RESULTS FOR STUDY GW10A: GROUND WATER PROTECTION LIST MONITORING FOR AZOXYSTROBIN, CHLOROTHALONIL, DICHLORAN, AND IPRODIONE

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GW10A

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ABSTRACT

The California Department of Pesticide Regulation's (DPR) Environmental Monitoring Branch (EMB) collected ground water samples from 184 wells in areas with high use of four agricultural fungicides—azoxystrobin, chlorothalonil, dichloran, and iprodione. None of the fungicide active ingredients were detected in ground water. Ninety-two of the wells sampled were located in high-use areas of azoxystrobin, a systemic fungicide that is primarily applied to rice, grapes, and almonds. Three of the wells located in the rice-growing region of Glenn County had detectable levels of azoxystrobin acid, a degradate of azoxystrobin. In this study, the application of azoxystrobin to rice was not the focus; a majority of the ground water samples collected were located in areas where other crops were grown. Additional studies should be conducted in the rice-growing region of California to determine if azoxystrobin or azoxystrobin acid are migrating to the ground water as a result of use on rice.

DPR also analyzed eighty of the ground water samples for hexazinone, tebuthiuron and its degradates, and the known ground water contaminants and degradates (3 CCR section 6800[a]): atrazine, bromacil, desethyl atrazine (DEA), desisopropyl atrazine (ACET), desmethylnorflurazon (DSMN), diamino chlorotriazine (DACT), diuron, norflurazon, prometon, and simazine. Fourteen of the ground water samples were collected from wells in Ground Water Protection Areas (GWPAs) that are known to be vulnerable to pesticide contamination. As expected all of these wells had pesticide residues. The 66 other ground water samples were collected from wells in sections that were outside of the GWPAs. Of these wells, nine wells had detectable levels of the pesticides or degradates. DPR is evaluating these data and is considering adding these sections to the list of GWPAs.

INTRODUCTION

In 2010–2011, the Environmental Monitoring Branch (EMB) of the Department of Pesticide Regulation (DPR) sampled wells for four agricultural fungicides and their main degradates to determine whether the fungicides have migrated to ground water in areas with high reported agricultural use and shallow depth-to-ground water (Dias, 2010). The four fungicides—azoxystrobin, chlorothalonil, dichloran, and iprodione—were selected for monitoring from the Groundwater Protection List (GWPL) (Title 3, California Code of Regulations [3 CCR] section 6800[b]) based on environmental fate and transport modeling as well as pesticide use reporting.

Statutory Authority
DPR's ground water monitoring program is mandated by the Pesticide Contamination Prevention Act (PCPA) (Statutes of 1985, Chapter 1298, Section 1). The PCPA was enacted in 1985 to prevent further pesticide pollution of California ground water that may be used for drinking water. The PCPA added sections 13141–13152 to the Food and Agricultural Code (FAC) which outlines procedures for

- Gathering physical and chemical data that describe the mobility, persistence, and environmental fate of agricultural use[1] pesticides proposed for registration,
- Establishing specific numerical values (SNVs [threshold values]) for mobility and persistence, and
- Placing agricultural use pesticides on the Groundwater Protection List (GWPL) (Title 3, California Code of Regulations [3 CCR] section 6800[b]) if they exceed the SNVs and are applied in specified ways.

The PCPA then requires DPR to monitor ground water for the GWPL pesticides to determine if these pesticides have migrated to ground water as a result of legal agricultural use. Since 1990, EMB has sampled more than 1,700 unique wells for 91 pesticides and pesticide breakdown products as part of GWPL monitoring.

Criteria for Inclusion on Groundwater Protection List
In California a pesticide must be placed on the GWPL if the pesticide has specific uses on the label and exceeds one of the mobility SNVs and one of the persistence SNVs (Table 1). As shown in Table 1, azoxystrobin and dichloran exceed both of the mobility SNVs—water solubility and Koc—and two of the persistence SNVs—hydrolysis and anaerobic soil metabolism. Chlorothalonil exceeds the Koc SNV for mobility and the hydrolysis SNV for persistence. Iprodione exceeds the water solubility SNV for mobility and the anaerobic soil metabolism SNV for persistence.

Pesticide Use Data for the Fungicides
Azoxystrobin is a systemic fungicide primarily used on rice and from early bloom to petal fall on grapes and almonds. 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 occurred 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. Statewide chlorothalonil use increased sharply from 1997 to 1998 but has remained fairly steady from 1999 to 2006 (Figure 1) (CDPR, 2010). Chlorothalonil is used widely throughout the state, but the highest-use counties are Fresno, Kern, San Diego, San Joaquin, and Ventura (Figure 3).

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[1] *FAC section 11408 defines "agricultural use" to mean the use of any pesticide or method or device for the control of plant or animal pests, or any other pests, or the use of any pesticide for the regulation of plant growth or defoliation of plants. It excludes the sale or use of pesticides intended for home use, use in structural pest control, industrial or institutional use, the control of an animal pest under the written prescription of a veterinarian, or use of a pesticides by local districts or other public agencies for disease vector control under certain conditions.*

Dicloran is a foliar fungicide used primarily on lettuce, grapes, and celery. 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. 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).

