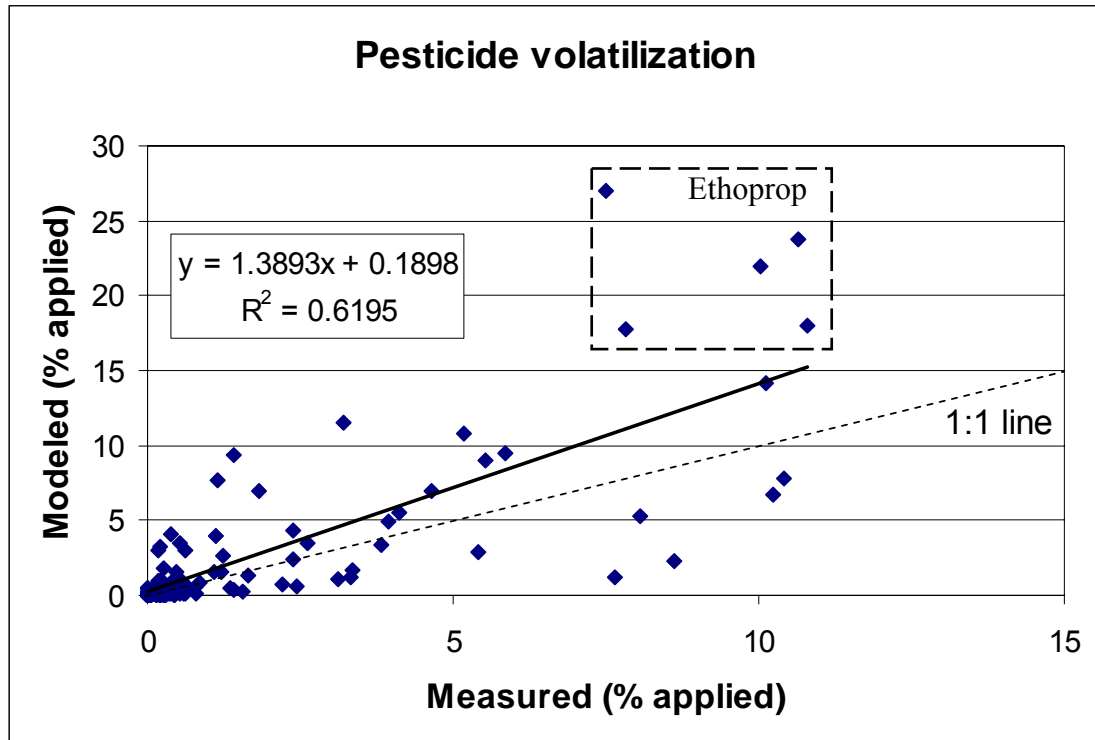


Figure 6.5. Pesticide volatilization.

CONCLUSIONS

The model performs reasonably well in terms of predicting pesticide loss in runoff, leaching and volatilization from turf systems. It also appears to provide adequate estimates of runoff and drainage volumes. Test results indicated that the model explains 75% of the observed variation in drainage, 63% for pesticide leaching, 65% for runoff volumes, 64% for pesticide loss in runoff, and 62% for pesticide volatilization. Considering that the model requires relatively few input parameter values, that the results arose from uncalibrated simulations, and that a wide variety of pesticides, turf, soil and climatic conditions were used in the tests, the model appears to perform satisfactorily under varied scenarios. It is possible that better results could be obtained by calibration the model with specific site data.

Given its relatively modest data requirements and adequate test results, TPM could be used for impact and risk assessment, total maximum daily load, and other water and environmental quality studies involving pesticides applied to turf. As an example, regional analyses of pesticide runoff from turf (such as that of Haith and Duffany 2007) could be expanded to include leaching and inhalation impacts.

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CHAPTER 7

CONCLUSIONS

In this chapter a summary of the chapters are provided, followed by the main conclusions arising from this research.

The literature review in Chapter 2 presents evidence that microbial decay is the major pathway of pesticide dissipation in turf. Analysis of dissipation studies from turf produced a set of half-lives that demonstrates that pesticide dissipation is considerably faster in well established turf than in soil. Use of these turf dissipation half-lives to represent microbial decay in simulation studies seems justified by evidence of large, highly active and adaptable microbial populations residing in the foliage and thatch layers of mature turf and their adaptability to use pesticides as sources of energy. However, care should be taken as these dissipation values are not likely to be representative of microbial decay for pesticides that are weakly sorbed to foliage and thatch, or in situations where the turf is not fully established and the microbial populations have not adapted to using the pesticide as a source of energy. Immature stands of turf are likely to produce higher pesticide losses to the surrounding environment, and reentry risks during the first few days after application may be considerable.

