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November 2021

Study 332: Protocol for characterizing the relative fate and movement of glyphosate, bromacil, and diuron in leaching-vulnerable soils

INTRODUCTION

Although not currently identified as a potential groundwater contaminant on the California Department of Pesticide Regulation's (DPR) Groundwater Protection List (GWPL) (Title 3 California Code of Regulations [3CCR] section 6800), glyphosate has the highest use compared to other herbicides throughout California (CDPR, 2019) and its use has increased over time (Figure 1). To better understand the potential for glyphosate to contaminate groundwater, DPR's Groundwater Protection Program (GWPP) will use zero-tension column lysimeters to characterize its movement and fate in the soil environment. Lysimeters are typically inserted into the soil to measure movement of water and solute. They are commonly used for agricultural purposes to account for evapotranspiration and drainage losses by determining the change in soil water storage over time, usually by weight differential. Lysimeters are also utilized to sample soil drainage solution to determine solute concentration in contaminant transport research. In this context, the solution is collected in a reservoir at the bottom of the lysimeter either by gravitational means or by an active tension process, such as by mechanically-induced suction pressure. Solution in soil can also be collected by capillary action through a porous, ceramic-type interface with the soil and a reservoir. European member-states have utilized soil lysimeters for higher-tier assessments of pesticide leaching potential to provide data for use in their pesticide registration processes (FOCUS, 2009). In California, pesticide registrants and GWPP use lysimeters to investigate aspects of pesticide movement in the soil.

STUDY OBJECTIVE

For this study, GWPP will use zero-tension column lysimeters to monitor the movement and fate of glyphosate in soil. Diuron, bromacil, and potassium bromide will be applied to the lysimeters, along with glyphosate, to gauge glyphosate's relative persistence and movement in the soil. Diuron and bromacil, regulated pesticides that are known groundwater contaminants, will provide benchmarks for comparing glyphosate's potential for movement to groundwater. Bromide is often used as a conservative tracer for the movement of water through soil and is expected to be helpful as a benchmark for glyphosate movement in soil. Measuring bromide movement in soil is also useful for calibrating soil hydraulic properties if location- and soil-specific modeling of glyphosate's movement in soil is investigated. At a minimum, this study will involve general modeling of glyphosate's potential to impact groundwater using the Leaching Estimation and Chemistry Model (LEACHM) model (Hutson, 2003 and 2005) in conjunction with GWPP's standard modeling scenario (Troiano and Clayton, 2009). This information would potentially complement the field-derived data and provide estimates of groundwater concentrations.

PERSONNEL

DPR's Environmental Monitoring Branch's GWPP will conduct this study under the general direction of Joy Dias, Environmental Program Manager, and Carissa Ganapathy, Senior Environmental Scientist Supervisor. Project Personnel will include:

Project Leader:	Alfredo DaSilva
Senior Scientist:	Murray Clayton
Laboratory Liaison:	Vaneet Aggarwal
Staff Chemists:	California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry

Please direct questions regarding this study to Alfredo DaSilva at (559) 297-5404 or by e-mail at Alfredo.DaSilva@cdpr.ca.gov.

STUDY PLAN

GWPP scientists will conduct this study at the University of California Kearney Agricultural Research and Extension Center (KARE), located in Parlier, California. The lysimeters will be filled with one of two coarse-textured soil types: Hanford sandy loam soil or Delhi sandy soil. Initial activities include the experimental plot layout and installation, followed by testing the functionality of the lysimeters and the irrigation system. A three-month testing period of the lysimeter and irrigation systems will allow for reconstitution of the soil within the lysimeters and precise calibration of the irrigation system. The layout of the soil types within each irrigation block will follow a completely randomized design, as shown in Figure 2.

GWPP scientists will apply glyphosate, bromacil, and diuron to each lysimeter at the maximum label rates. These three pesticides will be dispensed through a syringe directly to the soil surface within each lysimeter. Potassium bromide will also be applied using the same technique at a rate of 100 kg bromide ions/hectare. All four chemicals will be applied simultaneously and incorporated into the soil with 1 inch of water immediately following their application. Irrigation will be applied on a weekly basis for approximately 140 days as follows:

- The Northern experimental block will receive water applications that simulate drainage conditions at 125% of typical summer-time cumulative reference evapotranspiration (ETo). This level of water input represents efficient applications and is currently a mitigation measure considered protective of groundwater in leaching-vulnerable areas where excessive water inputs have resulted in pesticide movement to groundwater.