MATERIALS AND METHODS

Thirty-seven to 92 wells were sampled for each active ingredient. The samples were analyzed using either the chlorothalonil (tetrachloroisophthalonitrile) method (CDFA, 2010b) or the multi-analyte screen (ADI screen) (CDFA, 2010a) for the following parent pesticides and degradates:

- <u>Azoxystrobin:</u> methyl (E)-2-{2-[6-(2-cyanophenoxy) pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate
- <u>Azoxystrobin degradates:</u>
    - Azoxystrobin Z: methyl(Z)-2{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate (R-230310)
    - Azoxystrobin acid: (E)-2-[6(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylic acid (R-234886)
- <u>Dicloran:</u> (2,6-dichloro-4-nitroaniline)
- <u>Iprodione and its stereoisomer isoiprodione:</u>
    - Iprodione: 3-(3,5-dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidine-carboxamide
    - Isoiprodione: 3-(1-methylethyl)-N-(3,5-dichlorophenyl)-2,4-dioxo-1-imidazolidine-carboxamide (RP-30228)
- <u>Iprodione degradate:</u> 3,5-dichloroaniline (RP-32596)

Ground water sampling for ADI occurred in high-use sections of the following counties: Butte, Fresno, Glenn, Kern, Merced, Monterey, Santa Barbara, Santa Cruz, Stanislaus, Tulare, and Ventura. Although the fungicides were analyzed using a multi-analyte screen, each pesticide was targeted individually.

Chlorthalonil samples were collected from Fresno, Kern, Kings, Madera, Merced, San Joaquin, Stanislaus, and Tulare counties.

Depending on pesticide use patterns, additional samples were collected from selected wells and analyzed using a multi-analyte screen (triazine screen) for hexazinone, tebuthiuron and its four degradation products, and for the following pesticides and degradation products that are regulated as ground water contaminants (3 CCR section 6800[a]): atrazine, bromacil, desethyl atrazine (DEA), desisopropyl atrazine (ACET), desmethylnorflurazon (DSMN), diamino chlorotriazine (DACT), diuron, norflurazon, prometon, and simazine (CDFA, 2009). EMB periodically monitors for the known ground water contaminants and degradates to help assess the adequacy of DPR's mitigation measures and to determine if the Ground Water Protection Areas (GWPAs) need to be expanded. DPR has classified many sections within the state as GWPAs because they are vulnerable to pesticide contamination. Sections are classified as GWPA either because of the presence of verified pesticide residues in the ground water or because they have been determined to be vulnerability based on soil conditions and the depth to ground water. Areas that are vulnerable to ground water contamination from pesticide use generally have a shallow ground water table (less than 70 feet) and soils with either coarse textures with a potential for direct residue leaching or an impermeable layer with a potential for residue run-off to a site with more permeable soils (Troiano et al., 2000). Monitoring for hexazinone and tebuthiuron provides additional data on the potential source of the detections.

Selection of Sampling Locations

The sampling locations were chosen based on the pounds of fungicide-active ingredient applied in a one-square-mile section, soil vulnerability, depth to ground water, and well availability. Although some counties had higher overall use of a pesticide, priority was given to areas with clusters of high-use sections based on pesticide use reporting from 1997 to 2006. High-use sections were then evaluated for the presence of wells and whether or not the sections were GWPAs. Since GWPAs are known to be vulnerable to ground water contamination from pesticides, these sections were given higher priority than similar sections that were not GWPAs. If high-use sections were located outside the GWPAs, they were ranked based on depth to ground water. If a ground water sample tested positive for a pesticide, further sampling was undertaken to better characterize the extent of the ground water contamination.

Samples for the triazine screen were collected in sections that had historical use of the known ground water contaminants but were not GWPAs. A subsection of wells in Fresno and Stanislaus County GWPAs were also analyzed using the triazine screen.

Sampling and Analytical Methods

Where domestic wells were available, they were selected according to the well integrity procedures in 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, were sampled. Samples were collected using the methods described in SOP FSWA001.01 (Nordmark and Pinera-Pasquino, 2008a). Samples containing deionized water (field blanks) were collected at the same time as field samples and analyzed to confirm the validity of the positive results. Chemical analyses were performed by the CDFA Center for Analytical Chemistry (CDFA, 2010a; CDFA, 2010b; CDFA, 2009) and the methods were determined to be unequivocal (Aggarwal, 2011a; Aggarwal, 2011b; Fattah, 2008). The reporting limit was 0.10 parts per billion (ppb) for iprodione/isoiprodione and 3,5-dichloroaniline and was 0.05 ppb for the rest of the analytes (Table 5). Samples containing known amounts of pesticide disguised as actual samples (blind spikes) were prepared and analyzed in accordance with SOP QAQC001.00 (Segawa, 1995). Samples containing deionized water (field blanks) were collected at the same time as field samples and analyzed to confirm the validity of positive results (Orlando, 2007).

RESULTS

During this study, ground water samples from 184 wells were collected in 14 California counties—Butte, Fresno, Glenn, Kern, Kings, Madera, Merced, Monterey, San Joaquin, Santa Barbara, Santa Cruz, Stanislaus, Tulare, and Ventura (Appendix II).

Chlorothalonil Analytical Results

Sixty ground water samples were collected for chlorothalonil in high-use sections of eight counties—Fresno, Kern, Kings, Madera, Merced, San Joaquin, Stanislaus, and Tulare (Table 2). None of the ground water samples had detectable levels of chlorothalonil.

