CHAPTER 4

EFFECT OF TURFGRASS COVER AND IRRIGATION ON SOIL MOBILITY AND DISSIPATION OF MEFANOXAM AND PROPICONAZOLE

Abstract

Irrigation effects on pesticide mobility have been studied, but few direct comparisons of pesticide mobility or persistence have been conducted on turfgrass versus bare soil. The interaction of irrigation practices and turfgrass thatch on the soil mobility and dissipation of mefanoxam and propiconazole was studied. Twenty-cm diam. sampling cylinders were placed in either creeping bentgrass (Agrostis palustris Huds.) or bare soil. Mefanoxam [(R)-2-[(2,6-dimethylphenyl)-methoxyacetyl]amino]-propionic acid methyl ester] was applied at 770 g ai ha\(^{-1}\) and propiconazole (1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole) was applied at 1540 g ai ha\(^{-1}\) on 14 June 1999. Sampling cylinders were removed two hours after treatment and 4, 8, 16, 32, and 64 days after treatment (DAT). The sampling cylinders were removed and the cores sectioned by depth. Soil extracts were assayed by HPLC yielding a pesticide detection limit of 0.01 mg kg\(^{-1}\). Dissipation of mefanoxam was rapid, regardless of the amount of surface organic matter or irrigation. The half-life (t\(_{1/2}\)) of mefanoxam was 5-6 days in turf and 7-8 days in bare soil. Most mefanoxam residues found in soil under turfgrass were in the 0-1 cm section at 0, 4, and 8 DAT. Residues were found in the 15-30 cm soil layer at 4, 8, 16, 32, and 64 DAT, regardless of surface organic matter or irrigation. The t\(_{1/2}\) of propiconazole was 12-15 days in turfgrass and 29 days in bare soil. Little vertical movement of propiconazole was observed. The results of this study indicate that
chemical properties are important in determining if irrigation practices or turfgrass cover will affect soil mobility and dissipation of pesticides.

**Introduction**

Public awareness of possible environmental contamination resulting from the use of pesticides in turfgrass systems has increased in recent years (Balogh and Anderson, 1992). However, turfgrass is a unique system in that, except at establishment, pesticides are applied directly to the plant material and thatch, a layer of dead and living stems and roots between the green vegetation and soil surface. Movement of turf-applied pesticides into the soil is attenuated by the high organic carbon content of turfgrass thatch (Branham, 1994; Branham and Wehner, 1985).

Laboratory studies show that turfgrass leaves and thatch strongly sorb organic compounds and thus should have a significant impact on the fate of pesticides applied to turfgrass (Lickfeldt and Branham, 1995; Dell et al., 1994). Previous studies have shown that pesticides bind strongly to thatch (Dell et al., 1994; Niemczyk et al., 1988). Sears and Chapman (1979) showed that even a thin layer of thatch could significantly retard pesticide movement on high-sand soils. Retention of pesticides by thatch may result in reduced mobility of pesticides applied to turfgrass (Smith and Bridges, 1996; Stahnke et al., 1991).

Some pesticides dissipate more quickly in thatch compared to soil (Gardner et al., 2000; Gold et al., 1988; Hurto et al., 1979). Horst et al. (1996) found that the half-lives of metalaxyl, pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitro-benzenamine], chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate], and isazofos (O-[5-chloro-1-(1-methyl-ethyl)-1H-1,2,4-triazol-3-yl]O, O-diethyl phosphorothioate) applied to turfgrass were
16, 12, 10, and 7 days, respectively. This compares to previously published soil $t_{1/2}$ data of 70, 34, 30, and 90 days, respectively (Balogh and Anderson, 1992).

Mefanoxam is a newly released, resolved isomer of metalaxyl ($N$-(2,6-dimethylphenyl)-$N$-(methoxyacetyl)alanine methyl ester). Mefanoxam is a fungicide for the control of certain diseases in turfgrass and other crops. A considerable amount of work had been published concerning metalaxyl (Horst et al., 1996; Starrett et al., 1996). Metalaxyl has a water solubility of 8400 mg L$^{-1}$ and a $K_{oc}$ of 29-287 indicating the potential for considerable leaching through the turfgrass-soil profile. Metalaxyl has a variable $t_{1/2}$, ranging from 7-160 days (Balogh and Anderson, 1992).