- The Southern experimental block will receive water applications that simulate drainage conditions at 160% of typical summer-time cumulative ETo, representing typical applications from unpressurized surface delivery systems used in California (California Agricultural Technology Institute, 1988; Snyder et al., 1986). This level of water input produces excessive drainage water and has been shown to be responsible for pesticide movement to groundwater in leaching-vulnerable areas of California.

Irrigation will be indexed to ETo from CIMIS weather station #39 at KARE. Collection of daily weather station data will include ETo; mean, maximum, and minimum air temperature; and rainfall.

SAMPLING SCHEDULE AND METHODS

Background Samples

Prior to chemical application, GWPP scientists will collect background samples for pesticide and bromide residue analysis. These samples will include irrigation water, solution from lysimeter reservoirs, and soil adjacent to the lysimeters.

Solution

Background solution from the lysimeter reservoirs will be collected in the same manner as the post-application solution.

Soil

From the bare ground adjacent to randomly selected lysimeters, GWPP scientists will collect background soil core samples for bromacil, diuron, and bromide residue analysis. Samples will be collected at 6 inch increments to a depth of 3 feet using methods in Standard Operating Procedure (SOP) FSSO002.01 (Powell, 2021). Soil samples will be placed in a sealed jar and stored frozen on dry ice or in a freezer until chemical analysis. Samples for bromide residue analysis will be sealed in plastic bags and transferred to refrigerated storage until analysis.

Post-Application Sampling

Solution

After chemical application, the solution collected in each lysimeter reservoir will be extracted at 7-day intervals prior to the next weekly water application. The solution from each lysimeter will be analyzed for pesticides and bromide residues and the volume of the solution will be recorded to determine total drainage solution resulting from the water inputs.

Weekly sampling from the lysimeter reservoirs will consist of extracting all the solution from each lysimeter using an electric peristaltic pump. GWPP scientists will measure the total volume of each extraction; then the solution will be partitioned into a 125 mL opaque polyethylene container for glyphosate analysis and a 500 mL amber glass bottle for bromacil and diuron analysis. A 40 mL aliquot will be collected from each lysimeter reservoir for bromide analysis. All the samples will be placed on ice and transferred to refrigerated storage until chemical analysis. Between each solution extraction from the lysimeters, the pump tubing will be flushed with cleansing liquids identical to those used for soil sampling equipment in SOP FSSO002.01 (Powell, 2021).

Soil

Approximately 140 days after chemical application and 14 days after the final water application to the experimental blocks, GWPP scientists will core all lysimeters to their full depth to collect soil samples. These cores will be analyzed for bromacil, diuron, and bromide residues. Glyphosate analysis will not be conducted on soil samples due to the lack of an analytical method.

For soil sampling within the lysimeters, GWPP scientists will follow SOP FSSO002.01 (Powell, 2021). These cores will be sampled at 6-inch increments to a depth of 3 feet. However, the procedure differs from SOP FSSO002.01 (Powell, 2021) in that each 6-inch soil sub-core will be 12-inches in diameter (inside diameter of lysimeters) and extracted using shovels and trowels. Sanitization of the soil extraction equipment will be consistent with the methods used for bucket augers as stated in SOP FSSO002.01 (Powell, 2021). Soil from each 6-inch sub-core will be thoroughly mixed inside a plastic bag and one subsample of approximately 500 g will be transferred to a sealed jar on dry ice and maintained in frozen storage until pesticide analysis is conducted. The second subsample will be transferred to a sealed plastic bag and placed in cold storage until GWPP scientists perform the bromide residue analysis using SOP METH007.00 (Pinera-Pasquino, 2008).

CHEMICAL ANALYSIS AND QUALITY CONTROL

The CDFA Center for Analytical Chemistry's laboratory will conduct the pesticide analysis. The CDFA laboratory will analyze the water solution samples for bromacil and diuron using the Triazine Screen analytical method EM 62.9 (CDFA, 2020a) and for glyphosate using the Glyphosate Screen analytical method EMON-SM-05-045 (CDFA, 2020b). The CDFA laboratory previously developed a bromacil and diuron method for residues in soil (Method EM 29.7 [CDFA, 2002]). The method is currently undergoing validation for replacement instrumentation.

