

**Department of Pesticide Regulation  
Environmental Monitoring Branch  
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**Study #313: Fate and movement of pesticide residues in turf-overlaid soil**

**I. Introduction**

Pesticide terrestrial field dissipation (TFD) studies are routinely submitted to the Department of Pesticide Regulation (DPR) for evaluation during the pesticide product registration process. The Ground Water Protection Program (GWPP) at DPR reviews TFD studies to evaluate the fate and movement of pesticide active ingredients in the soil for their potential to impact ground water. These studies are typically conducted on bare soil sites that are void of vegetation. Occasionally these studies are conducted in the presence of turf, particularly for pesticides exclusively designated with this site use.

The review of a TFD study typically evaluates a chemical's potential to leach through soils as mediated by soil characteristics, evapotranspirative demands, and water inputs at the study site. Computer modeling is also conducted to reaffirm the results observed from the field studies. However, if deficiencies in the field studies exist, such as the absence of sufficient percolating water to produce leaching conditions then greater emphasis is placed on results from the computer modeling to assess the potential impact on ground water. This is achieved by simulating the fate and movement of pesticides from their site of application to a domestic well where well water concentrations are predicted. The current ground water modeling procedure utilizes the LEACHM pesticide fate and transport model (Hutson and Waganet, 1992) for simulating the upper vadose zone, and a second empirical-based model coupled to LEACHM for simulating the lower vadose and saturated zones (Troiano and Clayton, 2009). The LEACHM component centers on chemical applications directly to the soil surface. A mature grape crop is included in the scenario because grape is a major crop in the model-simulated area of eastern Fresno and Tulare counties where the ground water has been impacted by pesticides. Grape evapotranspiration and growth cycles are simulated and water inputs are adjusted accordingly to simulate targeted levels of drainage water. Modeling results from this scenario have been shown to agree with ground water monitoring data from the eastern Fresno and Tulare County area (Spurlock, 2000).

For simulating pesticide products applied to turf the GWPP employs a modeling scenario that in contrast to the grape scenario includes a shallower plant rooting depth, a permanent vegetative soil surface coverage, and increased organic carbon content in the soil surface layers. To compensate for a shallower plant rooting depth, individual water inputs are simulated in lesser amounts but at greater frequency in order to achieve targeted drainage levels. However, the turf scenario is still largely based on the standard grape modeling scenario where simulated pesticide

applications are directly to the soil surface and where adsorption isotherm coefficients and dissipation rate constants are typically derived from bare soil studies. Potential effects of pesticide residue movement through the turf foliage and thatch layer following a typical application above the verdure are not factored into the simulations. Furthermore, the turf modeling scenario has not been evaluated or verified against field measured data.

Studies submitted to DPR characterizing the soil persistence and mobility of an active ingredient applied to the bare soil surface for which turf is a proposed site of use do not account for potential turf effects. Observations from turf-based studies submitted to DPR indicate that residue movement in soil may be affected by the presence of the turf. For example, several TFD studies conducted on bare soil that were recently submitted to DPR supporting the registration of a pre-emergent herbicide indicated concerns of potential ground water contamination by the chemical. These concerns were based on residue persistence and on residue movement to the deepest soil coring layers for applications that were made to bare soil sites. In addition, submission of three prospective ground water studies revealed that residues of this chemical, including its degradation product, were detected in ground water monitoring wells following a single application also to the bare soil surface. In a subsequent field study with a coarse-textured sandy loam soil overlaid with well-established turf this same pesticide was confined to within 15 cm of soil surface despite experiencing greater water applications and deeper levels of percolating water compared to the field dissipation and monitoring well studies. This finding indicated that turf effects may be significant as it has been demonstrated that increased water applications to coarse-textured bare soil treated with pesticides result in residue movement to greater soil depths (Troiano et al., 1993).

