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STUDY GW13: PROTOCOL FOR GROUND WATER PROTECTION LIST MONITORING OF SELECTED RICE PESTICIDES

I. INTRODUCTION

Selection of Rice Pesticides

Section 13148 of the California Food and Agricultural Code directs the Department of Pesticide Regulation (DPR) to conduct ground water monitoring for pesticides that have been designated as having the potential to pollute ground water. These pesticides are identified on DPR's Ground Water Protection List (GWPL). DPR annually samples for several listed pesticides on the GWPL in areas where they are used to determine if they have migrated to ground water as a result of their legal agricultural use.

This GWPL monitoring study is focused on rice pesticides because of the following reasons:

- Rice production consists of continuously flooded fields that have pesticides applied directly to the water. This application practice may facilitate pesticide leaching into ground water (Clayton, 2011).

- Sampling efficiency is maximized because many of these pesticides are applied in a geographically constrained area; ninety-five percent of California's rice production occurs in the Sacramento Valley (CDPR, 2010).

- Many rice pesticides are included on the GWPL for ground water monitoring. Orthosulfamuron and propiconazole are included for sampling because they will be added to the GWPL in a future regulatory action. Molinate is also included in this monitoring because of its historical use and previous detections (Table 1 and Table 2).

- Ground water monitoring of the selected pesticides is sparse; only 2,4-D, azoxystrobin, molinate, and thiobencarb have been previously monitored by DPR (Table 2).

- Bentazon, a major rice herbicide, was detected in ground water associated with rice production areas in the 1980s. Following its detection, bentazon use on rice was cancelled. The definitive explanation for these detections has not been found. Bentazon is a fairly stable pesticide (Table 3) and a combination of environmental fate and local hydrogeologic areas (see section below on DPR's monitoring history) may have contributed to bentazon's detection in ground water.

The unique characteristics of rice pesticides (application to flooded fields, heavy presence on the GWPL, constrained geographical application area, and previous detection history) make them well-suited for a targeted ground water monitoring study in major rice production areas.

II. STUDY OBJECTIVES

- Monitor for 2,4-D, azoxystrobin, bensulfuron methyl, bispyribac-sodium, clomazone, halosulfuron-methyl, molinate, orthosulfamuron, penoxsulam, propanil, propiconazole, thiobencarb, and triclopyr in areas of rice production to determine if they have migrated to ground water as a result of their legal agricultural use.

- Investigate vulnerability of hydrogeological areas in rice country to pesticide leaching by comparing the sampling results of each area to the sampling results of the surrounding areas of high pesticide use.

III. PERSONNEL

The well sampling for this study will be conducted by the Environmental Monitoring Branch of DPR under the general supervision of Senior Environmental Scientist Lisa Quagliaroli. Project Personnel will include:

Project Leader: Rick Bergin
Field Coordinator: Craig Nordmark
Senior Scientist: Frank Spurlock
Laboratory Liaison: Sue Peoples (CDFA), Lisa Quagliaroli (CDFW)
Chemists: California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry, Staff Chemists; California Department of Fish and Wildlife (CDFW), Water Pollution Control Laboratory, Staff Chemists.

Please direct questions regarding this study to Rick Bergin at 916-324-0827, e-mail: <rbergin@cdpr.ca.gov>.

IV. STUDY PLAN

<u>Monitoring and Detection History</u>

U.S. Geological Survey and the California Department of Public Health
Many of the pesticides in this study have minimal ground water monitoring data (Table 2). Five of these pesticides, bispyribac-sodium, clomazone, halosulfuron-methyl, orthosulfamuron, and penoxsulam, have no reported ground water monitoring in DPR’s Well Inventory Database or the U.S. Geological Survey’s (USGS’s) National Water Quality Assessment (NAWQA) Database. DPR’s Well Inventory Database contains information on wells sampled for pesticides by public agencies in California; much of the data comes from the California Department of

Public Health. The NAWQA database contains data on the systematic collection of chemical, biological, and physical water quality data from 51 river basins and aquifers around the U.S.

DPR

Only four of these pesticides, 2,4-D, azoxystrobin, molinate, and thiobencarb, have been previously monitored by DPR. The lack of ground water sampling data by DPR for many of the selected pesticides is a major reason why they are included in this study (Table 2). Another rice pesticide, bentazon, is not included in this study because it has been recently monitored for by the USGS and has not been used on rice since 1989 (CDPR, 2013a). Bentazon is a rice herbicide that was detected in the late 1980's in California's rice-growing areas by DPR (Sitts, 1989). Several key findings from DPR's bentazon ground water monitoring are:

- Bentazon detections occurred in clayey, loamy, and sandy soils. Vertisol cracking clays were not correlated with bentazon detections (Johnson, 1989).