The hypothesis that the use of half-lives based on pesticide behavior in soils may lead to overestimation of runoff, volatilization and infiltration losses was tested in Chapter 3. Long term simulations showed considerably differences in the amounts of pesticide infiltrated and decayed when soil and turf half-lives were used to model pesticide persistence in the foliage and thatch layers. The results also indicated that the persistence of pesticides of low K_{oc} that have large differences between the soil

aerobic and the turf half-lives should be modeled with care, as decay rates based on dissipation from turf may overestimate pesticide decay. In these cases (as demonstrated in Chapter 6) the use of soil half-lives to model pesticide persistence may be advisable as this can lead more conservative estimates of pesticide transport from the system.

In Chapter 4, a surface deposit model for pesticide volatilization from turf was developed by adapting a previously developed model to incorporate surface and retained pesticide fractions. The approach used in developing the model was justified by several studies of dissipation of dislodgeable residues (sampled from the surface of the foliage) and pesticide volatilization. Default rates for the transfer between surface and deposited residues were developed based on selected dissipation rates (for pesticides with high K_{oc} and low vapor pressure), which were corrected for the effects of microbial decay. These rates were used to model daily volatilization for 6 pesticides. While the surface deposit model overpredicted volatilization (largely due to overpredictions for one of the pesticides), it did replicate the decline in daily volatilization better than the original model. The approach used in the surface deposit volatilization model allowed improved accuracy in the prediction of daily pesticide volatilization without increasing difficulties in model parameterization.

A general fate and transport model for pesticides applied to turf (Turf Pesticide Model – TPM) was developed by integrating the TurfPQ pesticide runoff model, the surface deposit volatilization model and a pesticide leaching component. The model was designed to require relatively few input parameters, and default parameter estimation methods were developed to facilitate its implementation. The model was tested using as wide a variety of turf, soil, climatic and management situations as possible. The model performed reasonably explaining 75% of the observed variation in drainage, 63% for pesticide leaching, 65% for runoff volumes, 64% for pesticide

loss in runoff, and 62% for pesticide volatilization. These results were obtained from uncalibrated simulations. Considering that the model requires relatively few input parameter values, and that a wide variety of pesticides, turf, soil and climatic conditions were used in the tests, the model appears to perform satisfactorily under varied scenarios. It is possible that better results could be obtained by calibration the model with specific site data.

Given its relatively modest data requirements and adequate test results, TPM could be used for impact and risk assessment, total maximum daily load, and other water and environmental quality studies involving pesticides applied to turf.

Main conclusions arising from this research are, firstly, that turf systems behave very differently to agricultural ones. This is due to the predominant role of turf's dense foliage and thatch on the fate and transport of pesticides. The large amount of organic matter covering the soil in mature turf systems governs pesticide dissipation processes by retaining very large fractions of the pesticide in the foliage and thatch, and by providing an environment in which large, active microbial populations can flourish. The combined effect is that most of the pesticide decay occurs in the foliage and thatch, and that microbial decay is the main dissipation process of pesticides applied to turf systems. Based on evidence found in the literature, other dissipation processes (volatilization, runoff, leaching, photolysis and removal in clippings) are relatively minor.

Secondly, empirical observations of enhanced microbial degradation suggest that accelerated decay in systems receiving repeated pesticide applications may play a significant role in the fate and transport of the pesticide. Some experimental observations indicate changes in the pesticide half-life of an order of magnitude or more for repeated pesticide applications. Enhanced microbial decay is not currently

included in any simulation model, and is addressed only tangentially in this research as some of the decay rates determined for turf systems resulted from experiments in which a pesticide was applied repeatedly. Quantification of decay rates that change according to management conditions may produce very different estimates of pesticide fate and transport, and of the risks associated with using these pesticides.

Thirdly, turf systems are complex, and the pesticide may be split into several fractions that exist simultaneously. As evidenced in the surface deposit volatilization model, identification of these fractions is important for model development. The assumptions used in model development should be made explicit and evaluated critically before the model is applied to specific scenarios in order to provide credible results.

