Department of Pesticide Regulation
Environmental Monitoring Branch
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STUDY GW10: PROTOCOL FOR GROUND WATER PROTECTION LIST MONITORING FOR ORYZALIN

I. INTRODUCTION

The Pesticide Contamination Prevention Act (PCPA) (Statutes of 1985, Chapter 1298, Section 1) added sections 13141–13152 to the Food and Agricultural Code to prevent pesticide pollution of California's ground water. The PCPA outlines procedures for (1) gathering physical and chemical data on pesticides, (2) establishing specific numerical values (SNVs [threshold values]) for specified types of those data that the PCPA associates with the potential of a pesticide to leach through soil to ground water, (3) identifying pesticides that "exceed" those SNVs, and (4) placing pesticides that "exceed" SNVs and are applied in specified ways on the Groundwater Protection List (GWPL) (Title 3, California Code of Regulations section 6800[b]). The PCPA then requires the Department of Pesticide Regulation (DPR) to monitor for GWPL pesticides to determine if they have migrated to ground water.

II. OBJECTIVE

The purpose of this study is to determine whether oryzalin has migrated to California ground water as a result of agricultural use. Sampling of ground water will be focused in Ground Water Protection Areas (GWPAs) where agricultural use of oryzalin is relatively high and where previous monitoring for oryzalin has not occurred.

III. PERSONNEL

GWPL well sampling will be conducted by the Environmental Monitoring Branch. Project personnel include:

- Project Leader: Kelly Aguirre
- Field Coordinator: Jane Herrig
- Project Supervisor: Lisa Quagliaroli
- Senior Scientist: Murray Clayton
- Q.A./Lab Liaison: Sue Peoples
- Chemists: California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry, Staff Chemists

Please direct questions regarding this study to Mark Pepple at 916-324-4086, e-mail: <mpepple@cdpr.ca.gov>.

IV. STUDY PLAN

a) Active Ingredient Selection

DPR is required to monitor ground water for the pesticides on the GWPL which currently includes 93 actively registered pesticides. Pesticides on the GWPL were prioritized for monitoring by identifying those pesticides that had the greatest potential to contaminate ground water based on use patterns and physical-chemical properties. Pesticides with heavy and/or increasing use with a higher potential to move to ground water, based on the LEACHM pesticide fate and transport model (Hutson and Wagenet, 1992), received a higher prioritization because they presented a greater threat to ground water.

DPR intends to monitor for the herbicide oryzalin (3,5-dinitro-N4,N4-dipropylsulfanilamide). Based on the current GWPL prioritization scheme, oryzalin is ranked as the fourth highest threat to California ground water after diuron, norflurazon, and metolachlor. Oryzalin was chosen for monitoring because of its high potential to migrate to ground water, but also to test the predictive capabilities of the current GWPL prioritization scheme.

DPR has previously sampled 131 wells for oryzalin in 1993, 1998, and 2006. None of these wells tested positive for oryzalin. However, approximately half of these wells were selected for the focused sampling of napropamide, which is a pesticide active ingredient and was a constituent in the oryzalin analytical screen. Spatially, very little overlap of use existed between oryzalin and napropamide and potential detections of oryzalin in ground water were not anticipated at sites monitored for napropamide. Of the oryzalin-focused sampling sites 52 wells were sampled within GWPAs, with only approximately half of these wells in sections where cumulative use between 1990 and 2008 exceeded 2,500 lbs. Prior to the 1998 sampling study oryzalin use in these sections would likely have been considerably lower. Ground water sampling conducted in 2006 was localized to relatively few leaching vulnerable areas. Further ground water monitoring of oryzalin is necessary due to its continued high use and the need to expand monitoring activities beyond those areas previously sampled.

In addition to oryzalin, well water samples will be analyzed for the currently regulated ground water contaminants listed in Title 3, California Code of Regulations section 6800(a) and some of their degradation products, with the exception of bentazon. Samples will also be analyzed for hexazinone and tebuthiuron because these pesticides have been also found in California ground water and their potential for regulated use is under consideration. This group of analytes and oryzalin are highly ranked as potential ground water contaminants by the GWPL prioritization scheme. Detections of the known ground water contaminants and oryzalin would provide some verification as to the predictive capabilities of the current prioritization scheme. In contrast, detections of the known ground water contaminants in the absence of oryzalin would indicate that further refinement of the prioritization scheme would need to be considered.