Azoxystrobin, Dichloran, and Iprodione Analytical Results

One hundred and twenty-four ground water samples were collected in 11 counties for the ADI screen—azoxystrobin, dichloran, iprodione, two azoxystrobin degradates, and an iprodione degradate. Although the sections were targeted for sampling based on the high use of one of the specific fungicides, there were sections with high use of more than one of the fungicides. The number of samples collected from high-use sections for azoxystrobin, dichloran, and iprodione are listed in Table 2.

None of the ground water samples had detectable levels of azoxystrobin, dichloran, iprodione, the iprodione degradate, or the azoxystrobin degradate azoxystrobin Z. Two ground water samples from sections with high use of azoxystrobin in Glenn County had detections of azoxystrobin acid, a degradate of azoxystrobin, at concentrations of 0.101 ppb (Loc 11-02) and 0.268 ppb (Loc 11-03). Based on these detections, ten additional ground water samples were collected: three around Loc 11-02, four around Loc 11-03, and three in other sections with high use of azoxystrobin and low depth-to-ground water. During this follow-up sampling only one ground water sample had residues of azoxystrobin acid. The ground water sample closest to Loc 11-03 had residues of azoxystrobin acid at concentrations of 0.263 ppb (Loc 11-17) (Appendix II).

Hexazinone, Tebuthiuron, and 3 CCR Section 6800(a) Pesticide Analytical Results

Ground water samples from eighty of the wells sampled for the ADI analysis were also analyzed using the triazine screen (Appendix II). Fourteen ground water samples from GWPAs were analyzed using the triazine screen. As expected, the ground water from all 14 of these wells—11 wells in Fresno County and three wells in Stanislaus County—had a high detection frequency of pesticide residues (Table 3). All of these samples had residues of DACT and one had residues of six pesticides and degradates. The remaining 66 ground water samples had a much lower detection frequency. Nine of the ground water samples had residues of one or more of the following pesticides or degradates: bromacil, diuron, simazine, ACET, and DACT (Table 4). Of this total, two samples contained residues of three or more pesticides or degradates, three samples contained a combination of two pesticides and degradates, and four samples contained only one pesticide or degradate. DPR is evaluating these data and is considering adding these sections to the list of GWPAs.

DISCUSSION

Azoxystrobin Acid Detections

Although many wells located throughout California in areas with high azoxystrobin use and low depth-to-ground water were sampled for azoxystrobin and its degradates, only residues of the degradate azoxystrobin acid were detected. The azoxystrobin acid detections only occurred in sections where azoxystrobin was applied to rice in Glenn County. Other areas that were sampled for azoxystrobin were located in areas where azoxystrobin was applied primarily on grapes or almonds (Figure 6). Although azoxystrobin is also used in rice in Butte County, the ground water samples that were collected in Butte County were not located in rice growing areas.

Both of the original positive ground water samples, Loc 11-02 and Loc 11-03, were collected in Runoff GWPAs that had been created based on previous detections of 6800(a) pesticides or degradates and both wells were located in sections where the depth-to-ground water was extremely shallow, less than 5 meters. One of the wells, Loc 11-03, was also located adjacent to sections where several wells had previously tested positive for bentazon (Figure 7) (Sitts, 1989). Bentazon is a pesticide that was found to contaminate ground water when used on rice. It is no longer registered for use on rice in California (3 CCR section 6457).

Azoxystrobin Acid Exposure Standards

In November 2010, DPR's Medical Toxicology Branch reviewed the detected concentrations of azoxystrobin acid and found that the U.S. EPA food tolerances for azoxystrobin are 1,000 times higher than the concentrations of the azoxystrobin acid detected in the wells. Available data suggests the azoxystrobin degradates are less toxic than the parent. The Medical Toxicology Branch concluded that, based on the available evidence on azoxystrobin acid, the detected concentrations are not expected to pose a threat the human health (Schreider, 2011; Appendix I).

Other Azoxystrobin and Azoxystrobin Acid Detections

Azoxystrobin and azoxystrobin acid have also been detected in other ground water monitoring studies. The U.S. Geological Survey (USGS) sampled 12 ground water sites for azoxystrobin and other fungicides in three geographic areas across the United States with high use of selected fungicides on potatoes. Azoxystrobin was detected in two of the wells with a maximum concentration of 0.0009 ppb (Reilly et al., 2012). Azoxystrobin was also detected at a concentration of 0.6 ppb in one well in Suffolk County, New York (NYSDEC, 2013) and in two wells in Teton County, Montana (Schmidt, 2008). None of these studies analyzed the ground water samples for azoxystrobin acid.

A study on the leaching of azoxystrobin and azoxystrobin acid from four Danish agricultural fields found that, although neither azoxystrobin nor azoxystrobin acid were detected at the site with sandy soil, they did leach through the loamy soils. While azoxystrobin was generally only detected in the drainage water during the first couple of months following application, azoxystrobin acid leached for a longer period of time and at higher concentrations. After the final azoxystrobin application at the site with the most leaching, azoxystrobin acid was detected in almost 30 percent of ground water monitoring wells with a maximum concentration of 0.10 ppb (Jørgensen et al., 2012). A study analyzing the leaching behavior of azoxystrobin and azoxystrobin acid in soil columns found that while azoxystrobin was fairly immobile in sandy loam soil columns, azoxystrobin acid was quite mobile (Ghosh and Singh, 2009).