APPENDIX

USER'S MANUAL
for the
Turf Pesticide Model (TPM)
Version 1.0

A fate and transport model for volatilization, runoff and leaching of pesticides applied to turf.

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INTRODUCTION

The Turf Pesticide Model is a fate and transport model that is capable of simulating volatilization, runoff and leaching losses of pesticides applied to turf. A complete description of the model equations and assumptions is available in Chapter 5. This document describes the data requirements of the model, the formats of the input and output files and how to run simulations.

Two input files are needed. The first is a parameter file that provides information pertaining to the pesticide, turf, soil and simulation characteristics. The second file contains daily weather data that consists of maximum and minimum air temperatures and the sum of natural precipitation and irrigation occurring during each day of the simulation. Information required for both files can be obtained from a variety of published sources or directly from field measurements. Default parameter estimation procedures are described in this document in order to ease implementation.

The Turf Pesticide Model was encoded in C++ and designed to allow flexibility in defining simulations. Short term simulations are those which run for periods of 1 day to any number of years. Long term simulations are predetermined to run for specified number of years in order to provide sufficient data for human and ecological risk assessment. Users can select daily, monthly, and/or annual output files.

INPUT FILE FORMATS

Both input files can be conveniently constructed in Excel, other spreadsheet programs or text editors and saved to a text file in which values are separated by spaces, which is the format read by TPM.exe.

Input parameter file

The input parameter file consists of 29 lines of information (Table A.1). The first 7 lines of the input parameter file define the characteristics of the simulation. Lines 8 to 15 describe physical and chemical characteristics of the pesticide. Lines 16 and 17 specify pesticide application dates and rates. Lines 18 to 23 describe the site and turf characteristics, and the soil is described in lines 24 to 29. A description of each line is follows Table A.1.

The example provided in Table A1 is an application of metalaxyl to a golf course green. The pesticide is applied at a rate of 1531 g A.I. ha⁻¹ on the 27th of September in 1995. The location of the golf course green is Riverside, CA, and the turf is creeping bentgrass (a cool season turf, which in this location continues to grow actively during the winter months). The soil consists of a sand-peat mixture and 2 layers of gravel. An upper layer of matt (consisting of roots and sand-peat mixture) is also included. The simulation is set to run for 6 months.

Table A.1. Input parameter file.

Line	Description	Entry
1	Daily weather file name (up to 50 characters long)	Example weather.txt
2	Output file name (up to 50 characters long)	Example metalaxyl
3	Specify simulation length (short or long term)	s
4	Select output: Daily Monthly Annual	y n n
5	Pesticide name (up to 50 characters long)	Metalaxyl
6	Start year month and day of simulation	1995 9 27
7	Number of months to simulate	6
8	Pesticide half life in turf (days)	7.3
9	Pesticide transfer half life from compartment 1 to 2 in turf (days)	1.14
10	Pesticide soil aerobic half life (days)	40
11	Pesticide Koc value (cm ³ /g)	171
12	Molecular weight of the pesticide	279.34
13	Vapor pressure of the pesticide at a reference temperature (kPa)	0.00000075
14	Reference temperature at which the vapor pressure was measured (°C)	25
15	Phase of the pesticide as applied (solid or liquid)	L
16	Total number of pesticide applications	1
17	Year Month Day Rate (g A.I./ha) for each pesticide application	1995 9 27 1531
18	Site latitude (decimal degrees)	33.97
19	CN ₂ value	35
20	Organic carbon content for foliage and thatch (kg/ha)	11403
21	Root factor	0.125
22	Growing season indicator (0 or 1), Jan to Dec	0 0 1 1 1 1 1 1 1 1 1 1
23	Monthly cover coefficients, Jan to Dec	0.65 0.65 0.85 0.85 0.85 0.85 0.85 0.85 0.85 0.85 0.85 0.65
24	Number of soil horizons	4
25	Depth of each soil horizon (cm, total depth cannot exceed 100 cm)	3 42 43 7
26	Organic matter content for each soil horizon (%)	5.3 0.52 0 0
27	Bulk density of each soil horizon (g/cm ³)	1.5 1.5 1.6 1.6
28	Field capacity of each soil horizon (cm/cm)	0.114 0.038 0.003 0.003
29	Wilting point of each soil horizon (cm/cm)	0.065 0.004 0.003 0.003