b) Active Ingredient Use Patterns

Oryzalin is an herbicide primarily used to control broadleaf weeds and grasses. Sites which account for the most use include almonds (23 percent [%] of total use), wine grapes (17%), other grapes (12%), pistachios (10%), and rights of way (10%). The label allows for application directly to the soil either through chemigation or broadcast spray. DPR’s Pesticide Use Reports indicate that oryzalin use throughout California and in GWPAs experienced a rapid decline starting in 1998 but returned to previous or higher levels of use after 2004 (Figures 1 and 2, respectively) (CDPR, 2010). The highest use of oryzalin within California counties and their GWPAs, has occurred in Fresno, San Joaquin, Tulare, Merced, and Madera (Figures 3 and 4, respectively).

c) Study Area Selection

Sections for ground water sampling were selected within GWPAs based on high oryzalin use, which happened to coincide, in most instances, with high use of one or more of the known California ground water contaminants. GWPAs have been identified by DPR as particularly vulnerable to groundwater contamination. Vulnerable areas generally have a shallow ground water table and soils with either coarse textures with a potential for direct residue leaching or an impermeable layer with potential for residue run-off to either a site leading to more permeable soils or to a structure providing access directly to ground water.

A total of 40 wells in high priority sections will be targeted for sampling (Table 1). Emphasis will focus on sampling wells that are at least one mile apart. If a well is not available in a high priority section, a well will be selected from an adjacent section provided it is within 0.2 miles of the target section and at least one mile from the nearest sampled well. If 40 wells cannot be sampled from high priority sections, alternative sections for sampling have been identified (Table 2). Proximity to almonds, wine grapes, other grapes and pistachios–crops with the heaviest reported use of oryzalin–will also be considered when selecting wells for sampling.

A positive detection of oryzalin in well water could result in the sampling of additional wells to characterize the extent of its movement to ground water.

V. SAMPLING AND ANALYTICAL METHODS

Where domestic wells are available, they will be selected according to procedures in the standard operating procedure (SOP) FSWA006.01 (Nordmark and Pinera-Pasquino, 2008b). Where domestic wells are unavailable, other types of wells, such as irrigation, municipal, stock, community, and small water system wells, will be sampled. Samples will be collected using the methods described in SOP FSWA001.01 (Nordmark and Pinera-Pasquino, 2008a). Samples containing deionized water (field blanks) will be collected at the same time as field samples and analyzed to confirm the validity of positive results. Chemical analysis will be performed by the CDFA Center for Analytical Chemistry in accordance with methods EM 62.9 (Hsu, et al., 2010) and EMON-SM-05-004 (Lee, 2010). Analytes, method detection limits, and reporting limits for this study are given in Table 3. Quality control will be conducted in accordance with SOP QAQC001.00 (Segawa, 1995).

VI. DATA ANALYSIS

Data obtained from the CDFA Center for Analytical Chemistry will be used to determine if oryzalin is migrating to ground water. These data will also be used to generate a study report detailing our findings. Analytical results will be provided to participating property owners within 12 to 16 weeks of sampling.

VII. TIMETABLE

- November 2010-December 2010: Conduct sampling for oryzalin
- January 2011-February 2011: Obtain analysis results from CDFA laboratory
- February 2011: Mail results to property owners
- March 2011: Write study memorandum

VIII. BUDGET

Table 4. Study Budget Estimate.

Budget Component	Units	Expense per Unit	Total Component Expense
Pesticide sample analysis – oryzalin	40 samples	$720	$28,800
Pesticide sample analysis – known CA contaminants	40 samples	$720	$28,800
Pesticide sample analysis – QC samples	~10 samples	$720	$7,200
Travel	~ 20 days	$130	$2600
PY	~ 0.2	$100,000	$20,000
Total			$86,100

REFERENCES

CDPR. 2010. Pesticide Use Reports. Available at: <http://www.cdpr.ca.gov/docs/pur/purmain.htm> (verified November 8, 2010). California Department of Pesticide Regulation, Sacramento, California.

Hsu, J., White, J., and Lee, P. 2010. EM 62.9. Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotraizine (DACT), Tebuthiuron and the metabolites Tebuthiuron-104, Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 in Well Water and River Water By Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm> (verified November 8, 2010). California Department of Pesticide Regulation, Sacramento, California.

Hutson, J.L. and R.J. Wagenet. 1992. LEACHM: Leaching Estimation and Chemistry Model: a process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Continuum Volume 2, Version 3. Water Resources Inst., Cornell University, Ithaca, New York.

Lee, P. 2010. EMON-SM-05-004. Determination of Napropamide and Oryzalin in Ground water by High Performance Liquid Chromatography with Ion Trap Mass Spectrometry. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm> (verified November 8, 2010). California Department of Pesticide Regulation, Sacramento, California.

