Degradation of Fungicides in Turfgrass Systems

Dr. Ron Turco

Purdue University

Goals:

- *Determine the character of the turfgrass leaf as a sorption material for fungicide.*
- *Determine the importance of microbial populations in controlling the degradation of fungicides on the turfgrass leaf surface.*
- *Investigate the significance of time on the fate of fungicides introduced into turfgrass ecosystems.*

Cooperators:

Clark Throssell
Zack Reiker

The study of microbial degradation of fungicides in turfgrass systems is important in order to understand the complete environmental fate of xenobiotic materials. This ongoing project investigates degradation as it may occur in the turfgrass canopy.

The turf leaf surface is an important sink for fungicides. It has been shown that a dense turf canopy can intercept over 95 percent of applied pesticides. Thus the turf canopy is a potentially important site for the degradation of xenobiotic materials including fungicides.

Review of last progress report:

Part 1. Fungicide dissipation results:

The concentration of fungicides in the extracted samples from the turf canopy was being determined using gas chromatography. Some manipulation of the samples was required in order to keep the concentrations of the detected fungicides within the limits of the standard solution concentrations. The first several samples that were going to be analyzed were those from the first and fifth two-week application cycles. These samples were chosen because they represent the first and fifth applications of fungicides that are applied every two weeks and the first and second applications of fungicides applied every eight weeks. It was thought that differences in degradation rates attributable to application frequency would most likely be observed at these sampling dates.

Part 2. Fungicide degradation results:

Oxidation of the degraded clipping samples showed that the majority (75%) of the applied radiolabeled fungicide was bound in the turfgrass leaves and probably unavailable for microbial degradation. The exact mechanism by which the fungicide became bound to the turf clippings was not clear. Determining the amount of residual parent material and metabolites formed was conducted using thin layer chromatography of ethyl acetate extracts of the degraded clippings. Because of the binding of the fungicide to the clippings, the amounts extracted from the leaf tissue was low. This kept the amount of radioactivity in the extracts spotted onto thin layer chromatography plates at a low level. Thus, plate counter-detection was impaired, and to a large extent, not useful in determining the presence of metabolite/parent compound-relationships. Few of the plate counter tracer graphs showed adequate amounts of activity that would allow for accurate quantification. This information, however, supports our conclusion that little of the fungicide is available in the environment. Most of the material appears to be retained in the leaf tissue.

Progress since May 1997

Part 1: Fungicide dissipation in the turfgrass canopy results

Analysis of the extracted fungicides showed that the dissipation rates on plots receiving fungicide applications were similar, regardless of frequency of application. Figure 15 shows the averages of all eight sampling cycles for iprodione, metalaxyl, and triadimefon. Although small changes in the dissipation rates were evident among the eight sampling cycles, the general trend of all sampling cycles was not conclusive support for the concept of

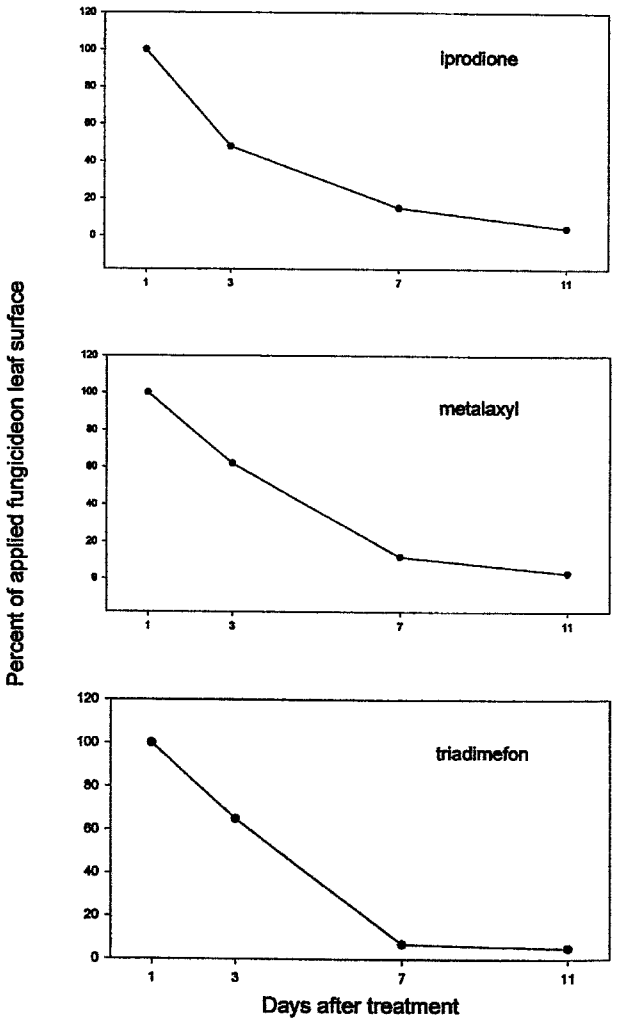

Figure 15. Averaged dissipation of iprodione, metalaxyl and triadimefon over eight application cycles.

enhanced biodegradation. The similarity of the dissipation curves suggests that little change in the loss mechanism of the fungicides is taking place.

Part 2: Fungicide degradation results:

A.) Quantifying the environmental fate of fungicides:

Table 10. Sampling cycle 5 recovery of 14C-fungicide from turfgrass clippings.