- Line 1: Daily weather input file name. The name can be 50 characters long and include spaces in the name. The filename extension must be specified.
- Line 2: Output file name. The name can be 50 characters long and include spaces in the name. The output filename extension is automatically set to “txt” to allow easy access using a text editor or direct import into Excel for analysis. Output is tab delimited text file.
- Line 3: Specify simulation length. Use “s” or “S” for short term simulations, and “l” or “L” for long term simulations.
- Line 4: Select output. There are 3 possible output files. Select the output files by using an “y” or “Y”, and exclude the unwanted files using “n” or “N”. Each letter must be separated by a space and follow this order: Daily output file, Monthly output file, Annual output file. All output files are tab delimited text files.
- Line 5: Pesticide name. Input the name of the pesticide used in the simulation, using up to 50 characters including spaces.
- Line 6: Start year, month and day of the simulation. Input numerical values in the following format: YYYY MM DD. Year, month and day entries must be separated by a space.
- Line 7: Number of months to simulate. This specifies the length of short term simulations (months). For long term simulations, input the number of years to simulate.
- Line 8: Pesticide half life in turf. Input a value representative of the pesticide’s half life (d) while on/in the turf foliage. Values for some pesticides and a general default value are provided in Chapter 2.
- Line 9: Pesticide transfer half life. Input the rate (d^{-1}) at which the pesticide is transferred between surface and retained residues in the turf foliage and thatch. Values for some pesticides and a general default value are given in Chapter 4.
- Line 10: Pesticide soil aerobic half life. Input the pesticide’s half-life in the soil (d), subject to aerobic microbial decay.
- Line 11: Pesticide Koc. This is the pesticide’s organic carbon partition coefficient ($cm^3 g^{-1}$).
- Line 12: Molecular weight of the pesticide. Input the molecular weight of the pesticide.

- Line 13: Vapor pressure of the pesticide. This is the pesticide's vapor pressure (mPa), measured at a specific reference temperature.
- Line 14: Reference temperature at which the vapor pressure was measured (°C).
- Line 15: Phase of the pesticide as applied (solid or liquid). Use solid ("s" or "S") for granular formulations and liquid ("l" or "L") for pesticides applied as sprays.
- Line 16: Total number of pesticide applications. For short-term simulations, input the total number of pesticide applications that occur during the entire simulation period. For long-term simulations, input the total number of pesticide applications that occur each calendar year.
- Line 17: Year Month Day Rate (g A.I./ha) for each pesticide application. For short-term simulations, input the year, month, day and rate of each pesticide application, separated by 1 space between each entry. For long-term simulations, input the month, day and rate of each pesticide application occurring within a calendar year, separated by 1 space between each entry.
- Line 18: Site latitude (decimal degrees). Input the site's latitude (measured in decimal degrees, e.g. 45.42°). Distinction of northern or southern hemispheres is not required by the program.
- Line 19: CN2 value. This value is determined based on the conditions of the turf cover and the hydrologic class of the underlying soil. Values for this parameter were developed by Haith and Andre (2000), and are presented in Chapter 5.
- Line 20: Organic carbon content for foliage and thatch (kg/ha). This can be determined based on the height of the foliage and the thickness of the thatch layer, based on the default method developed by Haith (2001), which is presented in Chapter 5.
- Line 21: Root factor. This factor determines the distribution of root density in the soil. It is defined as the depth of soil which contains 63% of the root mass (measured from the top of the soil downwards). The default value is 8 cm.
- Line 22: Growing season indicator. Input one value for each month of the year, starting with January. Use a value of 1 to indicate that the month belongs to the growing season, and a value of 0 if it does not. Growing season length can be determined using median freeze/frost dates, as demonstrated by Haith and Duffany (2007). Twelve values must be input even if the simulation length is shorter than 1 year, in order to maintain the correct format of the input parameter file.

Line 23: Monthly cover coefficients. Input a cover coefficient for each month of the year, starting with January. Default values are suggested in Chapter 5, and vary according to warm and cool season turfgrass. Twelve values must be input even if the simulation length is shorter than 1 year.