Nordmark, C. and L. Pinera-Pasquino. 2008a. SOP FSWA001.01. Obtaining and Preserving Well Water Samples. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa00101.pdf> (verified November 8, 2010). California Department of Pesticide Regulation, Sacramento, California.

Nordmark, C. and L. Pinera-Pasquino. 2008b. SOP FSWA006.01. Selection of a Suitable Wells and Study Sites for Ground Water Monitoring. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa00601.pdf> (verified November 8, 2010). California Department of Pesticide Regulation, Sacramento, California.

Segawa, R. 1995. SOP QAQC001.00. Chemistry Laboratory Quality Control. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf> (verified November 8, 2010). California Department of Pesticide Regulation, Sacramento, California.

ADDITIONAL TABLES AND FIGURES

Table 1. High priority sections for ground water sampling. Oryzalin use is cumulative from 1995-2007 (CDPR 2010).

COUNTY	CMTRS	ORYZALIN USE (LBS)
	10M13S21E22	3,611
	10M14S23E21	4,326
	10M14S23E22	3,248
	10M14S23E28	4,661
	10M14S24E32	2,989
	10M16S22E16	3,005
Fresno	10M16S22E31	2,832
Kern	15M25S25E17	10,328
	20M10S18E23	6,366
	20M11S15E22	5,107
	20M11S16E16	2,862
	20M12S15E13	3,475
	20M12S15E23	3,614
	20M12S15E24	2,854
	20M12S15E25	3,682
	20M12S15E26	3,222
	20M12S16E30	2,735
Madera	20M12S17E36	3,651
	24M06S10E36	3,494
	24M06S11E31	2,805
	24M06S13E06	4,203
	24M07S12E04	2,836
Merced	24M07S12E13	3,031
	39M01S07E07	4,031
	39M01S08E30	11,350
	39M02S07E01	3,292
	39M02S08E02	4,119
	39M02S08E07	3,964
	39M02S08E09	5,357
	39M02S09E06	2,785
	39M02S09E07	3,175
	39M02S09E09	3,035
	39M02S09E14	2,955
	39M02S09E15	4,551
	39M03N05E12	3,063
San Joaquin	39M04N06E03	3,440
	54M16S23E09	3,398
	54M17S23E02	3,638
	54M17S23E03	2,871
Tulare	54M21S26E11	3,615

Table 2. Alternate sections for ground water sampling. Oryzalin use is cumulative from 1995-2007 (CDPR, 2010).

COUNTY	CMTRS	ORYZALIN USE (LBS)
Fresno	10M13S17E14	2,520
	10M13S18E10	2,292
	10M13S18E33	2,060
	10M13S19E07	2,047
	10M15S24E07	2,548
	10M15S24E18	2,587
Kings	16M17S22E12	2,769
Madera	20M10S18E24	2,415
	20M11S16E05	2,292
	20M12S17E24	2,348
	20M12S17E32	2,340
	20M12S17E33	2,519
	20M12S18E27	2,205
	20M13S17E05	2,548
Merced	24M06S11E20	2,425
San Joaquin	39M01S07E21	2,453
	39M01S08E34	2,383
	39M01S08E35	2,151
	39M02S07E02	2,517
	39M02S07E24	2,267
	39M02S07E27	2,197
	39M02S07E35	2,251
	39M02S08E01	2,350
	39M02S08E03	2,338
	39M02S08E04	2,237
	39M02S08E08	2,096
	39M02S08E11	2,534
	39M02S08E12	2,318
	39M02S08E17	2,381
	39M02S08E18	2,459
	39M02S09E02	2,614
	39M02S09E17	2,692
	39M03N06E24	2,351
	39M03N07E18	2,459
	39M04N06E05	2,196
Stanislaus	50M02S09E28	2,182
Tulare	54M17S23E12	2,110
	54M17S23E15	2,684
	54M18S27E18	2,122
	54M19S26E05	2,064

Table 3. Department of Food and Agriculture, Center for Analytical Chemistry analytical method details.

Herbicide in Ground Water by LC/MS

Compound	Method Detection Limit (ug/L)	Reporting Limit (ug/L)
Oryzalin	0.036	0.05
DACT	0.0063	0.05
ACET	0.013	0.05
DEA	0.0110	0.05
Hexazinone	0.025	0.05
Simazine	0.0135	0.05
Bromacil	0.020	0.05
Prometon	0.012	0.05
Atrazine	0.015	0.05
DSMN	0.015	0.05
Norflurazon	0.0063	0.05
Diuron	0.043	0.05
Tebuthiuron	0.014	0.05
Tebuthiuron M-104	0.042	0.05
Tebuthiuron M-106	0.017	0.05
Tebuthiuron M-107	0.027	0.05
Tebuthiuron M-108	0.031	0.05

Figure 1. Total Oryzalin Use in California for Reporting Years 1995-2007 (CDPR, 2010).