- Sixty-eight percent of the detections occurred in sections with depth to ground water less than 10 feet. Only 11% of the contaminated wells were located in areas with ground water depths greater than 20 feet (CDFA, 1989).

- No other rice pesticides, such as molinate and thiobencarb, were detected in ground water even though they are applied at rates greater than bentazon's application rate. This indicates that point source contamination is unlikely (Johnson, 1989).

- Bentazon detections were associated with rice only; beans, peas, corn, and sorghum have no corresponding ground water detections of bentazon (CDFA, 1990).

Hydrogeologic Areas

However, given the points above, bentazon's ground water detections were never conclusively explained. The only commonality amongst the bentazon detections were their proximity to rice production, hence bentazon's restriction on rice. In 1995, Spurlock investigated the hydrogeological characteristics of the bentazon contaminated wells in the Sacramento Valley as part of a proposed ground water age-dating study to examine bentazon's ground water detections. It was hypothesized that three areas in the Sacramento Valley are associated with bentazon ground water detections due to their relatively coarse deposits and higher permeabilities (Olmsted and Davis, 1961; CDWR, 1978; Table 4). The associated areas are (Spurlock, 1995; Figure 1):

I. Stony Creek Alluvial Fan and Colusa Basin Transition Zone

The Stony Creek alluvial fan is on the west side of the Sacramento Valley; it spans from Orland to Willows. This fan contains more coarse-grained materials in the form of sheets and broad lenses, at depths of 40 to 125 feet, than other alluvial fans in the area. The fan is also populated by many abandoned gravel channels of Stony Creek. Some of these channels extend underneath the Colusa Basin to the southeast. Where the Stony Creek fan and the Colusa Basin meet is characterized by interfingering beds of coarse-grained alluvium and fine-grained basin deposits.

II. River Lands

This area includes the river bed, natural levees, and flood plains of the Sacramento River and its tributaries. The areas along active channels have highly permeable coarse sands and gravels as the finer-grained materials are deposited further away into the surrounding flood plains and basins. Wells adjacent to the Sacramento River are drilled through many layers of coarse material. The ground water in these areas is often shallow. On the west side of the valley, the flood plains interfinger with the finer-textured flood basins.

III. Upper Northeast Butte Basin

The Butte Basin is located between Chico and the Sutter Buttes. It contains fine textured soils of low permeability due to silt and clay deposition during river flooding. Like much of the east side of the Sacramento Valley, Butte Basin has an extensive hardpan. However, the northeastern portion of the Butte Basin is not underlain by hardpan and the fine textured deposits in this area are the thinnest basin deposits in the Sacramento Valley.

This information on the characterization of previous bentazon detections will be used to direct the sampling efforts in this study by focusing on the most hydrogeological permeable areas of Sacramento Valley rice country.

Sample Site Selection

The following counties will be targeted for well sampling: Butte, Colusa, Glenn, Placer, Sacramento, Sutter, Yolo, and Yuba. These counties are chosen because the targeted hydrogeological areas are located within their boundaries. Also, these counties comprise the majority of the Sacramento Valley rice growing area and, consequently, have the highest use of the selected rice pesticides (Table 5).

Sections will be prioritized for sampling based on the following criteria:

- Located in hydrogeological areas I, II, or III: At least initially, we will focus sampling in areas with the highest soil permeability. These are the primary sampling areas.

- High use sections outside of hydrogeological areas I, II, and III: We will compare the results of these samples to the samples from the primary areas. Sampling intensity of these surrounding areas will depend on the results from the primary areas and pesticide use intensity.

Up to 200 wells will be sampled in this study. Up to three wells may be sampled in each target section depending on the availability of wells. If wells are not available in a target section, wells may be sampled from within 0.2 miles of the surrounding sections. Sections with the highest pesticide use and shallowest ground water depth will be prioritized for sampling.

V. SAMPLING AND ANALYTICAL METHODS

Wells will be chosen in the designated areas following procedures described in standard operating procedure FSWA001.01 (Nordmark and Pinera-Pasquino, 2008). Domestic wells are preferable because they usually are accessible year round and tend to be shallower than irrigation or municipal wells. During collection of ground water samples, all efforts will be taken to bypass pressure tanks, hoses, and filters to sample water directly from the aquifer.