CONCLUSIONS

DPR sampled ground water from high-use areas throughout California for dichloran, iprodione, and chlorothalonil. None of these pesticides or their degradates were detected in the ground water samples indicating that current use patterns are not moving residues of these pesticides to ground water. Although azoxystrobin was not detected in any of the ground water samples, a major degradate, azoxystrobin acid, was detected in three wells adjacent to fields where azoxystrobin is used on rice. Azoxystrobin use on rice was not singled out during the selection of the wells in this study so it is not possible to determine if these three detections were isolated occurrences or if there is an aspect of applications to rice that moves azoxystrobin acid to ground water. A study focusing on the use of azoxystrobin in the rice-growing region of California should be conducted.

DPR also analyzed eighty of the ground water samples using the triazine screen. Fourteen of the ground water samples were collected from wells in GWPAs that are known to be vulnerable to pesticide contamination. As expected all of these wells had pesticide residues. The 66 other ground water samples were collected from wells in sections that were outside of the GWPAs. Of these wells, nine wells had detectable levels of the pesticides or degradates. DPR is evaluating these data and is considering adding these sections to the list of GWPAs.

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FIGURES[2]

Figure 1. Total azoxystrobin, chlorothalonil, dicloran, and iprodione use in California for reporting years 1997-2006 (CDPR, 2010).

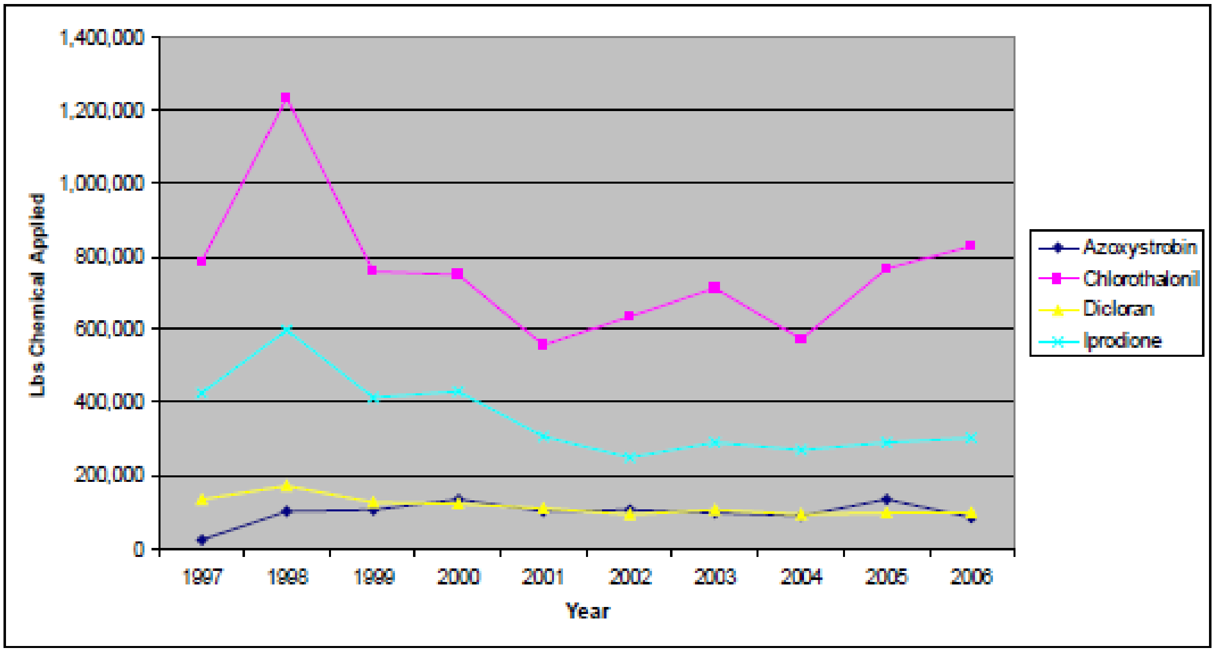
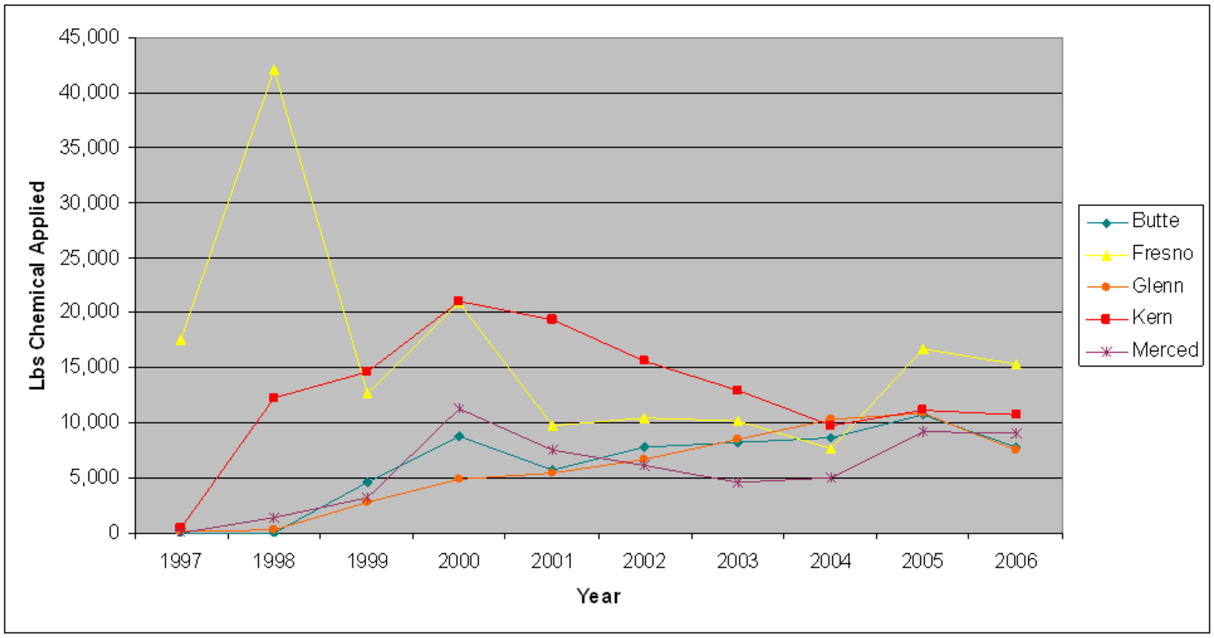