Reports from the published literature have been inconsistent as to the effects of turf on the mobility and persistence of pesticides in soil. Gardner and Branham (2001a) reported that leaching of the herbicide ethofumesate was reduced and its dissipation more rapid in turf-overlaid soil compared to bare soil. However, in the same study these findings were not consistent for the insecticide halofenozide. In a separate study, Gardner and Branham (2001b) indicated that the highly mobile fungicide mefenoxam exhibited similar levels of soil mobility in turf and bare soil and that a comparable amount of chemical likely leached below a soil coring depth of 30 cm. Despite this finding, mefenoxam remaining within the soil cores was reported to dissipate at a greater rate in turf plots compared to bare soil, which was attributed to enhanced microbial metabolism in the verdure and thatch layers. This assumption was later supported by results from Raturi et al. (2004) who noted that total carbon in the microbial biomass of two turf species was over 10-fold greater in thatch than in the immediate underlying soil. For the less mobile fungicide propiconazole where residues were retained close to the soil surface, Gardner and Branham (2001b) found, as with mefenoxam, no difference in residue movement in soil between turf and bare soil plots and that the residue degradation rate was considerably greater in turf compared to bare soil.

Dousset et al. (2010) investigated the effectiveness of turf cover to reduce movement of the pesticides diuron, tebuconazole and procymidone in a loamy-sand soil sensitive to leaching. They reported that soil adsorption coefficients for these pesticides in the 0 - 5-cm soil depth were considerably higher in turf-covered soil than in bare soil, and that these differences were consistent with the organic carbon ratio between the soils. As such, less chemical residue was

collected from leachate of the turf-covered soil than from the bare soil. The authors did note some irregularity with the soil movement of bromide, which was used as a tracer for water movement and where residue leachate recovery was expected to be similar between the bare and turf-covered soils. In several instances greater amounts of bromide was recovered from leachate of the bare soil compared to the turf-covered soil despite similar volumes of leachate recovered from both systems. The authors speculated that this result was due to adsorption of bromide to the turf vegetation in one instance and to soil compaction of the turf covered plots in the other. However, the potential impact of turf vegetation and soil compaction on movement of the pesticides was not mentioned. Dousset et al. (2010) did remark on several studies by others where the effect of turf cover was found both effective and ineffective at reducing chemical residue leachate compared to bare soil.

Magri and Haith (2009) reviewed numerous studies investigating pesticide decay processes and rates in turf, including residue retention in foliage and thatch. The authors cited various studies indicating that turf-applied pesticides are less susceptible to physical removal by runoff, infiltration into the soil, and volatilization. They noted two key reasons why pesticide dissipation is more rapid in turf compared to bare soil: 1) strong retention of pesticides in turf foliage and thatch can sustain large and highly active microbial populations that degrade pesticide residues as a source of energy, and 2) high pesticide inputs typically associated with turf maintenance, when compounded by the nature of turf's unaltered landscape, further increases microbial populations and their level of activity by conditioning their ability to degrade residues. Results from an earlier study by Petrovic and Larsson-Kovach (1996) supported these conclusions whereby leaching of the herbicide mecoprop in newly established, immature stands of turf void of thatch was ten-times greater than in established turf. Magri and Haith (2009) further concluded that high retention of pesticides in foliage and thatch is likely the most important factor governing pesticide dissipation in turf systems. Likewise, Gardner (2001) noted that despite the many processes affecting the environmental fate of pesticides in turf, the most important are sorption of residues to soil particles and organic matter, residue leaching or runoff, and degradation of residues by soil-borne microbes. He concluded that turf influences the effect pesticide properties have on residue leaching and dissipation rates, and that for the most part applications to turf do not persist or leach to the same extent as they do when applied to bare soil.