The current reporting limit for bromacil and diuron is 0.02 ppb in solution and 50 ppb in soil; the reporting limit for glyphosate and its degradation product, aminomethylphosphonic acid (AMPA), is 0.05 ppb in solution. The final reporting limits may be higher if there is interference in the sample or lower for soil samples due to newer instrumentation. The CDFA laboratory will provide reporting limits with the results and GWPP will include the reporting limits in the final report.

Analytical quality control procedures for these analyses will follow SOP QAQC001.01 (Peoples, 2019). According to guidelines in this SOP, DPR's laboratory liaison will also submit blind spikes to the CDFA laboratory. Quality control procedures for the analysis of bromide in soil and water will follow SOP METH007.00 (Pinera-Pasquino, 2008).

Note: the CDFA laboratory conducted a storage stability study of glyphosate and its degradate that showed the recovery percentage of the degradate declines considerably between 7 and 14 days. When the CDFA laboratory tested the storage stability with the preservative sodium thiosulfate on solution samples and at additional intervals, the recoveries declined after 10 days. Glyphosate demonstrated more stability than its degradate in both tests (Table 1). Solution samples will be delivered, extracted and analyzed within 7 days when they are not preserved, unless additional intervals are tested between 7 and 14 days for samples with no preservative. If GWPP scientists add a preservative to the solution upon collection, then the CDFA laboratory can extract and analyze samples by 10 days.

DATA ANALYSIS

GWPP scientists will compare the mass of glyphosate and AMPA recovered from the lysimeter reservoirs to the recovered residues of bromacil and diuron. These recoveries will indicate the potential for movement of glyphosate and its degradation product to groundwater relative to that of the known groundwater contaminants bromacil and diuron.

GWPP scientists will perform a mass balance analysis for bromide using the residues quantified from the soil cores sampled within the lysimeters and the solution extracted from the lysimeter reservoirs. An acceptable mass balance will provide options to calibrate the soil hydraulic-related properties of the LEACHM groundwater model to the study site. Recoveries of bromacil and diuron residues from the lysimeter reservoirs and from the soil within the lysimeters will provide data to validate the calibrated modeling scenario. A successful calibration and validation of the model will facilitate location- and soil-specific modeling of glyphosate fate and transport in soil, and provide estimates of groundwater concentrations should the simulations indicate residue movement to groundwater. Alternatively, GWPP scientists may conduct general modeling of glyphosate fate and transport in soil and to groundwater utilizing a more generalized modeling scenario, namely, the GWPP's LEACHM modeling scenario (Troiano and Clayton, 2009).

Results from the field and modeling components of the study will be evaluated together to provide an indication of the potential for glyphosate and its degradate to contaminate groundwater.

TIMETABLE OF ACTIVITIES

May – November 2021:

- Study planning.
- Install lysimeters.
- Install irrigation system and verify uniformity of water application.
- Conduct frequent irrigations over study plots until all lysimeter reservoirs experience collection of drainage solution to ensure their functionality and to standardize their soil water content.
- Calibrate water balance spreadsheets to enable water input scheduling and accurate predictions of solution movement to lysimeter reservoirs.

December 2021:

- Collect 18 soil samples for background pesticide and bromide analysis.
- Collect 13 solution samples from lysimeter reservoirs for background pesticide and bromide analysis, including one additional sample for analysis of irrigation water.
- Apply pesticides and potassium bromide to plots.
- Collect two samples of solution concentrate used for chemical application for pesticide and bromide analysis.

December 2021 – April 2022:

- Irrigate and extract solution from lysimeter reservoirs weekly.
- Collect 260 solution samples from lysimeter reservoirs for pesticide and bromide analysis.

May 2022:

- Collect 72 soil samples from within lysimeters for chemical and bromide residue analysis.

May – July 2022:

- Chemical analysis.

July – November 2022:

- Analyze data.
- Write study report.