Figure 2. Azoxystrobin use in the top five counties for reporting years 1997-2006 (CDPR, 2010).



[2] *DPR summarized pesticide use from 1997-2006. This range allows DPR to evaluate ten years of pesticide use data but also accounts for the time that it takes for pesticides to move to ground water from agricultural use. DPR has determined that it takes approximately 4 years for pesticide residues to travel through the vadose zone and 6 years to reach a well once in ground water (Troiano and Clayton, 2009).*

Figure 3. Chlorothalonil use in the top five counties for reporting years 1997-2006 (CDPR, 2010).

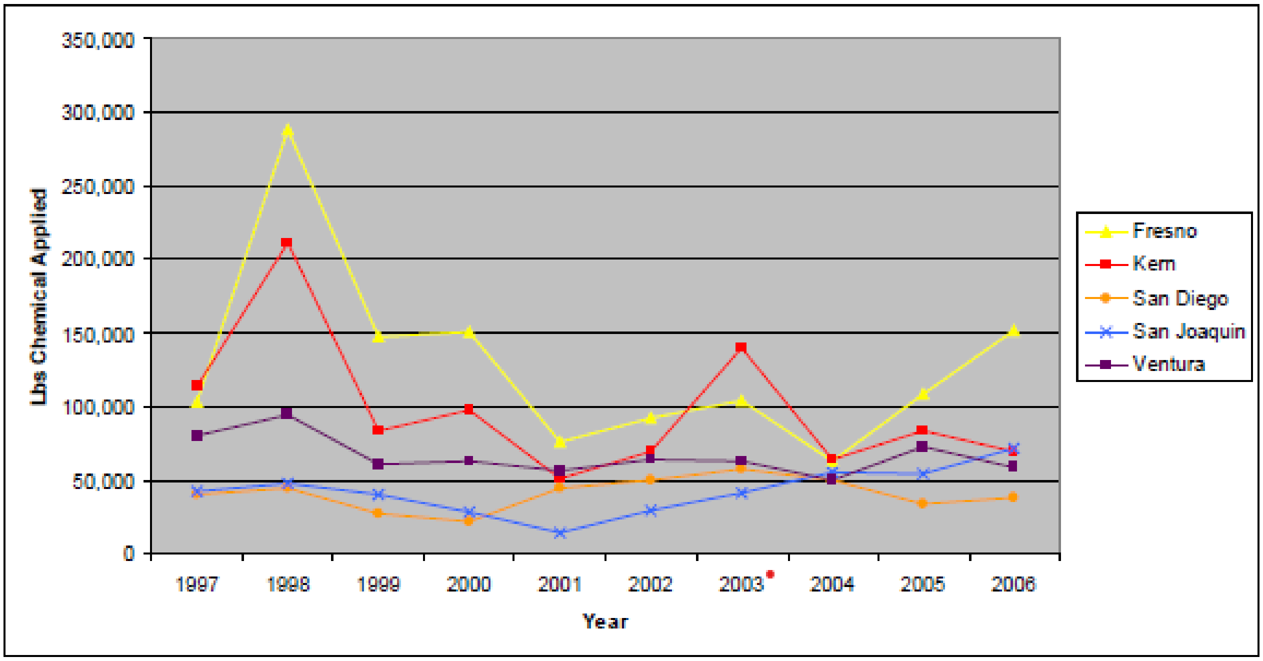


Figure 4. Dicloran use in the top five counties for reporting years 1997-2006 (CDPR, 2010).

