Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street, P.O. Box 4015
Sacramento, California 95812

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STUDY GW10: PROTOCOL FOR GROUND WATER PROTECTION LIST MONITORING FOR AZOXYSTROBIN, CHLOROTHALONIL, DICLORAN, AND IPRODIONE

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 azoxystrobin, chlorothalonil, dicloran, or iprodione have migrated to California ground water. Sampling of ground water will focus on areas where agricultural use of these compounds is relatively high and the potential for residue movement to ground water is greatest.

III. PERSONNEL

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

- Project Leader: Joy Dias
- Field Coordinator: Craig Nordmark
- 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, 1992), received a higher prioritization because they presented a greater threat to ground water.

DPR intends to monitor for the following fungicides using a multi-analyte screen (Pyatt, 2009):

- azoxystrobin (methyl (E)-2-{2-[6-(2-cyanophenoxy) pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate)
- iprodione (3-(3,5-dichlorophenyl)-N-(1-methylethyl)2,4-dioxo-1-imidazoline-carboximide) and its stereoisomer 3-(1-methylethyl)-N-(3,5-dichlorophenyl)-2,4-dioxo-1-imidazolidine carboxamide (RP-30228)
- dicloran (2,6-dichloro-4-nitroaniline)

In addition to monitoring for the parent compounds, DPR will also monitor for several main degradates (Pyatt, 2009):

1. Azoxystrobin Degradates
   - Methyl(Z)-2{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate (R-230310)
   - (E)-2-[6(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylic acid (R-234886)
2. Iprodione Degradates
   - 3,5-dichloroaniline (RP-32596)

DPR will also monitor for chlorothalonil (tetrachloroisophthalonitrile) if an analytical method is available by March 2011.

Depending on use patterns, some wells will be sampled for hexazinone, tebuthiuron, and the known ground water contaminants (Title 3, California Code of Regulations section 6800[a]) and some of their degradates. We periodically monitor for known ground water contaminants to help assess the adequacy of our mitigation measures and to determine if the Ground Water Protection Areas need to be expanded. Samples are also analyzed for hexazinone and tebuthiuron because those pesticides may be migrating to ground water (please see previous monitoring studies for hexazinone and tebuthiuron) and additional data is needed to formulate a regulatory decision, if necessary.

b) Active Ingredient Use Patterns

Azoxystrobin is a systemic fungicide primarily used from early bloom to petal fall on grapes, almonds, and rice. The label allows for application through chemigation or directly to soil. Data obtained from DPR's Pesticide Use Reports indicate that azoxystrobin use throughout California increased from 1997 to 1998, but has stayed fairly steady from 1998 to 2006 (Figure 1) (CDPR, 2010). The highest use of azoxystrobin occurs in Butte, Fresno, Glenn, Kern, and Merced counties (Figure 2).

Chlorothalonil is a broad-spectrum contact fungicide applied most heavily to tomatoes, potatoes, onions, and celery. The fungicide is primarily applied to seed beds, foliage and fruit, and can be applied to directly to the soil or through chemigation. Statewide chlorothalonil use increased sharply from 1997 to 1998, but has remained fairly steady from 1999 to 2006 (Figure 1) (CDPR, 2010). Chlorothlonil is used widely throughout the state, but the highest use counties are Fresno, Kern, San Diego, San Joaquin, and Ventura (Figure 3).

Dicloran is a foliar fungicide used primarily on lettuce, grapes, and celery. The label also allows for application directly to the soil or through chemigation. Dicloran statewide use has slightly decreased from 1997 to 2006 (Figure 1) (CDPR, 2010) with the highest use occurring in Monterey, Ventura, Tulare, Fresno, and Kern counties (Figure 4).