The broad diversity of pesticides and their physiochemical properties, soil types, and environmental conditions under which the above cited studies were conducted likely contributed to the inconsistency in reported results. Those studies reporting turf effects have largely attributed these to characteristics of the chemical such as soil adsorption potential and dissipation rates. Other studies indicated additional factors such as density of thatch or establishment period of the turf and intensity of water inputs or levels of percolating water created. Our proposed pilot study will investigate pesticide fate and movement in turf-overlaid soil relative to that in bare soil in a typical agricultural setting and under conditions conducive to potential residue movement to ground water. The study will be conducted in eastern Fresno County where the ground water is vulnerable to leaching residues and has been impacted by the use of agricultural pesticides. Sulfentrazone and sulfentrazone carboxylic acid (SCA), an agricultural use herbicide and its major breakdown product, respectively, will be the test subjects for this current study. This herbicide was chosen because it has product registrations in California with agricultural crop, rights-of-way, and turf uses and has been identified in the California Code of Regulations

section 6800(b) as having potential to pollute ground water due to its physiochemical properties and sites of application. Bromide, in the form of potassium bromide will be used as a tracer for the movement of water. The fate and transport of these chemicals will be evaluated under two levels of water input to create both low and high levels of percolating water. Zero tension column lysimeters will be utilized to characterize fate and movement of the chemicals in both the turf and bare soil plots.

From the data generated in this proposed pilot study either of two possible procedures could be developed as a methodology for evaluating the threat to ground water of turf-applied pesticides:

1. An assessment could be made in relative terms by proportionally adjusting simulated output from the GWPP's current ground water model, which is based on bare soil applications, by the ratio of leaching residues between turf and bare soil conditions as determined from the field study data. This would be possible because the current ground water modeling procedure dictates that the predicted well water concentration for any given pesticide is directly proportional to its mass leached below the crop root zone under equivalent drainage conditions.
2. Depending on the quality of the field-generated data, computer modeling scenarios could be developed to directly predict well water concentrations resulting from pesticide applications to turf and movement of residues to ground water. Successful simulation of turf effects and verification of model output by field-measured data would justify coupling of the simulated output to the GWPP's deep vadose- and saturated-zone empirical-based model to provide estimates of well water concentrations. In contrast to the first option this methodology is more challenging to develop, but would provide added benefit by allowing for adjustments to modeling parameters that deviate from the GWPP's standard modeling scenario. For example, scenarios could be modified to simulate alternative irrigation regimes or other management practice.

## **II. Study Objectives**

1. Compare and contrast the leaching of pesticide residues in turf-overlaid soil relative to bare soil under equivalent levels of percolating water in a coarse-textured soil vulnerable to pesticide leaching.
2. Develop a methodology for estimating the potential for ground water contamination resulting from pesticide applications to turf. In its simplest form the methodology will be based on the GWPP's current modeling scenario with adjustments to simulated output to account for turf effects. In a more advanced form the methodology will comprise of turf-specific modeling scenarios simulating residue fate and transport in soil and estimating residue concentrations in well water.

## **III. Personnel**

Project Leaders: Murray Clayton

Field Coordinator: Alfredo DaSilva  
Senior Scientist: John Troiano  
Project Supervisor: Sheryl Gill  
Laboratory Liaison: Sue Peoples for analyses conducted by the California Department of Food and Agriculture (CDFA)  
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#### **IV. Study Plan**

This study will be conducted at the University of California (UC) Kearney Agricultural Research and Extension facility in Fresno County on a coarse-textured soil bordering between a loamy sand and sandy loam. Zero tension column lysimeters will be used to characterize water and chemical movement in the turf and bare soil plots. UC Kearney personnel will assist with installation of the lysimeters and irrigation system, site weed control and application of chemicals via chemigation along with obtaining any necessary pesticide application permits and/or notifications to the County Agricultural Commissioner. DPR staff will be responsible for the construction of lysimeters, establishing and maintaining turf within the lysimeters, chemigation and irrigation of the plots, soil coring activities, solution sampling from lysimeter reservoirs, chemical analysis, data analysis, and reporting of results.

Each of two independent sites will have treatment plots aligned in a linear configuration. The two study sites will differ only in the amount of water they receive after chemical application, thereby producing either high or low levels of percolating water. The treatment factor within each study site will be the presence or absence of turf and will be arranged in a completely randomized design. Each site will consist of six treatment plots with three treatment plots containing established turf and the remaining three containing bare soil. Each treatment plot will be confined to within a single lysimeter. Adjacent lysimeters or plots within each study site will be separated by 2.25 m; the two study sites will be oriented in a parallel formation relative to each other and separated also by 2.25 m (Figure 1). Installation of the irrigation system and lysimeters, and establishment of the turf will occur approximately six months prior to chemical application to the plots.