Line 24: Number of soil horizons. Input the number of soil horizons for the simulation. Soil horizons may be delimited naturally (as observations in native soils) or artificially (for example to match depths of soil at which samples were taken). The program will internally split the entire soil profile into 1cm thick computational layers and assign soil property values to each layer based on the horizon to which they belong. Daily, monthly and annual output will be regrouped to match the input horizons.

Line 25: Depth of each soil horizon. Input the depth (cm) of each soil horizon, using 1 space to separate each value. Total depth of the soil cannot exceed 100 cm, otherwise an error message will be displayed and the program will ask that the input file be checked.

Line 26: Organic matter for each soil horizon. Input the percentage of organic matter in each soil horizon (measured on a weight to weight basis), using 1 space to separate values for each soil horizon.

Line 27: Bulk density of each soil horizon. Input the bulk density (g cm^{-3}) of each soil horizon, using 1 space to separate each value.

Line 28: Field capacity of each soil horizon. Input the field capacity (cm cm^{-1}) for each soil horizon, using 1 space to separate each value.

Line 29: Wilting point of each soil horizon. Input the wilting point (cm cm^{-1}) for each soil horizon, using 1 space to separate each value.

The input parameter file contains information for 1 pesticide. Multiple pesticides may be run sequentially by creating an input parameter file for each pesticide, and then listing them all in a batch file. Batch files are described in more detail in the section titled “Running TPM”.

Daily weather file.

The daily weather file contains the maximum and minimum air temperatures ($^{\circ}\text{C}$), and an entry for the sum of natural precipitation (cm) and irrigation (cm) occurring on each day of the simulation. The format of the file requires that each month start with the number of days in the month, followed on the next row by data for the first day. Weather data is ordered as follows: maximum daily air temperature, minimum daily air temperature, sum of precipitation and irrigation. An example is shown below.

4		
27.7	14.2	0.645
22	15	0.554
25.3	14.5	0.554
34.7	13.2	0.554
31		
32.9	14.3	0.554
36.6	14.5	0.554
34	16.3	0.554
35	13.6	0.554
31.3	13.2	0.554

Note that for short term simulations, the start and end months can be truncated, as long as the appropriate number of days is specified in the first line of data for the month. In the example above, the first month simulated will have only 4 days. The program's initial condition for soil water is that all soil layers start the simulation at field capacity. Truncating the start month will ensure that the simulation will start with the soil at field capacity on a specific day (e.g. the day when the pesticide is applied). Truncating the end month may save some simulation time and facilitate processing the output data. Users are cautioned, however, that monthly average and total values will be based on the number of days in each month, so that in the example above, monthly output will be based on only 4 days of simulation data.

Daily weather data can be obtained from many databases (NOAA, NRCC, etc.) or it can be generated using synthetic weather generators such as USCLIMATE (Hanson et al. 1994).

DEFAULT PARAMETER ESTIMATION

In this section, default values and parameter estimation procedures are explained. Default values should be used when more precise sources of data are unavailable, as is common when simulating scenarios that are not linked with field experiments.

Pesticide half-lives for turf foliage and thatch were developed in Chapter 2, and are given in Table A.2. For pesticides not included in this table, a general default turf half-life of 5 d may be used, as demonstrated in Chapter 3.

Pesticide transfer rates from surface to retained deposits in the turf foliage and thatch were developed in Chapter 4, and half-lives corresponding to these values are presented in Table A.3. A general default value of 1.14 d may be used for pesticides not included in this table.

Comprehensive sources of pesticide properties including soil aerobic half-lives, Koc values, molecular weights, vapor pressures and their measurement reference temperatures can be found in the ARS Pesticide Properties Database (ARS 2006) and The Pesticide Manual (Tomlin 2003). Soil aerobic half-life for some pesticides currently registered for use on turf are included in Table A.2.

Table A.2. Half-lives for pesticide registered for use on turf.

Pesticide	Turf dissipation (d)	Aerobic in soil (d)	
		ARS†	Tomlin‡
2,4-D	24.9	5.5	7.0
Benefin	61.6	51.0	35.8
Chlorothalonil	4.5		14.2
Chlorpyrifos	8.7	30.5	40.2
Diazinon	2.6	39.0	16.0
Dicamba	1.6	18.0	14.0
Dithiopyr	7.0		39.0
Ethofumesate	3.0	143.0	155.8
Halofenozide	64.0		426.8
Iprodione	3.6	50.0	70.0
Mecoprop	1.0		10.0
Mefenoxam	5.5		21.0
Metalaxyl	7.3	40.0	29.0
Pendimethalin	7.4	1300.0	105.0
Propiconazole	13.5	53.0	49.5
Triadimefon	4.5	6.0	12.0
Trichlorfon	3.3	6.4	
Vinclozolin	2.3		
Median	5.0	39.5	32.4
Mean	12.6	145.2	65.3
Max	64.0	1300.0	426.8
Min	1.0	5.5	7.0

† ARS PPD (2006).