Iprodione is a contact fungicide primarily used on almonds, carrots, grapes, and leaf lettuce. The label also allows for application directly to the soil or through chemigation. Iprodione use decreased from 1997 to 2003 but has been increasing from 2003 to 2006 (Figure 1) (CDPR, 2010). The counties with the highest iprodione use are Kern, Monterey, Fresno, San Luis Obispo, and Kings (Figure 5).

c) Study Area Selection

Potential study areas will be chosen based on the amounts of pesticide applied and/or soil vulnerability. 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 a site leading to more permeable soils. We will target up to 240 wells located in the highest use areas, giving priority to sections that also have vulnerable soils. In high use vulnerable sections up to three wells may be sampled depending on the availability of wells both in the targeted section and the surrounding sections. If wells are not available in a target section, wells may be sampled from within 0.2 miles of the surrounding sections. If we find a positive detection, further sampling may be undertaken to better characterize the extent of the ground water contamination.

The following high use counties will be targeted for well sampling: Fresno, Kern, Tulare, Merced, Monterey, and Ventura (Table 1). Additional counties may be sampled if they have high use sections in vulnerable areas. The fungicides azoxystrobin, dicloran, and iprodione will be analyzed as a multi-analyte screen, but each pesticide will be targeted individually. Chlorothalonil will be sampled for after an analytical method is finalized. If the laboratory determines that chlorothalonil has a long storage stability half-life, unused and unneeded back-up samples for previously sampled wells may be used for chlorothalonil analysis if they were collected in high use areas. Samples for hexazinone, tebuthiuron, and the known ground water

contaminants will be collected if a well targeted for fungicide use has historical use of the known ground water contaminants and is not located in a Ground Water Protection Area.

Table 1. Proposed number of wells targeted per high-use county and pesticide.

County	Azoxystrobin	Chlorothalonil	Dicloran	Iprodione	TOTAL
Fresno	15	25	0	20	60
Kern	15	25	10	5	55
Tulare	15	0	10	5	30
Monterey	0	0	20	20	40
Merced	15	0	0	10	25
Ventura	0	10	20	0	30
TOTAL	60	60	60	60	240[1]

V. SAMPLING AND ANALYTICAL METHODS

Where domestic wells are available, they will be selected according to procedures in SOP FSWA006.01 (Nordmark, 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, 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. Analytical method detection, analytes, method detection limits, and reporting limits for this study are given in Table 3. Details of the chemical analysis methods and method detection/reporting limits for newly developed methods will be provided in the final report. 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 pesticides are 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

- May 2010-June 2011: Conduct sampling for azoxystrobin, chlorothalonil, dicloran, and iprodione.
- July 2010-August 2011: Obtain analysis results from CDFA laboratory.
- When sampling is concluded: Mail results to property owners.
- November 2011: Write study memorandum.

[1] If these pesticides are detected during this study, additional samples may be taken to better characterize the extent of the ground water contamination.

VIII. BUDGET

Table 2. Study Budget Estimate.

Budget Component	Units	Expense per Unit	Total Component Expense
Pesticide sample analysis – initial samples	≤ 360 samples[2]	$720	$259,000
Pesticide sample analysis – QC samples	≤ 90 samples	$720	$65,000
Pesticide sample analysis – New AI detection follow up	≤ 60 samples	$720	$43,000
Travel[3]	≤ 240 days	$130	$31,000
PY	≤1.5	$150,000	$150,000
Total			$548,000

[2] The initial sample estimate is based on the assumption that we will sample up to 240 wells for azoxystrobin, chlorothalonil, dicloran, and iprodione and up to 120 wells for the known / suspected ground water contaminants.
[3] The travel estimate is based on the following assumptions: 300 wells will be sampled and a two-person team will sample 10 wells during a 4-day week.

IX. REFERENCES

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Segawa, R. 1995. SOP QAQC001.00. Chemistry Laboratory Quality Control. Available at: <http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf> (verified March 25, 2010). California Department of Pesticide Regulation, Sacramento, California.