The lysimeters will be similar to those used by Clayton et al. (2016) who utilized design features and installation procedures that mitigated some limitations associated with their use. These limitations included the development of preferential flow pathways within the units and disturbance of the soil structure and soil horizons during installation. Another factor known to impact the functionality of these devices is the existence of a saturated lower boundary condition within the confined soil. However, this phenomenon has been quantified and its effect on water and residue movement normalized using computer modeling (Clayton et al., 2016). A coarse-textured soil was chosen because of its association with high residue movement through the soil profile as a result from irrigation input (Troiano et al., 1993), and to also minimize the potential

for preferential flow and saturated lower boundary conditions within the lysimeters (Clayton et al., 2016).

After the irrigation system is verified for uniformity of water application, frequent irrigations will be conducted across the sites until drainage water is extracted from all lysimeters to confirm their functionality and to standardize the soil-water content in each plot.

A single application of sulfentrazone will be applied at maximum labeled rates to all the plots at each study site. Potassium bromide also will be applied simultaneously with sulfentrazone as a tracer for water movement at a rate of 100 kg bromide ions/ha. Chemical application will be by chemigation, which will be followed by 12 mm of water for incorporation of residues into the soil.

Irrigation will be applied to both study sites at 1-week intervals for a period of approximately 12 weeks using a pressurized drip system. One study site will receive water input amounts that are reflective of unpressurized surface delivery systems where application efficiencies as low as 60% have been reported in California (California Agricultural Technology Institute, 1988; Snyder et al., 1986) and elsewhere in the United States (Rogers et al., 1997). This application efficiency equates to water inputs of approximately 160% of evapotranspirative demand. At this level of water input, simulated output from the GWPP's standard ground water model for a coarse-textured soil in the Fresno and Tulare County area resulted in deep drainage levels averaging approximately 20 mm per week during a typical 6-month irrigation season. Accordingly, treatment plots at this study site will receive weekly water inputs targeted to also produce drainage levels of approximately 20 mm per week. The remaining study site will receive lower water inputs based on application efficiencies of 80%, equating to inputs at 125% of evapotranspirative demand to produce less percolating water. This higher water application efficiency is reflective of the GWPP's mitigation measure for preventing residue movement to ground water in leaching vulnerable areas of California (Troiano and Clayton, 2009). At this level of water input simulated output from the ground water model estimated deep drainage levels averaging approximately 10 mm per week during the typical 6-month irrigation season. Therefore, treatment plots at this study site will receive weekly water inputs targeted also to produce drainage levels of approximately 10 mm per week.

Water inputs will be indexed to reference evapotranspiration, which is available from a California irrigation management information system weather station located within 500 m of the study sites. A water balance model using the methodology of Allen et al. (1998) that partitions water inputs into the fractions of evapotranspiration, drainage and changes in soil-water content will provide estimates for irrigation input in order to obtain targeted drainage levels. Within each study site a water balance model will be utilized for each of the treatments.

Sampling activities (methodology provided in Protocol Section V) will occur in the following sequence:

- Prior to chemical application samples will be collected to be analyzed for sulfentrazone, SCA and bromide background residue levels. These samples will include soil cores adjacent to a treatment plot near the center of each study site, solution extracted from

each lysimeter reservoir, water from the irrigation system, and vegetative clippings from the turf plots.