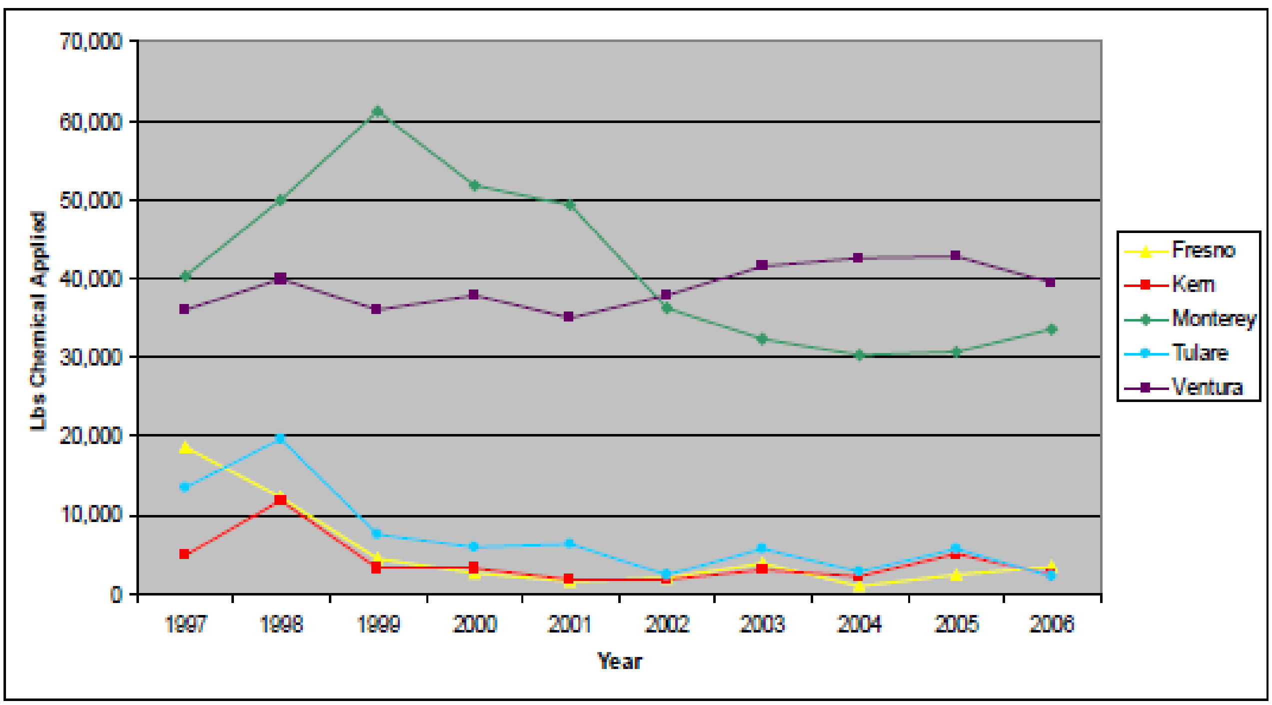


Figure 5. Iprodione use in the top five counties for reporting years 1997-2006 (CDPR, 2010).

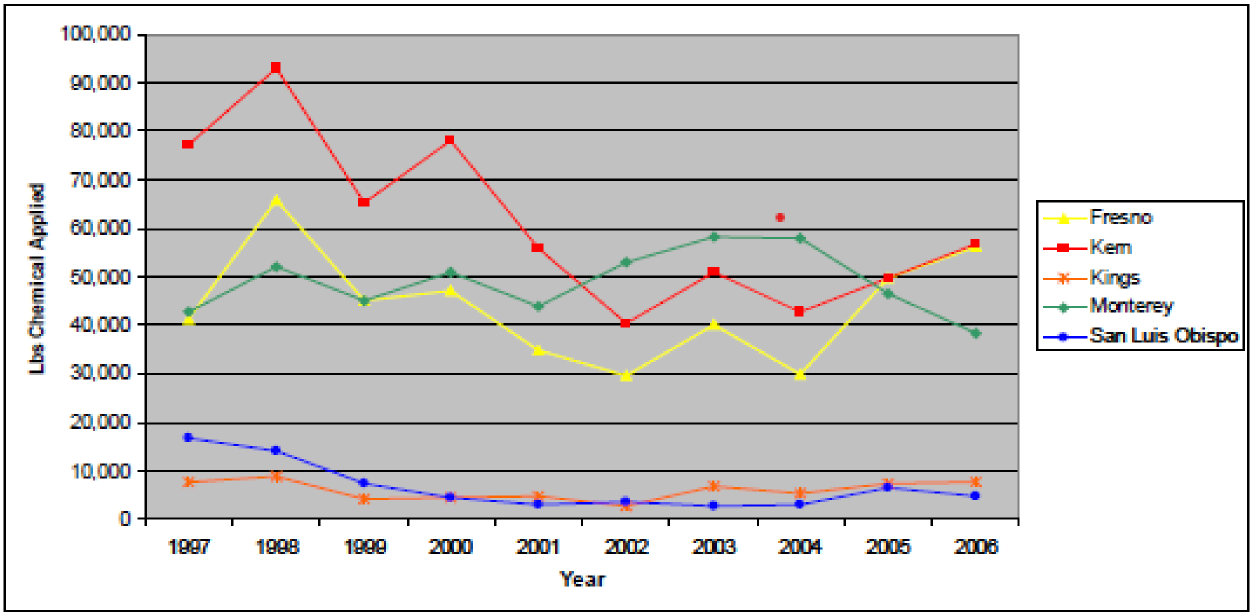


Figure 6. Azoxystrobin use by county and crop for reporting years 1997-2006 (CDPR, 2010).