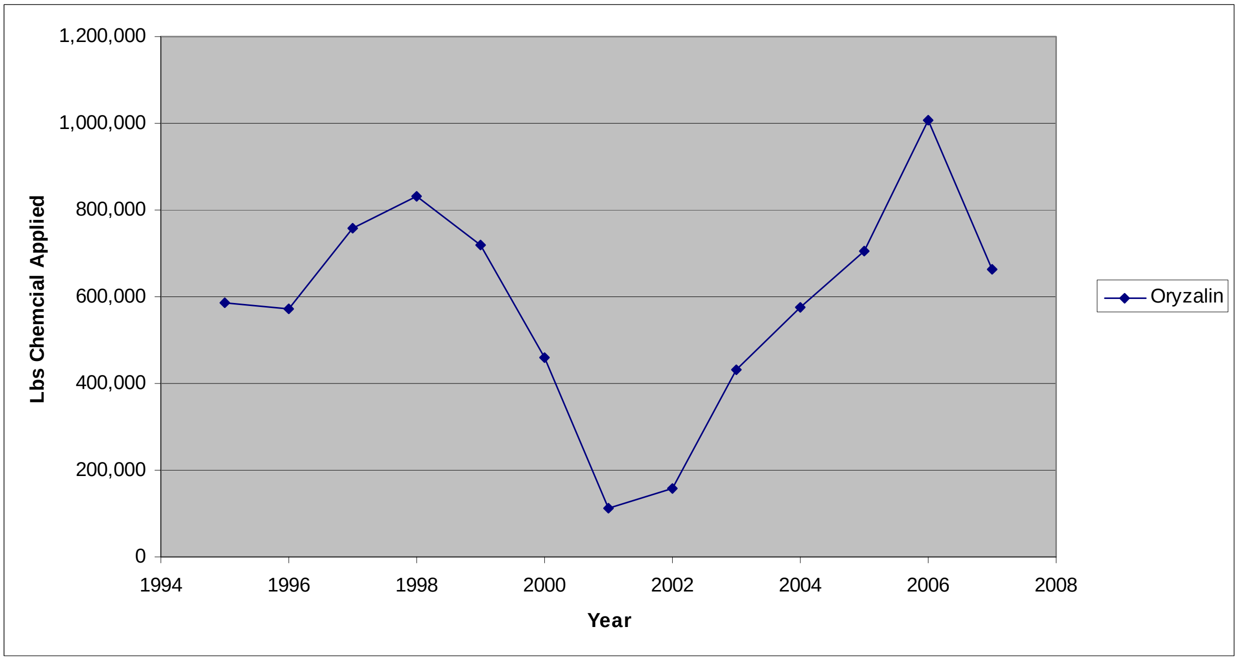

Figure 2. Total Oryzalin Use in California Groundwater Protection Areas for Reporting Years 1995-2007 (CDPR, 2010).