Propiconazole is a triazole fungicide used to control several pathogens. Propiconazole has a water solubility of 110 mg L$^{-1}$ and a $K_{oc}$ of 387-1,147 indicating the potential for some leaching through the turfgrass-soil profile. Propiconazole is persistent, with a $t_{1/2}$ of 109-120 days (Balogh and Anderson, 1992).

Our objective was to investigate the effect of surface organic matter and irrigation on the mobility and persistence of mefanoxam and propiconazole. Since the pesticides have different chemical and physical properties we also attempted to determine if the effect of thatch can be generalized or is more compound-specific.

**Materials and Methods**

**Field Procedures**

Field experiments were conducted in 'Penneagle' and 'Seaside II' creeping bentgrass turf in 1999 at the University of Illinois Landscape Horticulture Research Center in Urbana,
Illinois. The soil was a Flanagan silt loam (fine, smectic, mesic Aquertic, Argiudoll, 52 g kg\(^{-1}\) organic matter, 1.38 g cm\(^{-3}\) bulk density, and pH 6.5). Creeping bentgrass thatch was 10 to 14 mm thick and had a bulk density of 0.53 g cm\(^{-3}\), 241 g kg\(^{-1}\) organic matter and pH 6.7. Bare soil plots were prepared by stripping the sod from the plot with a sod-cutter.

Sampling cylinders were constructed of 20-cm-diam. schedule 40 polyvinylchloride (PVC) pipe cut into 30 cm lengths and beveled at one end to ease insertion into the soil. Sampling cylinders were inserted into each plot on 11 June 1999 using a hydraulic press (Alden Enterprises, Okemos, MI) attached to a tractor.

Mefanoxam (Subdue Maxx®) was applied to the plots on 14 June 1999 at 770 g ai ha\(^{-1}\). Propiconazole (Banner Maxx®) was applied to the plots on 14 June 1999 at 1540 g ai ha\(^{-1}\). The pesticides were applied with a backpack sprayer equipped with a TEEJET 8006E (Spraying Systems Co., Wheaton, IL) nozzle at a height of 36 cm, with an effective spray width of 30 cm. The pesticides were applied in 1120 L water ha\(^{-1}\) at 276 kPa. Irrigation (0.4 cm) was applied to the plots immediately after treatment.

The experimental area was mowed three times per week at 1.8 cm with a reel mower and clippings were not returned. Half of the plots were irrigated with 1 cm of water 5 times per week (high irrigation schedule). The other plots (low irrigation schedule) were watered as necessary to replace 80% of estimated evapotranspiration (Figure 9).

**Sampling and Analysis of Pesticides**

Sampling cylinders were removed from three replicate blocks of each level of turf organic matter 2 hours after treatment and 4, 8, 16, 32, and 64 days after treatment (DAT).
Figure 9. Rainfall and irrigation from date of pesticide application to last sample collection date. Pesticide application date was 14 June 1999

Sampling dates were 14 June, 18 June, 22 June, 30 June, 16 July, and 17 August. Verdure and thatch were separated from the cores that had turfgrass. The soil cores were partitioned into 0 to 1, 1 to 3, 3 to 5, 5 to 15, and 15 to 30-cm soil depth sections. Samples or sub-samples were
weighed, placed in glass mason jars with aluminum foil-capped lids, and stored at -20° C until residue analysis.

Pesticides were extracted from soil, verdure, and thatch. Soil samples were thawed and a representative 20 g sample placed in 500 mL Erlenmeyer flasks. Pesticides were extracted from the soil by shaking with ethyl acetate (100 mL) for 3 hours on a platform shaker at 200 RPM. The extract was vacuum filtered by passing through Whatman G6 glass fiber filter.

Twenty grams of thatch or 3-10 g verdure were extracted by shaking with ethyl acetate (100 mL) for 4 hour on a platform shaker at 200 RPM. The extract was vacuum filtered by passing through Whatman G6 glass fiber filter paper.

