California Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1220 N Street, Room A-149
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RUNOFF AND LEACHING OF SIMAZINE AND DIURON USED ON HIGHWAY RIGHTS-OF-WAY

I. INTRODUCTION

Herbicides are used to control vegetation on California rights-of-way (ROW) by state and county agencies, railroads, irrigation and water districts, and private landowners. The California Department of Transportation (Caltrans) is responsible for vegetation control on state and interstate highway ROW.

According to Landscape Specialists in Caltrans Districts 3 and 10, preemergent herbicides are applied to highway ROW primarily during the rainy season (October through March). During the dry months, contact herbicides are applied. Thus the highest concentrations of preemergent herbicides are present when rain is likely, creating the potential for herbicides to be leached into the soil or carried from application sites in storm runoff. The design of ROW drainage may enhance the possibility that storm runoff will enter ground or surface waters: highway roadbeds are usually sloped so that rainwater runs off and away from the pavement, running over the treated shoulder; channels may conduct the runoff toward surface water bodies, or collect it in infiltration areas such as basins and trenches, to be detained until it evaporates or infiltrates into the soil; in some infiltration areas, infiltration is enhanced by the presence of dry wells. Thus if preemergent herbicide are present in runoff water, the potential for contamination of ground or surface water would seem to be great.

According to the Vegetation Control Program plans submitted by Caltrans districts to the Division of Maintenance, each district uses around a dozen different herbicide active ingredients in its program. The most heavily used in all districts, in terms of pounds of active ingredient applied, is glyphosate, a contact herbicide. After glyphosate, the most commonly used herbicides in most districts are oryzalin, simazine, diuron, bromacil and oxyfluorfen. Of these, the preemergent herbicides simazine, diuron and bromacil have been detected in groundwater by monitoring for the Pesticide Contamination Prevention Act.

Caltrans and other states' Departments of Transportation have studied pollutants in highway storm runoff extensively (e.g., Driscoll et al., 1990; Hoffman et al., 1985; Mar et al., 1982; Racin et al., 1982), but none of this research has looked at pesticides in runoff. The Environmental Hazards Assessment Program of the California Department of Pesticide Regulation (CDPR), in cooperation with Caltrans personnel, will conduct a study investigating the movement of simazine and diuron from treated highway

ROW in storm runoff. This will be the first of several studies to be conducted by the CDPR on the environmental impact of herbicides used on ROW.

Glenn County has been selected as the study location. Five herbicides (simazine, diuron, atrazine, prometon and bentazon) have been detected in well water in Glenn County (Cardozo et al., 1989), suggesting vulnerability of the area to groundwater contamination.

If this study shows that these herbicides do leave the ROW by runoff or leaching, further research should be done to assess the magnitude of the problem. ROW treated by other agencies should be investigated as well, since Caltrans' use accounted for just 26% of reported simazine use and 27% of reported diuron use on Glenn county ROW, according to pesticide use reports filed with the county agricultural commissioner for FY 90-91. It should also be determined whether runoff and leaching occur more in particular soil types, climates, or ROW drainage designs, so that recommendations may be made to help mitigate the problem.

II. OBJECTIVES

1. Determine what percentages of the simazine and diuron applied to highway shoulders leave the treated shoulder in storm runoff, and what percentages leach below the soil surface on the shoulder.

2. Determine whether simazine and diuron are leaching into the soil beneath infiltration areas.

3. Determine whether simazine and diuron are contained in highway storm runoff entering surface waters.

III. PERSONNEL

This study will be conducted by Environmental Hazards Assessment Program personnel under the overall supervision of Randall Segawa, Senior Environmental Research Scientist.

Study Group Leader: Sewell Simmons

Project Leader: Sally Powell

Senior Scientist: John Troiano

Field Coordinator: Jesus Leyva

Laboratory: California Department of Food and Agriculture
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Chemist: Duc Tran

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Caltrans Liaison: Robert Johnson

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IV. STUDY DESIGN

Objective 1: Runoff experiment

The first objective will be addressed by an experiment in which simulated rainfall is applied to the highway shoulder at intervals of 0, 2 and 4 weeks after the application of simazine and diuron.