Chemical analysis will be performed by both the CDFA Center for Analytical Chemistry and the CDFW Water Pollution Control Laboratory. CDFA will analyze for 2, 4-D and azoxystrobin (and degradates) using method EMON-SM-05-012 (CDFA, 2008) and method EMON-SM-05-018 (CDFA, 2010), respectively. CDFW will analyze for bensulfuron-methyl, bispyribac-sodium, clomazone, halosulfuron-methyl, molinate, orthosulfamuron, penoxsulam, propanil, propiconazole, thiobencarb, and triclopyr. The reporting limit is set at 0.05 ug/L for all analytes but one; orthosulfamuron has a reporting limit of 0.10 ug/L (Table 6). SOP QAQC001.00 (Segawa, 1995) guidelines will be followed for analytical laboratory quality control and for collecting quality assurance samples in the field.

VI. DATA ANALYSIS

Data obtained from CDFA and CDFW will be used to determine if pesticides are migrating to ground water. Detections in the primary and surrounding areas will be used to assess regional vulnerability to ground water contamination. These data will also be used to generate a study report detailing our findings.

VII. TIMETABLE

- September 2013-March 2014: Conduct sampling.
- October 2013-April 2014: Obtain analysis results from CDFA and CDFW laboratories.
- August 2014: Complete study report.
- Communication
    - Provide notice to the County Agricultural Commissioner, DPR Enforcement Branch Regional Office, the California Rice Commission, and the local Farm Bureau two weeks prior to initiating monitoring in a county. Additional notice will be provided if there is a six-month lapse in monitoring within a county.
    - Provide results to property owners within 30 days of receipt.
    - Provide results to state and local agencies when sampling is concluded and results have been reviewed and approved by the project team.

VIII. BUDGET

Budget Component	Units	Expense per Unit	Total Component Expense
Pesticide sample analysis – CDFW	≤ 335 samples	$450	≤ $150,750
Pesticide sample analysis – CDFA	≤ 335 samples	$720	≤ $241,200
Travel	≤ 160 days	$130	≤ $20,800
Person Years	≤ 1	$100,000	≤ $100,000
Total			≤ $512,750

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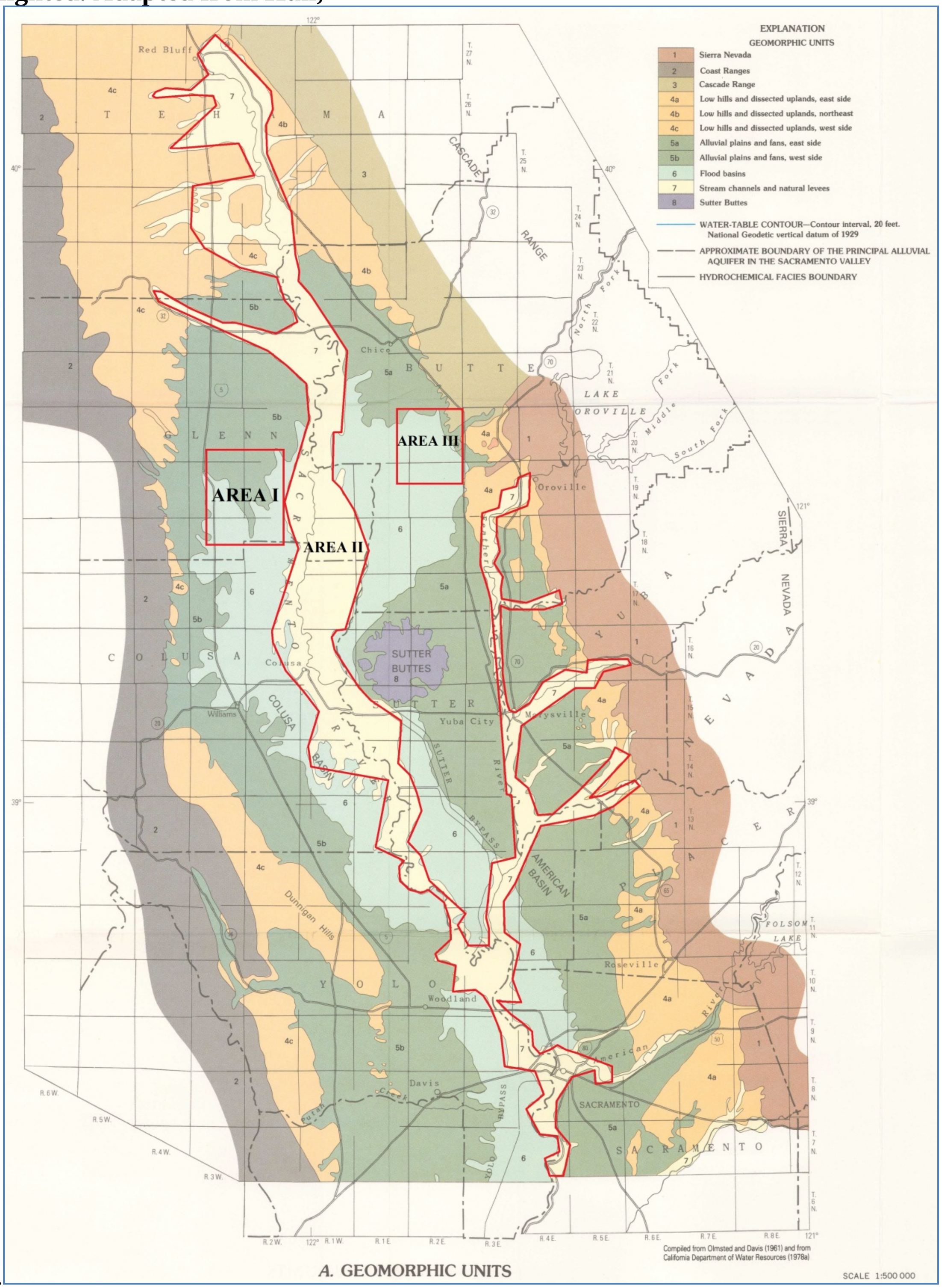
X. FIGURES