‡ The Pesticide Manual (Tomlin 2003).

Blank entries denote no available information.

Table A.3. Transfer half-lives by pesticide.

Pesticide	Transfer rate k_t (d)
Chlorpyrifos	0.88
DCPA	7.70
Dieldrin	1.54
Dithiopyr	0.90
Isofenphos	0.87
Pendimethalin	3.15
Triadimefon	2.04
Overall Average	1.14

Application rates can be obtained from pesticide labels, which have been compiled in the Greenbook: Turf and Ornamental Reference for Plant Protection, published annually by Vance Communication Corporation. Rates indicated in these product labels must be converted to units of grams of active ingredient applied per hectare for input into TPM.

The number of applications and their timing throughout the year is more problematic to determine. A thorough review was conducted by Haith and Duffany (2007), who derived typical preventative application rates and timings for several locations. Citing from their work:

“Herbicides applications depended on the chemical's use for either pre-emergent or post-emergent weed control. Pre-emergent chemicals were applied once on the first day of the growing season. Post-emergent herbicides were applied in the middle of each of the first two months of the growing season and once in the last or next to last month of growing season if allowed by the label.

Fungicide applications were based on preventative control of diseases such as dollar spot, summer patch, brown patch, and leaf spot. For golf surfaces, applications were generally started in the middle of the second growing month, and if permitted by label, continued every 15 days through the middle of the next to last growing month. When label limits applied, or in the case of lawns, applications were every 30 days.

As with fungicides, repetitive preventive applications are assumed for insecticides, which are used to control a range of pests (grubs, chinch bugs, cutworms, webworms, billbugs) which occur mainly in late spring and summer. This suggested a mid-month application starting in the second growing season month and label permitting, continuing through September. For lawns, a single insecticide application was made in the middle of the third growing season month.”

The methodology presented by Haith and Duffany (2007) may be followed for long term studies or in other cases where more precise management data is unavailable.

Determination of growing season length is also discussed in Haith and Duffany (2007), and is based on data for the first freeze and last frost of a location near to the study site. This data can be obtained from Koss et al. (1988) for many locations in the U.S.

Soil information can be obtained from datasets such as SSURGO (NRCS). Basic soil description data, such as the percentages of sand, clay and organic matter for each soil horizon, can be used as inputs to the Soil Water Characteristics software (Saxton 2007) to generate estimates of each horizon's bulk density, field capacity and wilting point.

RUNNING TPM

TPM.exe requires the 2 input data files described previously. Both must be placed in the same folder as the executable. The current version of TPM is set up to run batch files. A batch file is simply a list of the input parameter files that one would like to run sequentially. The list can contain from 1 to 100 input parameter files. An example of a batch file containing 2 input parameter files is as follows:

```
Metalaxyl 1995 input.txt  
Chlorothalonil 1995 input.txt  
end
```

Batch files can be created in any text editor and saved as txt files. Batch file names can be up to 50 characters long, including spaces. Contents of the batch file must end with the word "end" to terminate the simulations and exit TPM.exe.

TPM.exe can be run by double-clicking on TPM.exe in Windows Explorer. A window will open and the program will ask which batch file you wish to run. Enter the batch file name (including its extension) and hit Enter to run the program. The TPM window is shown in Figure A.1. In this example, the batch file is called "test.txt".