Fungicide	Pre-extraction [§]	Post-extraction	Extractable	Mineralized
	----------	----------	%	----------
Triadimefon	100	56	42	2
Metalazyl	100	67	30	3
Iprodione	100	62	33	5

[§] Data normalized to reflect pre-extraction as 100% of total fungicide amount.

An example of the mass-balance of fungicide fates is depicted in Table 10. Pre-extraction oxidation is used to determine the amount of radiolabel ("C-labeled fungicide) that is extractable from the leaf surface of the degraded clippings. After shaking with ethyl acetate to remove the extractable fungicide, a post-extraction oxidation was performed to determine the amount of fungicide that is non-extractable and thus not available for microbial degradation. Based on pre and post-oxidations, results showed that, on average, only 36 percent of the fungicide ormetabolites were extractable. This means that almost two-thirds of the applied fungicide remained bound to the leaf surface, unavailable for microbial degradation or loss into the environment. The poor extraction efficiency in addition to a presumed complexing of the fungicides with extracted plant material, such as chlorophyll, is assumed to have resulted in the limited detection and quantification of metabolites using thin layer chromatography.

B.) Short-term sorptive properties of fungicides and leaf tissue:

Results of the 48-hour sorption study are displayed in Figure 16. The two-phased nature of fungicide extractability over time suggests variability in adsorption to the leaf surface. The extractability of the three fungicides over time remained relatively unchanged for the first 24 hour. The reason for the variation in recoverable fungicide for the first 24-hour period is unknown. It is possible that either diurnal cycles of metabolism unique to the plant are at work or simply uncontrollable sampling error occurred. Changes do however occur in the extractable amounts of all three fungicides after the 24-hour sampling. In the 24 hour period between the 24-hour sampling and the 48-hour sampling, the extractable amounts of triadimefon, metalaxyl, and vinclozilin decreased by 97, 65, and 80 percent of applied amounts, respectively. Irreversible binding to the leaf surface or uptake into the leaf is thought to drive this phenomenon. The drastic immobilization of fungicide can partially explain the limited microbial mineralization that resulted from the degradation study and the inefficient extractions of the degraded clipping samples. Thus, the highly sorptive nature of turfgrass leaf tissue is important in sequestering iprodione, metalaxyl, and triadimefon and limiting the amount of free chemical in the environment. Dilution of the fungicides by the growth of the plant between samplings was determined not to effect the concentrations of the extracted fungicides.

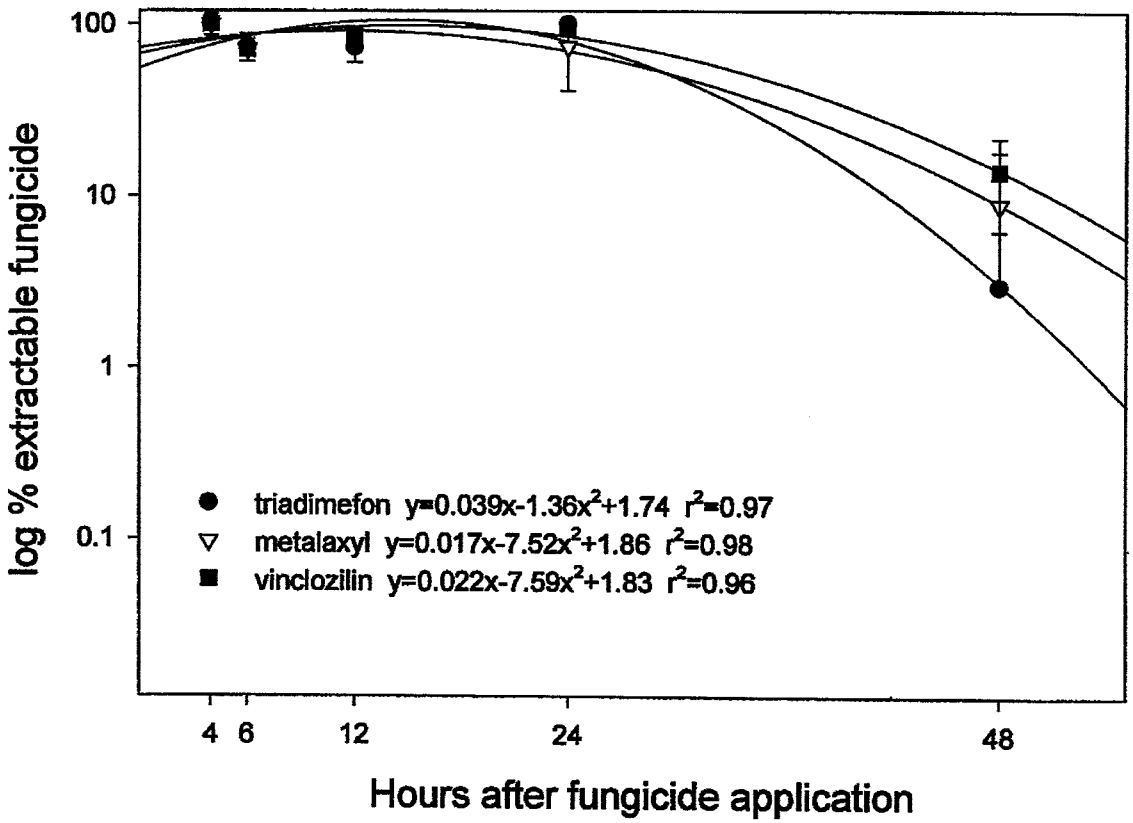

Figure 16. Percent of extractable fungicide at 4, 6, 12, 24, and 48 hours after application.