Ethyl acetate was removed by rotary evaporation at 40° C. The evaporatory flask was rinsed 3 times with 5 mL methylene chloride and the rinsate transferred to KD tubes. The methylene chloride was evaporated to 2 mL using a reacti-vap (Pierce, Inc., Rockford, IL). The extract was then passed through a 0.45 micron nylon membrane filter (GelmanSciences, Ann Arbor, MI) and transferred to an autosampler vial for analysis on a high pressure liquid chromatograph (Beckman Coulter, Fullerton, CA).

Mefanoxam and propiconazole were separated on a 15 cm, 4.6 mm i.d. column with a bonded 5 μm C-18 phase (Beckman Coulter, Fullerton, CA). Mefanoxam was separated from verdure, thatch, and soil impurities by injecting 40μL into a mobile phase of 30:70 (acetonitrile:water). After 8 min the mobile phase was increased to 100% acetonitrile over a 10 min period. Mefanoxam was detected with a UV-Vis detector (Beckman Coulter, Fullerton, CA) at 210 nm with a retention time of 14.3 min. Propiconazole was separated from verdure, thatch, and soil impurities by injecting 40μL into a mobile phase of 55:45 (acetonitrile:water).
After 5 min the mobile phase was increased to 100% acetonitrile over a 6 min period. Propiconazole was detected with a UV-Vis detector (Beckman Coulter, Fullerton, CA) at 210 nm with a retention time of 9.4 min.

Mefanoxam residues were quantified by peak area measurements in comparison with a 10 µg mL⁻¹ external standard. Propiconazole residues were quantified by peak height measurements in comparison with a 10 µg mL⁻¹ external standard. The limit of detection for both pesticides was 10 µg kg⁻¹.

Calibration standards were included after every sixth extract. A control sample fortified at 1 mg kg⁻¹ and a method blank were included with each batch of 22 samples. Mefanoxam recovery from soil, verdure, and thatch samples averaged 91% with a coefficient of variation of 6%. Propiconazole recovery from soil, verdure, and thatch samples averaged 90% with a coefficient of variation of 5%. The amount of mefanoxam or propiconazole remaining in each soil profile was estimated from data on the concentration of pesticide present in a soil core section and the mass of the core section.

The experiment was designed as a split-split-plot with irrigation as the whole plot, organic matter as the sub-plot and turf-soil core as the sub-sub-plot. On each sampling date, data were subjected to analysis of variance (SAS Institute, 1990). Half-life values were estimated by regressing the log of pesticide residues remaining versus time.

**Results**

Dissipation of mefanoxam was rapid, regardless of the amount of surface organic matter present or amount of irrigation applied (Figure 10). The calculated $t_{1/2}$ in turfgrass was 6 days ($R^2 = 0.99, P = 0.001$) under high irrigation and 5 days ($R^2 = 0.99, P = 0.002$) under low
irrigation. The calculated $t_{u2}$ in bare soil was 8 days ($R^2 = 0.95, P = 0.022$) under high irrigation and 7 days ($R^2 = 0.99, P = 0.006$) under low irrigation.

There was rapid vertical movement of mefanoxam through the soil profile, regardless of surface organic matter content or irrigation regime. Irrigation regime did not affect the distribution of mefanoxam in the soil on any sampling date. Differences in the distribution of mefanoxam residues in the soil layers due to surface organic matter cover were observed at 2 HAT and 4, 8, and 16 DAT, but not at 32 or 64 DAT (Table 8).

Most of the mefanoxam was found in the thatch on plots containing turfgrass or in the 0-1 cm soil layer on bare soil plots at 0 and 4 DAT (Figure 11). By 8 DAT, however, the majority of mefanoxam applied to the turf plots was found in soil. Residues were found in the 15 to 30
cm soil depth at 4, 8, 16, 32, and 64 DAT, regardless of surface organic matter or irrigation applied. However, due to rapid dissipation, the total amount of mefanoxam recovered on any date in the 1 to 3, 3 to 5, 5 to 15, and 15 to 30 cm soil sections did not exceed 15% of the total amount applied.