Three sites have been selected on highways where Caltrans applies simazine and diuron in the fall as part of its regular vegetation control program, and where the herbicide-treated strip is 8 feet wide, the most common width for Caltrans shoulder applications. A site consists of a 73-foot length of shoulder along one side of the highway. Each site will be divided into 4 7-ft-long runoff plots with 15 feet between them. The runoff plots will extend for 17 feet from the edge of the pavement. (Three plots are needed for the experiment; the fourth is reserved as a spare.)

Caltrans typically applies simazine and diuron as a tank mixture of 2 lbs of Princep Caliber 90 and 4 lbs of Karmex 80W, respectively, in 50-100 gallons of water per acre. Applications usually begin in mid- to late-October, after some rain has moistened the ground. For this study, Caltrans personnel will make special applications in late September to increase the time before rain occurs. The shoulder area will be wetted prior to the application using a water tank truck. If rain does occur, the experiment will be continued, but the results will be interpreted differently.

Three 3-ft background soil cores will be taken at each site before the application, one core adjacent to each runoff plot. Each sample will be analyzed for herbicide concentrations, soil texture and soil bulk density.

To measure the actual herbicide application rate, kimbies will be left on the ground between the runoff plots during the herbicide application. In order to compare the application rates achieved in the special applications made for this study to those achieved in regular Caltrans applications, Caltrans personnel will place kimbies at three different locations during regular applications. These applications will occur in mid- to late-October.

At 0, 2 and 4 weeks after the special herbicide application, simulated rain will be applied to one new runoff plot at each site. Rain will be applied to the plot at 0.5 in/hr for one hour. Rainfall intensity-duration-frequency curves for Red Bluff (U.S. Dept. of Commerce Weather Bureau, 1955) show a 2-year return period for 1-hr intensities of 0.65 in/hr and 2-hr intensities of 0.45 in/hr. Two weeks after the first rain application to each plot, the same plot will receive a second "rainfall" of the same duration and intensity.

A rainfall simulator using two Spraying Systems Co. 1/4 HH14WSQ Fulljet nozzles has been assembled and tested in a pilot study. The simulator was built according to the specifications of Bubenzer, Molnau and McCool (1985), who found it produced drop size distributions and drop impact velocities similar to storms with rainfall intensities of 2.5 to 10 mm/hr (0.1 to 0.4 in/hr). Other nozzles that have typically been used in rainfall simulation produce drop characteristics similar to much higher-intensity rainfall.

The total volume of water running off the plot will be captured. Composite samples of the runoff will be taken for chemical analysis.

At the end of the experiment (six weeks after the herbicide application) and again at the end of the rainy season (in about April), one 3-ft soil core will be taken in each plot and analyzed for herbicide concentrations and bulk density.

Simazine and diuron concentrations in runoff and soil will be converted to mass of herbicide and to percentage of the total mass of herbicide applied to the plot. All sample concentrations will be corrected for extraction efficiency. Mean percentage of herbicide mass application recovered in runoff from the first and second rain events, and in the top 3 feet of soil, will be presented for each time interval. Results will be presented graphically and in tabular form; no statistical inference will be done because the small number of replicates makes the power of such procedures too low to be meaningful. The mass of herbicide that would leave the shoulders in runoff and the mass that would leach into the soil on the shoulders, given rainfall events similar to those simulated, will be estimated per mile of state highway in Glenn county.

Objective 2: Leaching in infiltration areas

The second objective will be addressed by taking soil cores repeatedly over the course of the rainy season at up to three sites where runoff water is detained for infiltration into the soil. Such sites could be freeway interchanges, roadside ditches lacking outlets, or infiltration basins. A 10-ft soil core will be taken in each site after Caltrans' regular fall application of simazine and diuron (in mid- to late-October). An additional core will be taken at each site at four-week intervals through March 1992 (if no rain has occurred in the interval, the sample will not be taken). The first core taken at each site will be split for soil textural analysis.