- For modeling purposes, soil cores would normally be collected to characterize soil hydraulic conductivity, soil-water retention parameters, textural composition, total organic carbon content and bulk density. However, these soil parameters have already been characterized for the study sites (Clayton et al., 2016).
- Following chemical application, solution will be extracted from lysimeter reservoirs at weekly intervals for a period of approximately 12 weeks, occurring on the same day, but just prior to the weekly water applications. The extracted solution will be measured for total volume and analyzed for sulfentrazone, SCA and bromide residues. These samples will provide the primary data for characterizing the fate and movement of residues between turf and bare soil and for calibrating a turf-based computer model.
- Offcuts of leaf vegetation from the turf plots will be analyzed for sulfentrazone, SCA and bromide residues, which will be sampled when required to trim and maintain the turf vegetation at a reasonable length. A final sample of leaf vegetation will be analyzed for chemical residues when the field study is concluded. These data will provide accountability for residue dissipation should they be subject to plant uptake.
- The turf and bare soil plots within each lysimeter will be cored to collect soil samples approximately 16 weeks following chemical application, which will correspond to 4 weeks after the final water application to the study sites. The period between final water application and soil sampling will provide for partial drying of the normally saturated soil at the lower boundary of the lysimeter, which will aid in soil coring and sample collection activities. These soil samples will be analyzed for sulfentrazone, SCA and bromide residues and will provide the primary data for characterizing the fate and movement of residues between turf and bare soil and for calibrating a turf-based computer model.

## **V. Sampling Methodology**

- Soil to be analyzed for sulfentrazone, SCA and bromide background residues will be sampled using methods in soil sampling protocol FSSO002.00 (Garretson, 1999). These cores will be sampled to a depth of 3 feet in 6-inch increments. Upon extraction each 6-inch subsample will be divided with the fraction to be analyzed for sulfentrazone and SCA placed in a sealed jar and maintained in frozen storage. The fraction to be analyzed for bromide will be sealed in a plastic bag and maintained in refrigerated storage.
- Soil within the lysimeters to be analyzed for sulfentrazone, SCA and bromide will be sampled at the conclusion of the field study following the general methodology in soil sampling protocol FSSO002.00 (Garretson, 1999). The cores will be sampled to a depth of 3 feet in 6-inch increments. Each 6-inch sub-core will be 12 inches in diameter, corresponding to the inside diameter of lysimeters and extracted using trowels. Sanitizing of the trowels will be consistent with those methods used for bucket augers as stated in

sampling protocol FSSO002.00 (Garretson, 1999). Soil from each 6-inch sub-core will be thoroughly mixed inside a plastic bag and one of two subsamples of approximately 500 g transferred to a sealed jar and maintained in frozen storage until analysis for sulfentrazone and SCA. The remaining subsample will be transferred to a second plastic bag and placed in cold storage prior to analysis for bromide.

- Sampling from lysimeter reservoirs will consist of extracting all solution from each lysimeter using a peristaltic pump. Each extraction will be measured for total volume then partitioned into two vessels, one for sulfentrazone and SCA analysis and the other for bromide analysis. The samples will be transferred to refrigerated storage until chemical analysis. Between each solution extraction the transfer tubing will be flushed with cleansing liquids identical to those used for soil sampling equipment in protocol FSSO002.00 (Garretson, 1999).

## VI. Chemical Analysis and Quality Control

Pesticide analysis will be conducted by the CDFA Center for Analytical Chemistry where an analytical method is being developed for sulfentrazone and SCA. Analytical quality control procedures for these chemicals will follow recommendations from chemistry laboratory quality control protocol [QAQC001.00](#) (Segawa, 1995). Analysis for bromide residues in soil, lysimeter solution and vegetation, and quality control procedures for this analysis will follow those recommended in protocol [METH007.00](#) (Pinera-Pasquino, 2008).

## VII. Data Analysis

A generalized linear mixed model will statistically test each chemical within each study site or irrigation level for treatment effects (turf verses bare soil), thereby evaluating for significant effects of turf on overall chemical dissipation from the soil profile. For significant effects, a comparison of treatment means will indicate the magnitude of turf effects on chemical dissipation. The model will also test for interaction effects of treatment and soil depth, which will indicate the effects of turf on the movement and distribution of chemicals in the soil profile. The SAS software procedure PROC MIXED (Littell et.al., 2006) will allow for modeling treatment and soil depth as fixed effects and soil cores as the random effect. Soil cores will be treated as the random effect because their location is arbitrary with respect to the study design and the results would then be relevant to locations other than just the study sites.