Table 8. Analysis of Variance (ANOVA) on total mefanoxam residues in verdure, thatch, and soil profile components on different sampling dates during 1999.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Day 0</th>
<th>Day 4</th>
<th>Day 8</th>
<th>Day 16</th>
<th>Day 32</th>
<th>Day 64</th>
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<td>0.2268</td>
<td>0.4174</td>
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<td>0.0007</td>
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<td>0.0607</td>
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</tbody>
</table>

† I = high or low irrigation, O = bare soil or creeping bentgrass turf, C = core (verdure, thatch, and 0 to 1, 1 to 3, 3 to 5, 5 to 15, and 15 to 30 cm).

‡ Probability of greater F ratio (P > F) for surface organic matter content and soil profile components.

The $t_{12}$ of propiconazole varied due to surface organic matter cover (Figure 12). The calculated $t_{12}$ in turfgrass was 12 days ($R^2 = 0.99, P = 0.001$) under high irrigation and 15 days ($R^2 = 0.99, P = 0.001$) under low irrigation. The calculated $t_{12}$ in bare soil was 29 days ($R^2 = 0.90, P = 0.003$) under high irrigation and 29 days ($R^2 = 0.86, P = 0.007$) under low irrigation.

There were differences in the distribution of propiconazole in the soil layers due to organic matter cover on all sampling days (Table 9). There was little vertical movement of
Figure 11. Distribution of mefanoxam residues among verdure, thatch, and different soil depths over time in 1999. Horizontal bars represent standard error of the means.
Figure 12. Total propiconazole residue in verdure, thatch, and soil as a function of sampling time in 1999.

Propiconazole in the soil (Figure 13). When propiconazole was applied to turf, at least 95% of the residues were recovered from the verdure and thatch on all sampling dates. At least 87% of propiconazole residues applied to bare soil were recovered from the 0 to 1 cm soil layer. Small amounts of propiconazole were found in the 1 to 3, 3 to 5, and 5 to 15 cm soil layers when applied to bare soil. Propiconazole applied to turfgrass was detected in trace amounts in the 1 to 3 and 3 to 5 cm soil layers 16 DAT. No propiconazole applied to turfgrass was found below 0 to 1 cm in soil on any other sampling date.
Figure 13. Distribution of propiconazole residues among verdure, thatch, and different soil depths over time in 1999. Horizontal bars represent standard error of the means.
Table 9. Analysis of Variance (ANOVA) on total propiconazole residues in verdure, thatch, and soil profile components on different sampling dates during 1999.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Day 0</th>
<th>Day 4</th>
<th>Day 8</th>
<th>Day 16</th>
<th>Day 32</th>
<th>Day 64</th>
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</tr>
<tr>
<td>(C)ore</td>
<td>6</td>
<td>0.0001</td>
<td>0.0001</td>
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<td>O x C</td>
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</table>

† I = high or low irrigation, O = bare soil or creeping bentgrass turf, C = core (verdure, thatch, and 0 to 1, 1 to 3, 3 to 5, 5 to 15, and 15 to 30 cm).
‡ Probability of greater F ratio (P > F) for surface organic matter content and soil profile components.

Discussion

The total amount of irrigation/rainfall recorded on the plots throughout the study differed by nearly 2:1 (Figure 9). However, no differences in soil mobility or dissipation due to precipitation were observed with either pesticide.

Previous work has shown that soil mobility of certain pesticides applied to turfgrass is not affected by irrigation or precipitation events (Cisar and Snyder, 1996; Niemczyk and Krueger, 1987). However, Niemczyk and Krause (1994) found that the mobility of some preemergence herbicides was correlated to major rainfall events.

Because of its high water solubility and low soil $K_{oc}$, irrigation and rainfall can have a significant impact on leaching of metalaxyl. Metalaxyl leached through 40 cm lysimeters that received 100 mm of precipitation (Odanaka et al., 1994). Horst et al. (1996) found at least 28% of applied metalaxyl in soil under Kentucky bluegrass, and it moved through the entire 60-cm
soil column. Metalaxyl movement through 25-cm soil columns was 0, 9, 73, and 83% of applied material after being subjected to 5, 10, 15, and 20 cm, respectively, of simulated rainfall (Sharom and Edgington, 1986).