Soil concentration and bulk density measurements will be used to calculate the mass of herbicide in soil at each depth. All sample concentrations will be corrected for extraction efficiency.

Objective 3: Discharge of runoff to surface water

In some cases, highway runoff collected in roadside ditches is discharged directly into surface water such as a creek. Frequently the same ditch will serve to carry agricultural drainage water, so it would not be possible to attribute to highway runoff any pesticide found in the ditch water. However, if one or more sites can be found where highway runoff is discharged directly into surface water and where no agricultural drainage water enters the system, then the discharge will be sampled during rain events.

All sample concentrations will be corrected for extraction efficiency. The total volume of water discharged during the rain event and the herbicide concentration of the discharge will be measured and used to estimate the mass of herbicide discharged into the surface water body during the event. In addition, the total area draining into the ditch and the total herbicide application to that area will be estimated (using theoretical application rates) and used to express the mass of herbicide discharged as a percentage of the mass applied to the drainage area.

Table 1. Total number of samples

Study	Type of sample	Number of samples
Runoff experiment		
	Background soil (3-ft cores)	
	3 sites x 3 cores x 4 depths	36
	Kimbies (runoff experiment)	
	3 sites x 6 kimbies	18
	Kimbies (Caltrans application)	
	3 sites x 6 kimbies	18
	Background water (from tank truck)	6
	Runoff water	
	3 sites x 3 weeks x 2 rain apps x 2 samples	36
	Post-runoff soil (3-ft cores)	
	3 sites x 3 weeks x 4 depths	36
	Final soil (3-ft cores)	
	3 sites x 3 weeks x 4 depths	36
Leaching study		
	Soil (10-ft cores)	
	3 sites x 5 times x 11 depths	165
Discharge		
	Water	2-10

Note: Each sample will be analyzed for both simazine and diuron. 69 soil sample will have accompanying samples to be analyzed for soil texture.

V. SAMPLING METHODS

Objective 1: Runoff experiment

Soil: 3-ft soil cores will be taken using 6-in stainless steel cylinders inserted into an auger driven by a motorized drilling rig. A stainless steel collar will be placed to prevent surface dirt from falling into the hole. The top foot of soil will be sampled in 6-in increments, the remainder in 1-ft increments, i.e., by combining the contents of two cylinders. After a cylinder (or two, depending on the depth being sampled) is removed from the auger, it will be weighed with the soil in it. The tare weight of the cylinder and the total weight of the cylinder and soil will be recorded for bulk density estimation. The soil will be removed from the cylinder into a plastic bag, where it will be mixed. Then a 1-pt Mason jar will be filled for chemical analysis. With the first core taken at each site, 150 g of the remainder will be sealed in an 8 by 12-in plastic bag for transport to Fresno for textural analysis. The holes left by drilling will be filled with bentonite. Samples for chemical analysis will be transported on dry ice, and stored frozen until analysis.

Kimbies: At each site, three 1-sq-ft kimbies will be placed in the space between the first 2 plots, on a line perpendicular to the pavement and equidistant between the plots. The 3 kimbies will be placed at equal intervals across the 17 ft width of the runoff plots. Three more kimbies will be similarly placed between the third and fourth plots. Kimbies will be attached to plastic-covered cardboard sheets which have been placed on the ground and weighted down. Twenty minutes after completion of the herbicide application, individual kimbies will be removed from the cardboard backing, folded and wrapped in aluminum foil, sealed in manila envelopes, and placed on dry ice for transport to the lab. The sampling crew will wear respirators while collecting the kimbies.

Runoff: While artificial rainfall is being applied to a plot, the runoff will be channeled to a collection point by sheet metal barriers driven into the ground along the sides of the plot and in a V shape at the bottom of the plot. Runoff will flow through a 3-inch opening at the vertex of the V, running over a Teflon sheet into a metal collecting vessel set into the ground. As the vessel fills, water will be removed with a Nalgene hand pump and poured into stainless steel buckets. When runoff ceases, the volume of collected water will be measured, the collected water will be thoroughly mixed and two 1-L amber glass bottles filled for chemical analysis. Runoff samples will be transported on wet ice.