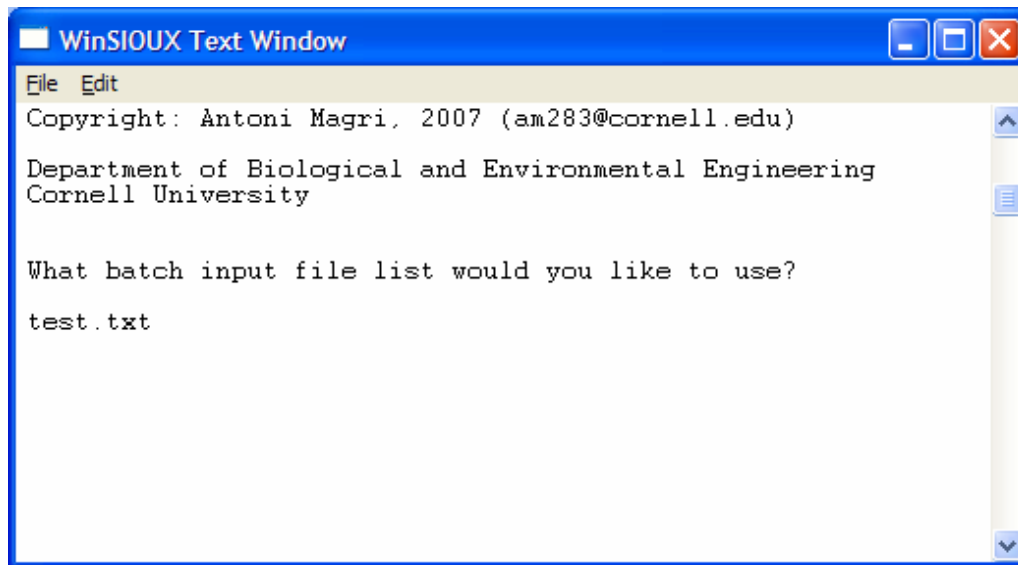


Figure A.1. The TPM program window.

As the simulations are run, a list of the input files being read and the output files being written will be displayed in the window. When the end of the batch file is encountered, a message stating that all the input parameter files listed in the batch file have been processed will appear. The program will then ask if the output contained in the TPM window should be saved or not. If “Yes” is selected, a text file containing the window’s contents can be saved to disk. If “No” is selected, the window will close. Saving or not saving the TPM window’s output will not modify the simulations’ results, which are stored in separate files.

TPM OUTPUT FILES

All output files are formatted as tab delimited text files, and have a “txt” extension to facilitate opening them in a variety of software for post-processing and analysis. For example, the output files can be opened directly in Microsoft Excel by selecting the default import options or by right-clicking on the output file in Windows Explorer and selecting Open with → Microsoft Office Excel (if this option is available).

Daily output file.

The daily output file contains data output for each day of the simulation. Dates are identified in the first 3 columns, titled: “Year”, “Month”, and “Day”. A running count of the days lapsed since the start of the simulation is output to the 4th column, titled “Days from start”.

Input data is included in columns 5 and 6, which include the average daily temperature and the sum of precipitation and irrigation, respectively.

The amount of runoff (expressed as a depth of water measured in cm), and the amount of snowmelt (cm of water) are contained in columns 7 and 8. These are followed by estimates of potential evapotranspiration (PET), and ET (which is PET corrected by a cover coefficient), in columns 9 and 10. The amount of water infiltrated into the soil (cm) is shown in column 11.

Output columns 1 to 11 for the metalaxyl application described in Table A1 is shown in Table A4.

Table A4. Example daily output - columns 1 to 11.

Year	Month	Day	Days from start	Avg. Temp (C)	Precip (cm)	Runoff (cm)	Snow (cm)	PET (cm)	ET (cm)	Infiltration (cm)
1995	9	27	1	21.0	0.65	0	0	0.40	0.34	0.65
1995	9	28	2	18.5	0.55	0	0	0.26	0.22	0.55
1995	9	29	3	19.9	0.55	0	0	0.34	0.29	0.55
1995	9	30	4	24.0	0.55	0	0	0.53	0.45	0.55
1995	10	1	5	23.6	0.55	0	0	0.48	0.41	0.55
1995	10	2	6	25.6	0.55	0	0	0.55	0.46	0.55

Columns 12 to 17 show, in order, the amount of pesticide on the turf at the beginning of the day, pesticide volatilized, lost in runoff, infiltrated into the soil, degraded on the turf, and left on the turf at the end of the day (all in g ha^{-1}). Example output is shown in Table A5.

Table A5. Example daily output - columns 12 to 17.