X. TABLES AND FIGURES

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

Fungicide in Ground Water by LC/MS

Compound	Method Detection Limit (ug/L)	Reporting Limit (ug/L)
Azoxystrobin	0.0165	0.05
Azoxystrobin Acid	0.0298	0.05
Azoxystrobin Z-metabolite	0.0187	0.05

Fungicide in Ground Water by GC/MS

Compound	Method Detection Limit (ug/L)	Reporting Limit (ug/L)
Iprodione/Isoiprodione	0.0317	0.05
3,5-dichloroaniline	0.0739	0.10
Dicloran	0.0255	0.05

Herbicide in Ground Water by LC/MS

Compound	Method Detection Limit (ug/L)	Reporting Limit (ug/L)
DACT	0.0063	0.05
ACET	0.0130	0.05
DEA	0.0110	0.05
Hexazinone	0.0250	0.05
Simazine	0.0135	0.05
Bromacil	0.0200	0.05
Prometon	0.0120	0.05
Atrazine	0.0150	0.05
DSMN	0.0150	0.05
Norflurazon	0.0063	0.05
Diuron	0.0430	0.05
Tebuthiuron	0.0140	0.05
Tebuthiuron M-104	0.0420	0.05
Tebuthiuron M-106	0.0170	0.05
Tebuthiuron M-107	0.0270	0.05
Tebuthiuron M-108	0.0310	0.05

Figure 1. Total Azoxystrobin, Chlorothalonil, Dicloran, and Iprodione Use in California for Reporting Years 1997-2006 (CDPR, 2010).

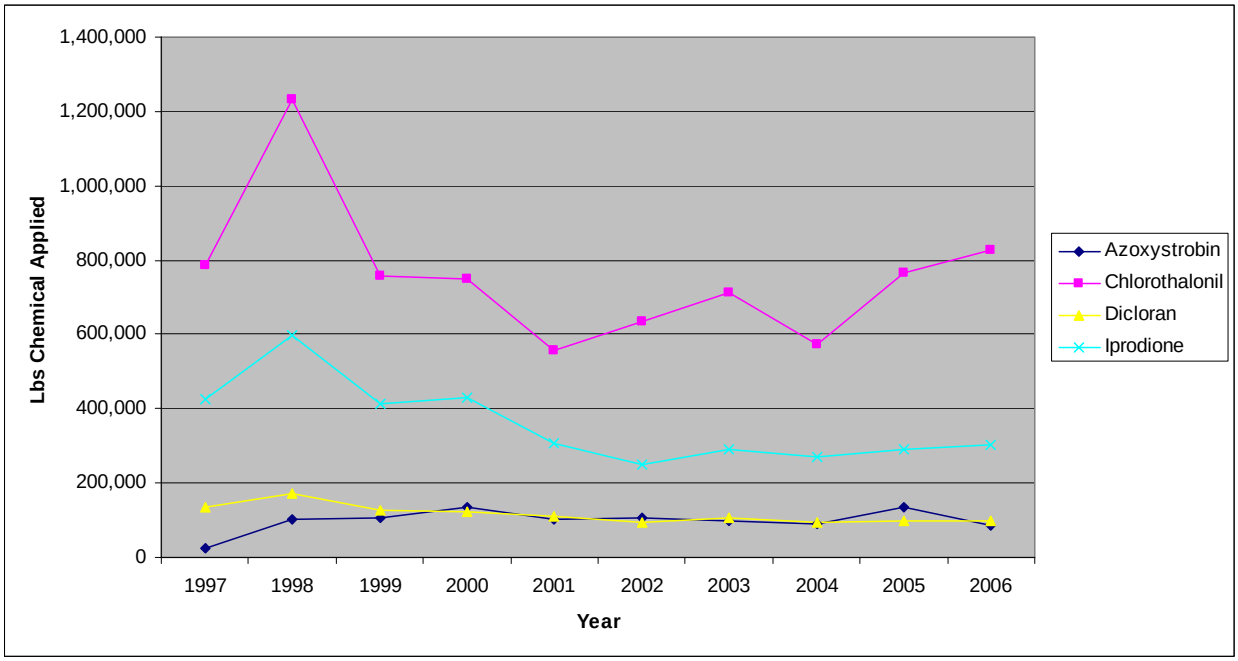

Figure 2. Azoxystrobin Use in the Top Five Counties for Reporting Years 1997-2006 (CDPR, 2010).