Objective 2: Leaching study

Soil: Methods for collecting and handling soil samples will be identical to those used in the runoff experiment. For the leaching study, however, the cores will be taken to a depth of 10 feet. The top foot of soil will be analyzed in 6-in increments, the remainder in 1-ft increments. The holes left by drilling will be filled with bentonite immediately after the samples are taken.

Objective 3: Discharge to surface water

Water: For each drainage ditch to be monitored, a flow-splitting sampler will be constructed. This sampler, developed by Clark and Mar (1980), requires no power source and can operate unattended. It consists of a rectangular open-channel flume that directs the water flow through a series of baffles that split the flow into progressively smaller fractions. The final fraction is diverted into a collection vessel. For this study we will collect 1.0%, the smallest sampling fraction tested by Clark and Mar. The sampled fraction will be held in a galvanized steel tank. Rain gauges will be placed at each site. Each of the first 1-3 rainstorms after regular Caltrans applications of simazine and diuron will be sampled. Local contacts will notify EHAP personnel when rain is occuring in the area. A sampling crew will drive to the site to wait for the end of the storm. The captured water will be thoroughly mixed and two 1-L amber glass bottles filled for chemical analysis. The volume of captured water will be measured in order to estimate the total runoff produced by the storm.

VI. CHEMICAL ANALYSIS/QUALITY CONTROL

Water will be analyzed for simazine and diuron using the short screen developed for CDPR groundwater monitoring. The method uses gas chromatography and has a detection limit of 0.1 ppb for both chemicals. Results will be reported in ppb. One matrix blank and one matrix spike will be analyzed with each extraction set.

Soil will be analyzed for simazine and diuron using the screen developed for CDPR compliance monitoring. The method uses solid phase extraction and gas chromatography and has a detection limit of 4 ppb for simazine and 40 ppb for diuron. Results will be reported in ppb on a dry weight basis. One matrix blank and one matrix spike will be analyzed with each extraction set.

Kimbies will be analyzed for simazine and diuron using gas chromatography. A method validation study will be done using five replicate samples spiked with both simazine and diuron at each of three levels (.5, 1 and 1.5 times the target application rate). Results will be reported in mg per sample. One matrix blank and one matrix spike will be analyzed with each extraction set.

Because this is a research study and because the analytical methods for simazine and diuron are well established, no secondary laboratory will be used.

VII. TIMETABLE

<u>Runoff experiment</u>

Runoff site preparation and background soil coring	September 16-20
Herbicide applications and first runoff trials	September 23-27
Second runoff trials	October 7-11
Third runoff trials	October 21-25
Final runoff trials and soil coring	November 4-8
Chemical analysis	Sept.23-Dec.9
Soil texture analysis	Sept.23-Dec.9
Data analysis	December-January
Draft of runoff section of report	February

<u>Leaching study</u>

Site selection	September 3-13
Soil coring #1	late October
Soil coring #2	late November
Soil coring #3	late December
Soil coring #4	late January
Soil coring #5	late February
Chemical analysis	November-March
Soil texture analysis	November-March

Discharge study	
Site selection	September
Sampler construction and installation	October
Sample collection	November-December
Chemical analysis	November-January
Draft combined report	April
Final combined report	May

VIII. BUDGET

Runoff study

Sampling apparatus		$ 1000
Per diem	4 people x 15 days x $84	5040
Vehicles	4 vehicles x 250 miles x 6 trips x $ .25	1125
Chemical analysis	186 field samples + 24 QC = 210 samples x $200	42000
		$49540

Leaching study

Per diem	4 people x 5 days x $84	$ 1680
Vehicles	3 vehicles x 250 miles x 6 trips x $ .25	1125
Chemical analysis	165 field samples + 20 QC= 185 samples x $200	37000
		$39805

Discharge study

Sampling apparatus		$ 1500
Vehicles	1 vehicle x 250 miles x 8 trips x $ .25	500
Chemical analysis	10 field samples + 4 QC = 14 samples x $200	2800
		$ 4800

IX. REFERENCES

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