Year	Month	Day	Initial Metalaxyl on turf (g/ha)	Metalaxyl volatilized (g/ha)	Metalaxyl lost in runoff (g/ha)	Metalaxyl infiltrated (g/ha)	Metalaxyl degraded on turf (g/ha)	Metalaxyl left on turf (g/ha)
1995	9	27	1531.0	11.1	0.0	49.0	133.2	1337.6
1995	9	28	1337.6	3.2	0.0	37.0	117.5	1180.0
1995	9	29	1180.0	2.1	0.0	32.6	103.7	1041.6
1995	9	30	1041.6	1.9	0.0	28.8	91.6	919.4
1995	10	1	919.4	0.8	0.0	25.4	80.9	812.3
1995	10	2	812.3	0.5	0.0	22.4	71.5	717.9

In the next section of output, the following columns of information are given for each soil horizon: “Soil water” is the amount of water (cm) in the soil horizon at the beginning of the day; “Soil water for pesticide” is the amount of water (cm) in the horizon that is available for pesticide redistribution into adsorbed and dissolved portions (which occurs after water and pesticides have entered from the soil horizon above); “Percolation” is the amount of water (cm) that drains from the horizon; “Actual ET” is the amount of water (cm) extracted from the horizon through evapotranspiration; “Pesticide in” is the pesticide mass entering the horizon (g ha^{-1}); “Pesticide out” is the amount of pesticide leached from the horizon (g ha^{-1}); “Pesticide before degrad” is the pesticide mass in the horizon before microbial decay takes place

(g ha⁻¹); “Pesticide after degrad” is the amount of pesticide remaining in the horizon after microbial decay has occurred (g ha⁻¹); and finally, “Pesticide degraded in layer” is the mass of pesticide lost from the horizon due to microbial decay (g ha⁻¹).

These 9 columns are repeated for every soil horizon that was included in the input parameter file. Soil horizons are identified by a number in square brackets (e.g. [1] to indicate the 1st or top horizon of the soil). Example output is shown in Table A6 and A7.

Table A6. Example daily output - columns 18 to 21.

Year	Month	Day	Soil Water for			
			Soil Water [1] (cm)	Pesticide [1] (cm)	Percolation [1] (cm)	Actual ET [1] (cm)
1995	9	27	0.34	0.88	0.54	0.11
1995	9	28	0.34	0.83	0.48	0.07
1995	9	29	0.34	0.81	0.46	0.09
1995	9	30	0.34	0.76	0.41	0.14
1995	10	1	0.34	0.77	0.43	0.13
1995	10	2	0.34	0.75	0.41	0.15

Table A7. Example daily output - columns 22 to 27.

Year	Month	Day	Pesticide IN [1] (g/ha)	Pesticide OUT [1] (g/ha)	Pesticide	
					before degrad [1] (g/ha)	after degrad [1] (g/ha)
1995	9	27	49.0	0.0	49.0	48.2
1995	9	28	37.0	0.0	85.1	83.6
1995	9	29	32.6	0.1	116.2	114.2
1995	9	30	28.8	0.1	142.8	140.4
1995	10	1	25.4	0.2	165.6	162.8
1995	10	2	22.4	0.3	185.0	181.9

The last 2 columns of the daily output file show the amount of drainage from the soil (cm) and the amount of pesticide leached in the drainage (g ha⁻¹), as shown in Table A8.

Table A8. Example daily output - final 2 columns.

Year	Month	Day	Pesticide	
			Leachate volume (cm)	leached (g/ha)
1995	9	27	0.31	0.0
1995	9	28	0.33	0.0
1995	9	29	0.27	0.0
1995	9	30	0.11	0.0
1995	10	1	0.14	0.0
1995	10	2	0.09	0.0

Monthly output file.

The monthly output file presents a summary of the daily output. Data columns are the essentially same as described for the daily output file. Variables included are the average daily temperature for the month, and totals of the precipitation + irrigation, runoff, snowmelt, PET, and ET. Initial pesticide on turf corresponds to the total amount applied during the month. Pesticide volatilization lost in runoff, infiltrated, and degraded on turf are the total amounts for each month. Lastly, the total monthly drainage and pesticide leached from the soil are included. The detailed information for each soil horizon is not included in the monthly output file.

Annual output file.

The annual output file follows the same format as the monthly output file. The annual average temperature and the annual amount of pesticide applied to the turf are given. All other output columns represent annual totals for each variable.

The example input and output files are provided with the TPM.exe model, and can be viewed in detail by opening them in a text editor, in Microsoft Excel, or in similar spreadsheet software.

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