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Figure 1. Agricultural use of glyphosate in California from 1990 to 2020 (CDPR, 2021)

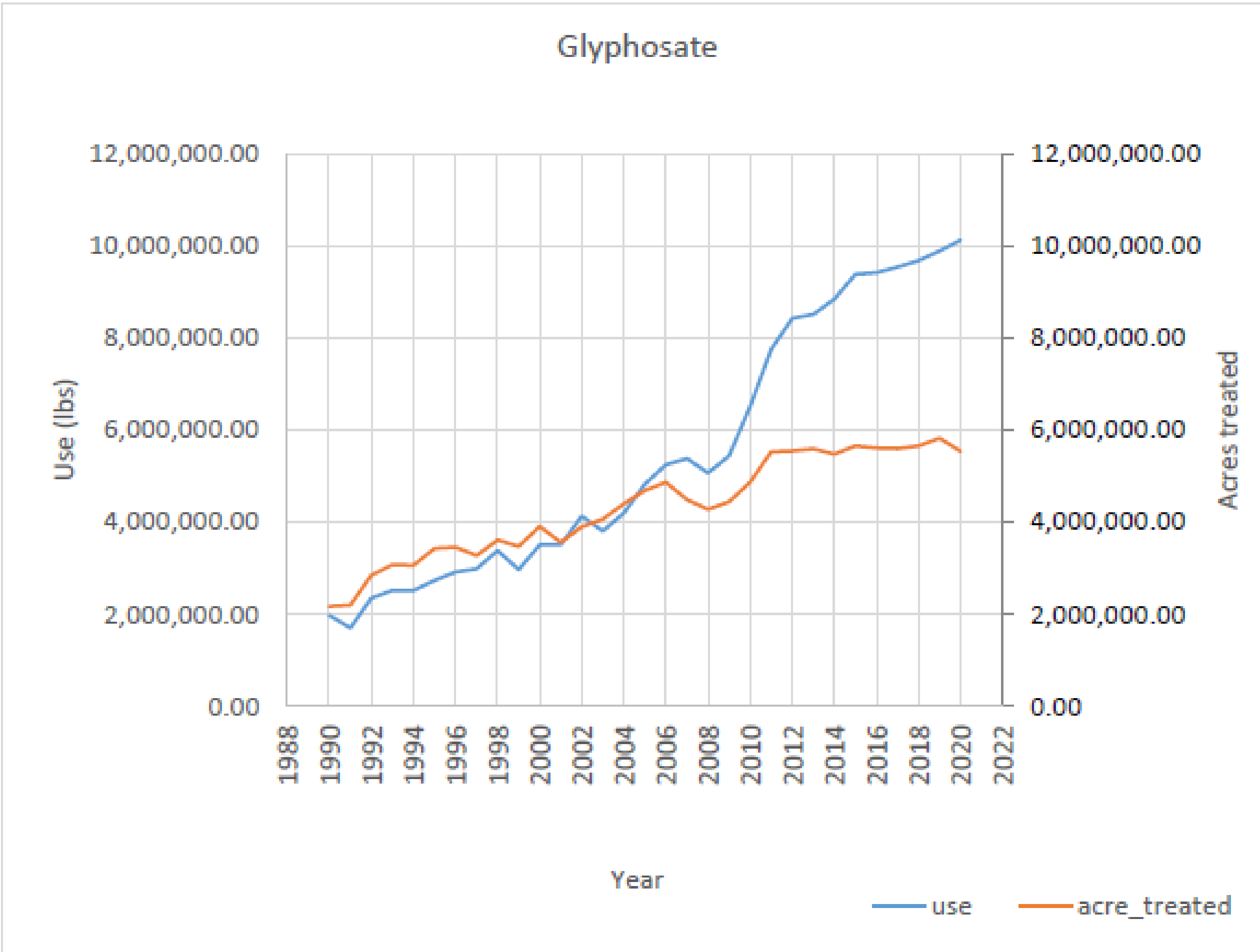

Figure 2. Lysimeter plot layout at the U.C. Kearney Agricultural Research and Extension Center