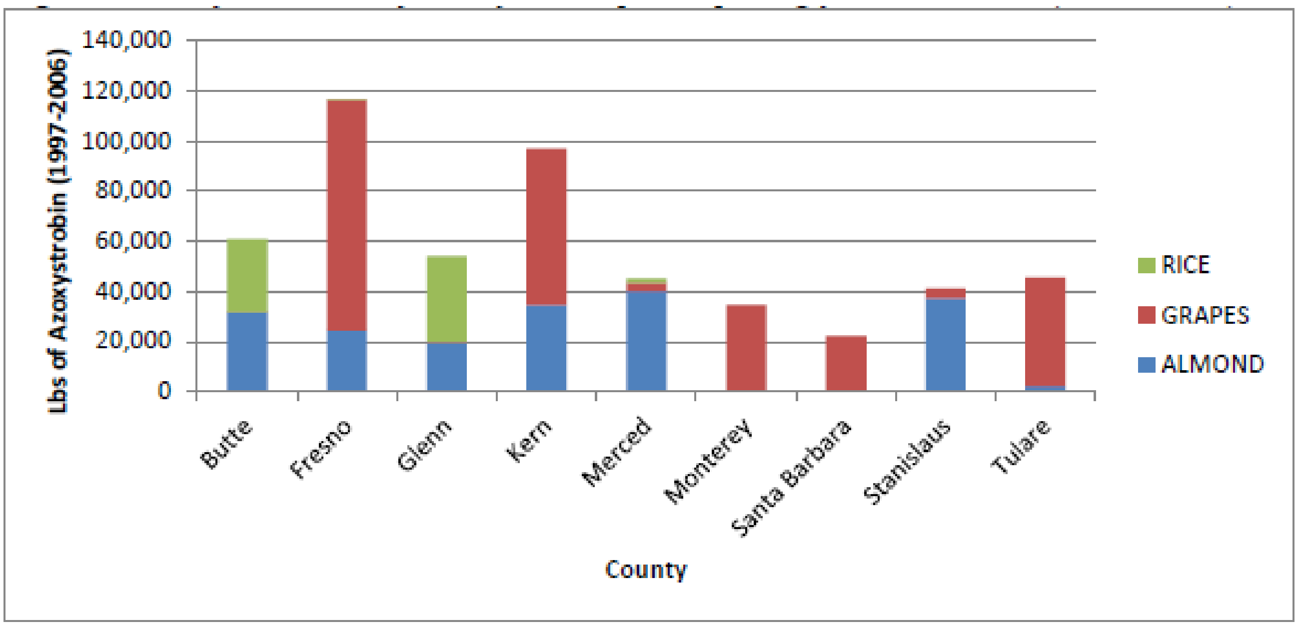
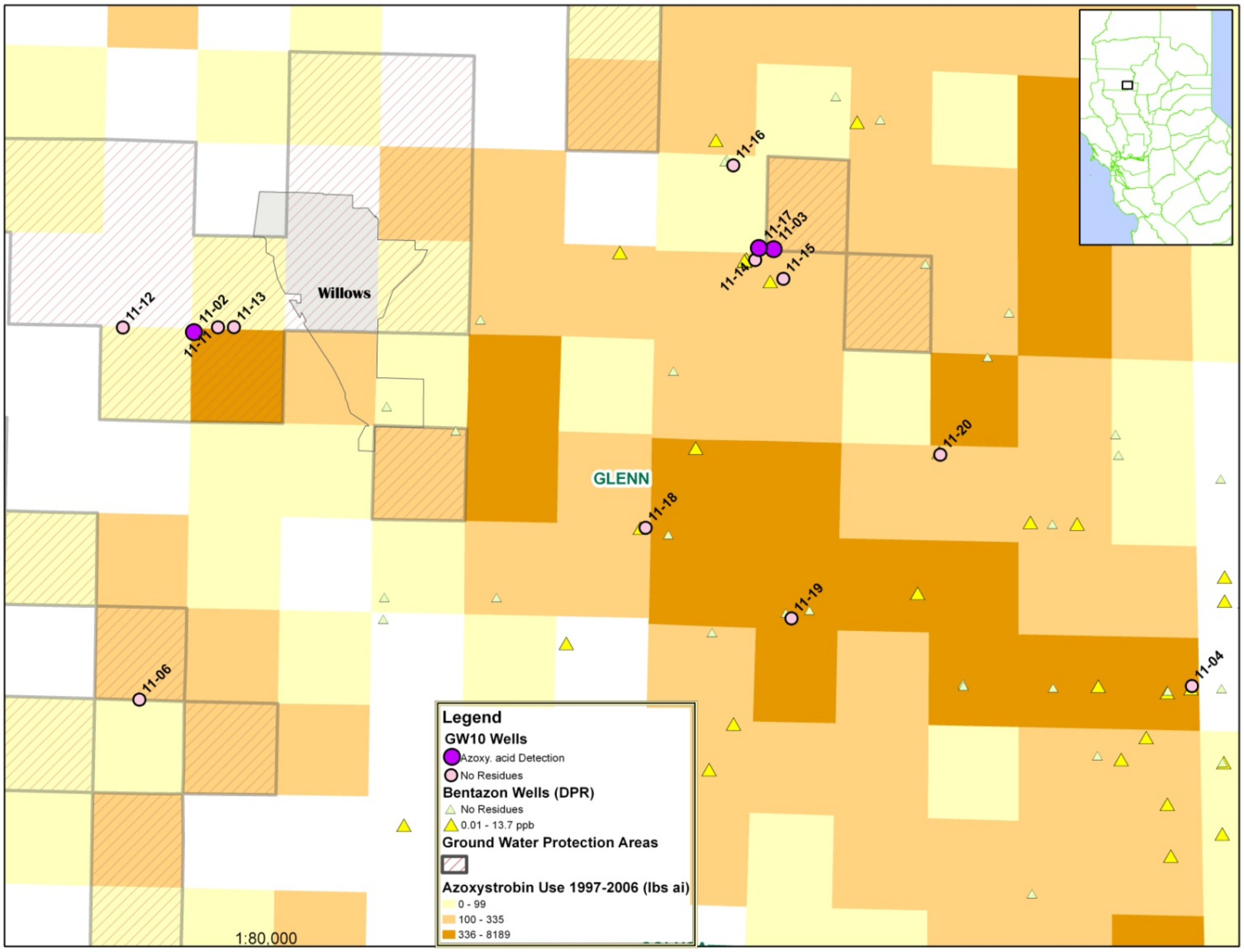


Figure 7. Map of current azoxystrobin acid detections and historical bentazon detections in Glenn County.