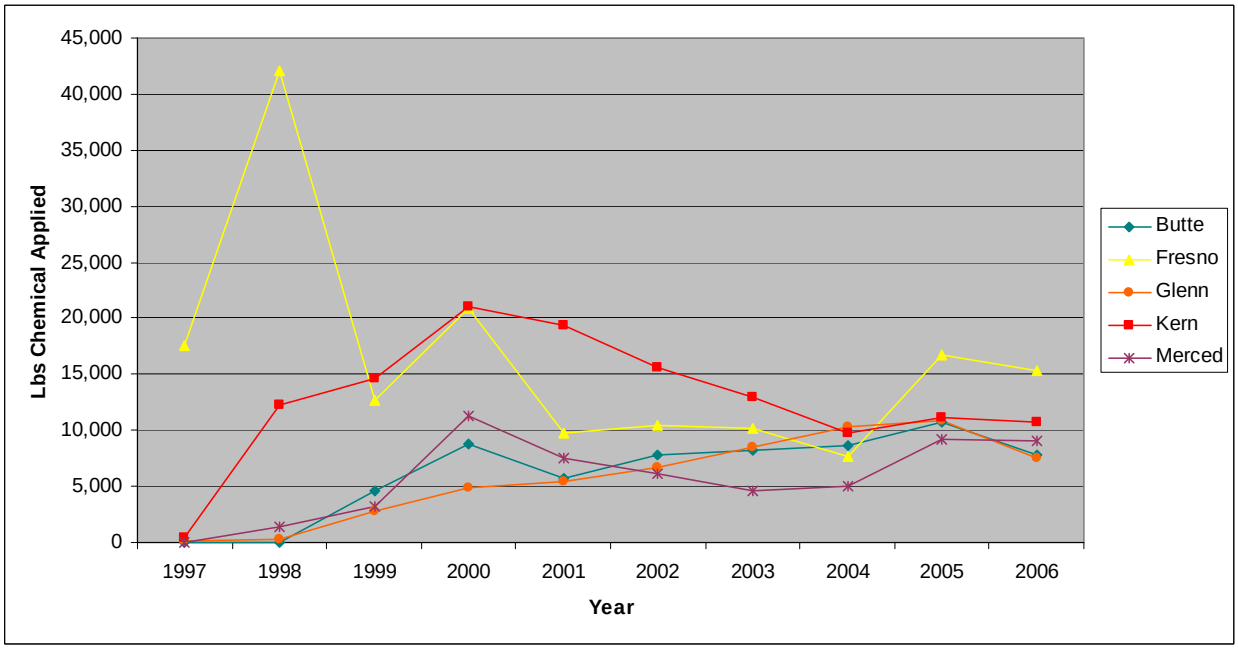

Figure 3. Chlorothalonil Use in the Top Five Counties for Reporting Years 1997-2006 (CDPR, 2010).