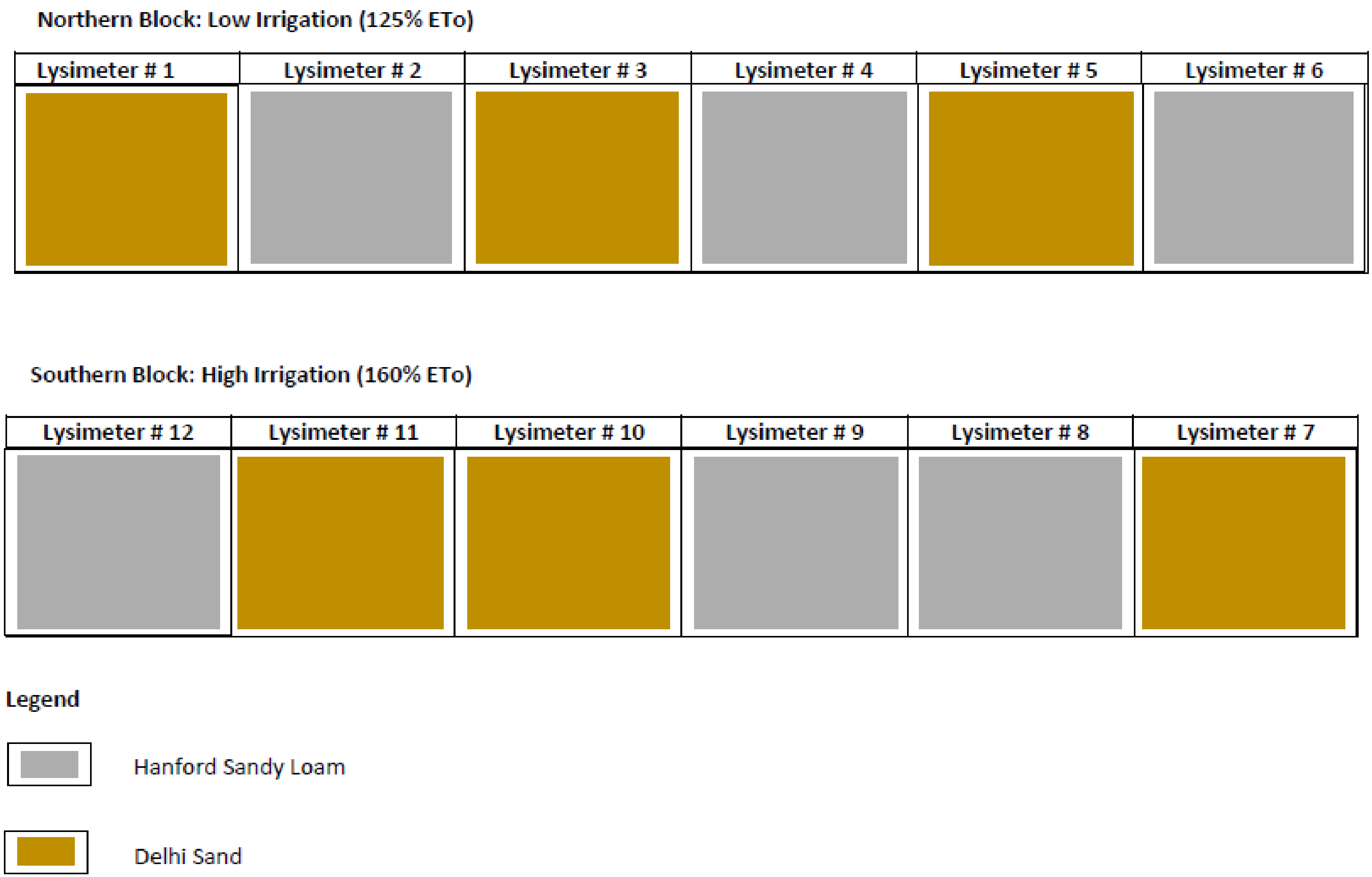

Table 1. Percent recovery (%) storage stability study results for glyphosate and its degradate AMPA without and with a preservative. Studies conducted by CDFA in 2019 and 2020.

Without Sodium Thiosulfate	**Day 0**	**Day 2**	**Day 3**	**Day 7**	**Day 9**	**Day 10**	**Day 13**	**Day 14**	**Day 17**	**Day 21**	**Day 22**
Glyphosate	103	116	90.8	107	-	-	-	86.9	-	-	-
AMPA	94.4	104	89.4	94.5	-	-	-	69.6	-	-	-

With Sodium Thiosulfate	**Day 0**	**Day 2**	**Day 3**	**Day 7**	**Day 9**	**Day 10**	**Day 13**	**Day 14**	**Day 17**	**Day 21**	**Day 22**
Glyphosate	83.1	93.9	94.7	102	113	113	113	106	70.6	70.2	75.4
AMPA	83.3	87.9	91.3	87.8	81.0	81.9	75.6	69.2	111	110	106