Mixed Model Table	
Source of Variation	Degrees of Freedom
Treatment (turf vs bare soil)	1
Soil Depth	5
Treatment x Soil Depth	5
Error	24
Total	35



PROC MIXED also allows for modeling of the variance component and it is anticipated that this modeling will be necessary because of autocorrelation between chemical residue mass and soil depth. Various models will be evaluated with information criteria such as AIC (Akaike Information Criterion) used to determine the most appropriate model.

Parameterization of soil hydrology is necessary for modeling pesticide fate and movement in soil. Soil hydraulic conductivity and soil-water retention curves have already been established for the soil at this study site by physical measurement (Clayton et al., 2016), and these data will be used for this current study. Other hydrology-related parameters that are problematic to measure such as longitudinal dispersivity, tortuosity and boundary layer pressure head at the base of the lysimeters have previously been estimated for this site by model optimization processes (Clayton et al., 2016), and these data also will be utilized accordingly. Suitability of these data will be evaluated by comparing model-simulated output against field measurements for bromide residue distributions in the soil profile and recoveries from lysimeter reservoirs, and volume of water or solution extracted from the reservoirs. The root mean square error (RMSE) and visual comparison of these data will be used to assess the suitability of the previously optimized parameter values. In the event of disagreement between simulated and field-measured data, recalibration of the model-optimized parameters will be attempted and then evaluated using the same assessment procedure.

For simulations of sulfentrazone, chemical-specific parameters required for modeling purposes will be obtained from DPR's Pesticide Chemistry Database. However, if disagreement exists between simulated and field-measured data then parameter optimization procedures will be used in an attempt to improve the agreement. The procedure will be similar to that used by Clayton et al. (2016) and will likely focus on the soil adsorption isotherm coefficient and dissipation half-life value as these parameter values can be highly variable due to their association with soil. The RMSE and visual comparison also would be used to assess the new parameter values.

## **VIII. Estimated Timetable of Activities**

August 2016:

Construction and installation of lysimeters and irrigation system.

December 2016:

Evaluation of lysimeter integrity and functionality.

Testing and calibration of the irrigation system for uniformity of water application.

Compiling of weather data, water inputs and water extractions from lysimeters in preparation for calibration of water balances.

July 2017:

Development and calibration of water balance spreadsheets for scheduling water inputs to the study sites.

September 2017:

Sampling of soil cores, lysimeter solution and irrigation water for background sulfentrazone and bromide residues.

September 2017:

Chemigation of sulfentrazone and potassium bromide to study plots.

October 2017:

First irrigation (immediately after chemigation).

October 2017 (7 days later):

First extraction of solution from lysimeters for chemical analysis.

Second irrigation.

October 2017 (7 days later):

Second extraction of solution from lysimeters for chemical analysis.

Third irrigation.

Sequence continues at 7-day intervals.

December 2017:

Eleventh extraction of solution from lysimeters for chemical analysis.

Twelfth and final irrigation.

December 2017 (7 days later):

Twelfth and final extraction of solution from lysimeters for chemical analysis.

January 2018 (approximately 3 weeks later):

Sampling of soil from lysimeters for chemical analysis.

January 2018:

Chemical analysis of samples.

April 2018:

Data analysis, model development and reporting of study results.

## IX. Budget

Budget component	Units	Expense/unit (\$)	Total expense (\$)
Contracted cooperator	1	40,000	40,000
Pesticide soil analysis of background residues	12	864	10,368
QA/QC for background residues	1	864	864
Pesticide soil analysis	72	864	62,208
QA/QC for pesticide soil analysis	7	864	6,048
Pesticide analysis of chemigation solution	2	864	1,728
QA/QC for pesticide analysis of chemigation solution	1	864	864
Pesticide analysis of lysimeter reservoir solution	144	864	124,416
QA/QC for pesticide analysis of lysimeter reservoir solution	14	864	12,096
Equipment & supplies (lysimeters)	8	0	0
Equipment & supplies (other)	1	2,000	2,000
Travel	1	2,000	2,000
PY	0.25	100,000	25,000
Total			287,592

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Figure 1. Randomized layout of turf and bare soil plots in each study site.