Starrett et al. (1996) found that depth and frequency of application of irrigation water can impact the movement of mobile pesticides such as metalaxyl. The authors found 7.7% of the applied metalaxyl in the leachate from columns containing Kentucky bluegrass that received heavy irrigation (four, 2.54-cm applications). In contrast, 0.2% was measured in leachate from the soil columns receiving light irrigation (16, 0.64-cm applications). In this study, irrigation regime was varied by frequency of application, not amount at application. It is likely that a high irrigation regime consisting of fewer, larger amounts would have resulted in increased leaching of mefanoxam as shown by Starrett et al (1996).

Turfgrass cover did not affect mobility of mefanoxam. In a previous study, metalaxyl recovered in leachate from plots with varying amounts of turfgrass cover was 36.4, 26.7, 14.1, and 16.5% on plots with turfgrass densities of 0, 33, 66, or 100%, respectively (Petrovic et al., 1996). However, based on our soil distribution data, the amount of mefanoxam reaching leachate, if measured, would have been similar on plots with turfgrass or bare soil. Different soil or climate conditions may have accounted for these differing observations.

The $t_{1/2}$ for mefanoxam was 6-10 days, which is in close agreement with previous studies in turf (Horst et al, 1996). The $t_{1/2}$ was slightly faster in turf than in bare soil, which may be attributed to more rapid microbial degradation of residues in the verdure and thatch. Sharom and Edgington (1982) reported that metalaxyl was stable in sterilized soils but degraded in unsterilized soils, indicating that degradation by microorganisms is an important factor.
governing the fate of metalaxyl. However, since mefanoxam is not strongly bound by thatch, the higher microbial activity in thatch may be circumvented.

The $t_{1/2}$ of propiconazole in this study was between 10 and 30 days, which is much lower than what is previously reported in Balogh and Walker (1992). Bai and Liu (1987) observed a $t_{1/2}$ of about 5 days when propiconazole was applied to wheat (*Triticum aestivum* L.). Similar results were found by Garland et al. (1999) who observed half-lives of 8-10 days when propiconazole was applied to leaves of a peppermint crop.

Very little downward movement of propiconazole was observed, which is in agreement with previously published studies (Kim and Suh, 1998; Liu and Weber, 1986). Kim and Suh (1998) found only 4.4% of applied propiconazole was in leachate from a sandy loam soil after 16 weeks. The majority (97%) of the material remained in the upper 20 cm of the profile. Similar results were reported by Liu and Weber (1986). When applied to wheat, significantly more residues were found on straw and leaves than were found in soil (Bai and Liu, 1987).

Other avenues of pesticide fate include runoff, volatilization, and photodegradation (Frederick et al., 1996). Our study was conducted on plots with little slope which minimized the possibility for runoff losses. Volatilization can be a significant mode of loss of metalaxyl (Petrovic et al., 1996). However, volatilization of propiconazole is of minor significance (Balogh and Anderson, 1992).

A study conducted by Petrovic et al. (1996) measured pesticide residues in leachate on plots with various amounts of turfgrass cover. A thorough review of the literature indicates that the present study is one of the first to directly examine the mobility and dissipation of pesticides in turfgrass compared to bare soil, with climate and soil type held constant.
Post-treatment irrigation practices may not be as important in determining the soil mobility of pesticides as is soil moisture at application time or large precipitation events within 14 days of application. The results of this study indicate that the effect of turfgrass cover or irrigation practices may be more important in determining leaching and dissipation of moderately mobile pesticides. However, pesticides with high water solubilities and low soil $K_{oc}$ values, such as mefanoxam, are prone to leaching, and pesticides with lower water solubilities and higher soil $K_{oc}$ values, such as propiconazole, are less prone to leaching, regardless of turf cover or precipitation.

Literature Cited