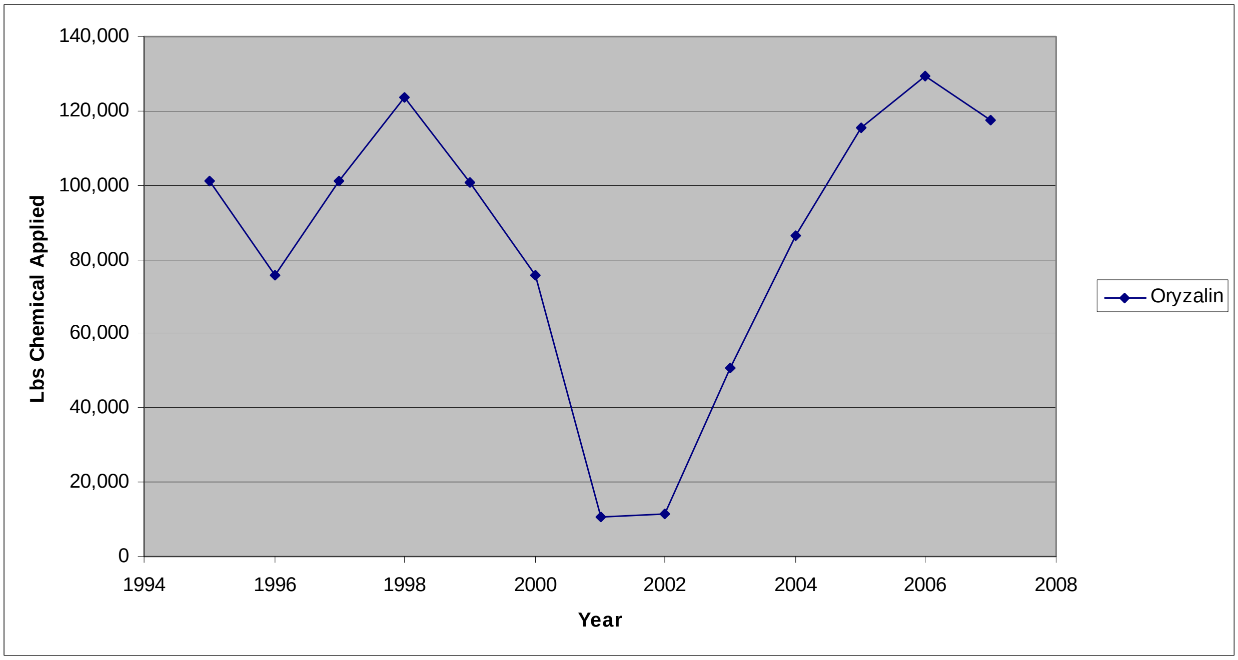

Figure 3. Total Oryzalin Use in Top Five Counties for Reporting Years 1995-2007 (CDPR, 2010).

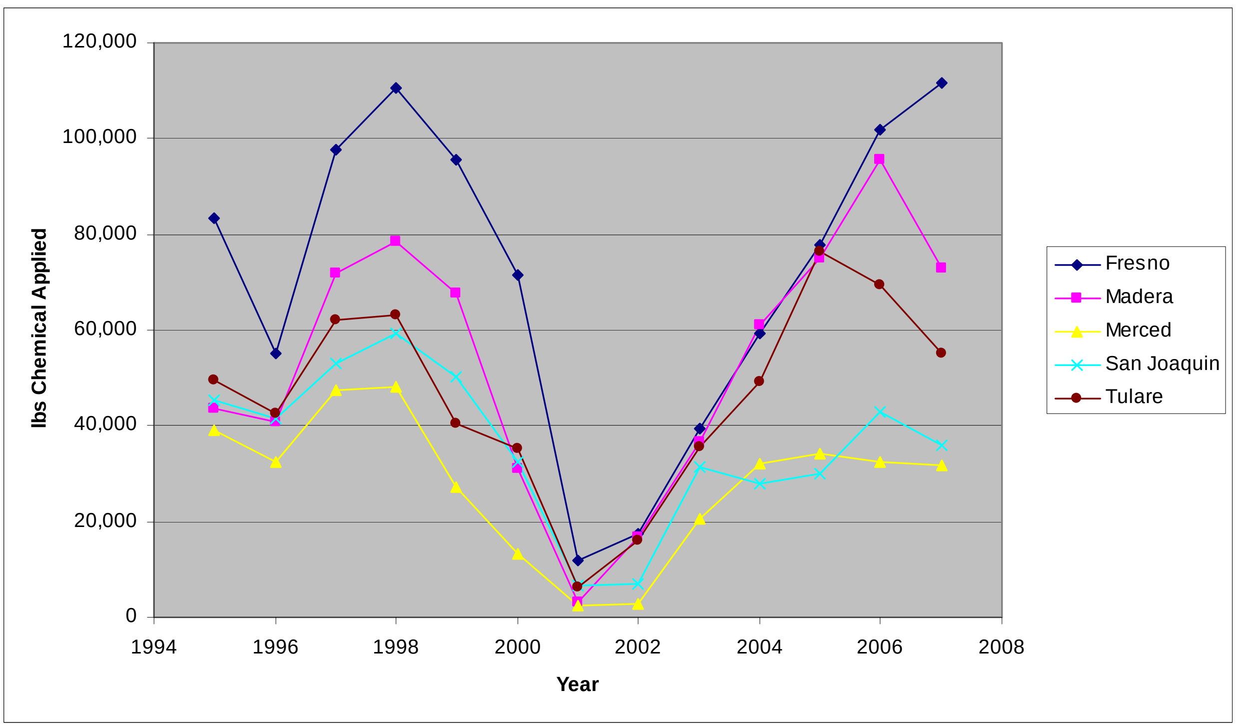

Figure 4. Oryzalin Use in Groundwater Protection Areas for the Top Five Counties for Reporting Years 1995-2007 (CDPR, 2010).