TABLES

Table 1. The specific numerical value thresholds (3 CCR section 6804) and the physical-chemical properties of the four fungicides (Bergin, 2012). The numbers in **bold** exceed the threshold values (SNVs) that indicate the pesticide has the potential to contaminate ground water.

	Mobility		**Persistence**		
	Water solubility (ppm)	**Koc (cm3/g)**	**Hydrolysis (days)**	**Aerobic soil metabolism (days)**	**Anaerobic soil metabolism (days)**
SNV	> 3	< 1900	> 14	> 610	> 9
Azoxystrobin	**6**	**581**	**> 31**[a]	112	**119**
Chlorothalonil	1	**1790**	**> 49**[a]	35	8
Dicloran	**6**	**804**	**> 72**[a]	549	**66**
Iprodione	**12**	W*	5	64	**32**

[a] = No degradation occurred during the study. The half-life is greater than the value listed, which is the length of the study.
* = The data requirement was waived because of rapid degradation, rendering it unable to measure.

Table 2. Number of wells sampled in each county that were targeted for chlorothalonil, azoxystrobin, dichloran, or iprodione. Some wells were located in sections that were targeted for multiple pesticides.

	Number of Wells Sampled				
County	**Chlorothalonil**	**Azoxystrobin**	**Dichloran**	**Iprodione**	**Total**
Butte	0	7	0	4	**7**
Fresno	14	10	3	14	**31**
Glenn	0	16	0	0	**16**
Kern	8	6	0	8	**18**
Kings	1	0	0	0	**1**
Madera	6	0	0	0	**6**
Merced	7	11	0	11	**18**
Monterey	0	7	14	14	**17**
San Joaquin	6	0	0	0	**6**
Santa Barbara	0	3	3	3	**3**
Santa Cruz	0	0	1	1	**1**
Stanislaus	9	11	1	11	**20**
Tulare	9	18	8	12	**32**
Ventura	0	3	7	6	**8**
Total	**60**	**92**	**37**	**84**	**184**

Table 3. “Triazine” detections in the 14 wells sampled in GWPAs.

	Bromacil	**Diuron**	**Norflurazon**	**Simazine**	**ACET**	**DACT**	**DSMN**
# Positive Wells	1	2	2	7	10	14	12
Detection Frequency %	7	14	14	50	71	100	86
Maximum Detected Concentration (ppb)	0.29	0.161	0.302	0.172	0.514	0.854	1.124
Minimum Detected Concentration (ppb)	0.29	0.147	0.274	0.05	0.085	0.055	0.059

Table 4. "Triazine" detections in the 66 wells sampled outside of GWPAs.

	Bromacil	Diuron	Simazine	ACET	DACT
# Positive Wells	2	3	3	4	6
Detection Frequency %	3	5	5	6	9
Maximum Detected Concentration (ppb)	0.071	0.137	0.121	0.212	0.322
Minimum Detected Concentration (ppb)	0.051	0.05	0.069	0.054	0.09

Table 5. Department of Food and Agriculture, Center for Analytical Chemistry analytical method details.

Compound	**Method**	**Method Detection Limit (ug/L)**	**Reporting Limit (ug/L)**
Azoxystrobin	LC/MS	0.0165	0.05
Azoxystrobin Acid	LC/MS	0.0298	0.05
Azoxystrobin Z-metabolite	LC/MS	0.0187	0.05
Iprodione/Isoiprodione	GC/MS	0.0317	0.10
3,5-dichloroaniline	GC/MS	0.0739	0.10
Dicloran	GC/MS	0.0255	0.05
DACT	LC/MS	0.0063	0.05
ACET	LC/MS	0.0130	0.05
DEA	LC/MS	0.0110	0.05
Hexazinone	LC/MS	0.0250	0.05
Simazine	LC/MS	0.0135	0.05
Bromacil	LC/MS	0.0200	0.05
Prometon	LC/MS	0.0120	0.05
Atrazine	LC/MS	0.0150	0.05
DSMN	LC/MS	0.0150	0.05
Norflurazon	LC/MS	0.0063	0.05
Diuron	LC/MS	0.0430	0.05
Tebuthiuron	LC/MS	0.0140	0.05
Tebuthiuron M-104	LC/MS	0.0420	0.05
Tebuthiuron M-106	LC/MS	0.0170	0.05
Tebuthiuron M-107	LC/MS	0.0270	0.05
Tebuthiuron M-108	LC/MS	0.0310	0.05

APPENDIX I and II

Medical Toxicology Branch memorandum outlining the potential health effects of azoxystrobin acid in well water (page 19) and Sampling results for GW10a in ppb (pages 20-26) are available upon request at GWPP@cdpr.ca.gov.