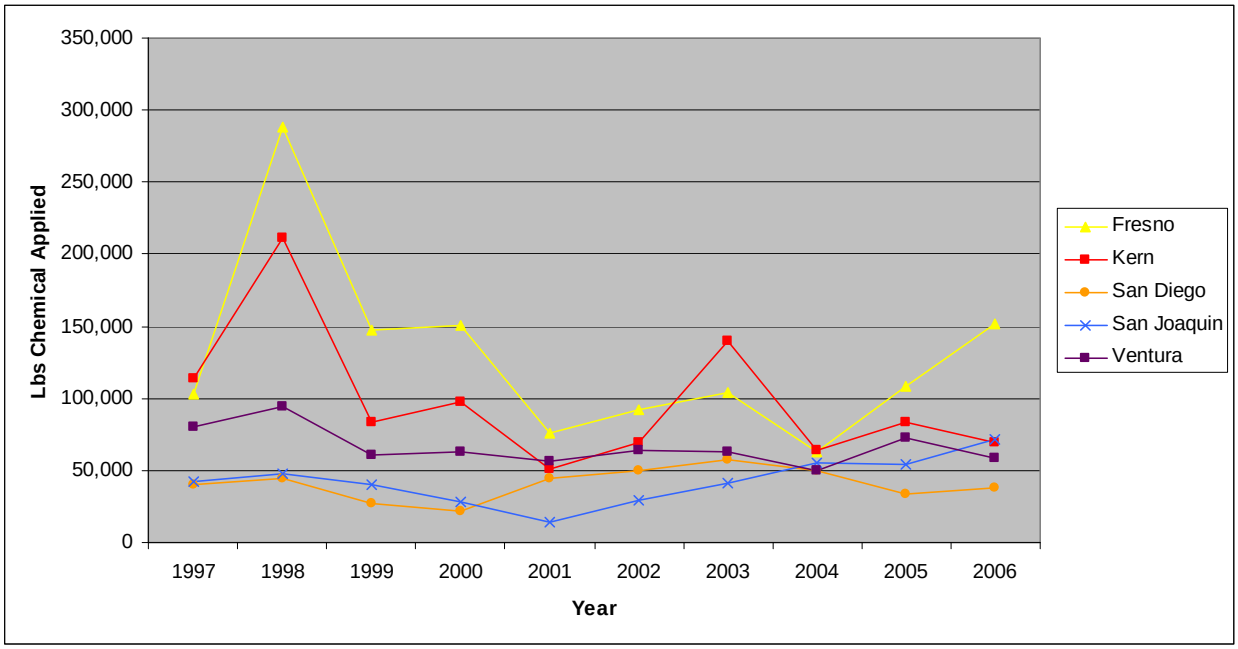

Figure 4. Dicloran Use in the Top Five Counties for Reporting Years 1997-2006 (CDPR, 2010).

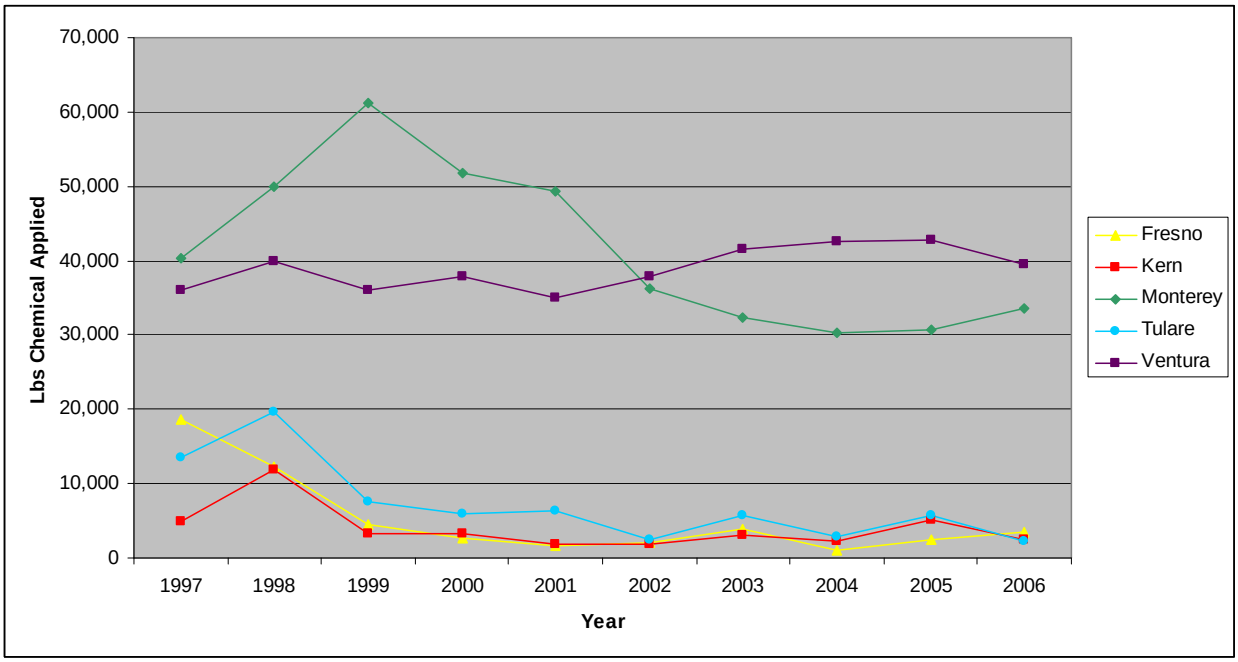

Figure 5. Iprodione Use in the Top Five Counties for Reporting Years 1997-2006 (CDPR, 2010).