Figure 1. Geologic Map of the Sacramento Valley. Targeted Hydrogeologic Areas Highlighted. Adapted from Hull,



1984.

XI. TABLES

Table 1. Yearly Use of Selected Rice Pesticides from 1990 to 2010 (CDPR, 2013a).

	Total Pounds of Pesticide Applied to Rice												
Year	**2,4-D, dimethylamine salt**	**Azoxystrobin**	**Bensulfuron methyl**	**Bispyribac-sodium**	**Clomazone**	**Halosulfuron-methyl**	**Molinate**	**Orthosulfamuron**	**Penoxsulam**	**Propanil**	**Propiconazole**	**Thiobencarb**	**Triclopyr, triethyl-amine salt**
1990	4,807	0	24,242	0	0	0	1,529,110	0	0	11,827	0	99,184	0
1991	6,735	0	19,752	0	0	0	1,147,765	0	0	10,370	0	73,164	0
1992	7,203	0	31,354	0	0	0	1,386,778	0	0	16,935	0	187,733	0
1993	21,926	0	26,169	0	0	0	1,533,101	0	0	26,297	0	263,898	0
1994	35,920	0	26,444	0	0	0	1,540,143	0	0	35,623	0	411,065	0
1995	67,795	0	25,868	0	0	0	1,411,137	0	0	40,022	0	571,074	41
1996	58,023	0	23,381	0	0	0	1,442,186	0	0	89,354	0	638,270	2,702
1997	65,221	402	17,966	0	0	0	1,179,403	0	0	154,868	0	907,864	17,229
1998	11,982	321	11,572	0	0	0	1,004,905	0	0	525,352	2	727,298	60,463
1999	7,783	4,206	8,268	0	0	0	915,597	0	0	843,970	8	731,717	73,935
2000	8,582	7,316	7,224	0	0	0	1,026,220	0	0	1,360,972	0	1,006,327	80,110
2001	13,844	8,822	3,041	0	0	0	742,857	0	0	1,390,264	0	645,914	56,180
2002	9,809	16,273	2,421	2,529	550	2	881,182	0	0	1,469,046	0	843,773	60,113
2003	7,358	14,389	1,286	2,441	33,766	5	539,870	0	0	1,383,394	0	587,156	49,656
2004	6,742	25,981	1,697	3,379	49,715	162	367,155	0	0	1,691,133	0	521,556	56,292
2005	5,296	16,635	784	2,069	39,199	274	171,302	0	2,643	1,418,100	747	448,182	46,483
2006	3,268	15,658	719	1,673	61,363	192	141,420	0	2,615	1,497,127	694	310,346	41,865
2007	5,218	22,332	795	1,959	79,711	120	75,235	0	2,962	1,855,547	705	289,033	52,534
2008	2,268	30,917	1,095	3,123	90,694	185	19,653	288	2,752	1,906,705	600	263,499	54,168
2009	5,513	40,244	2,735	2,790	93,897	193	12,508	452	3,098	2,134,130	2,278	320,473	59,457
2010	2,829	33,158	2,714	2,824	90,605	157	0	336	4,503	1,993,353	1,914	258,402	58,191
Comments	Herbicide. Decrease due to drift issues with cotton/broadleaf crops (USDA, 1998). Foliar only.	Fungicide. Controls rice blast; use varies with disease pressure. Foliar only.	Herbicide. ALS inhibitor. Widespread resistance= use decline. Foliar/water applied.	Herbicide. ALS inhibitor. Some drift issues with walnuts. Foliar only.	Herbicide. Applied into water. New mode of action combats resistance.	Herbicide. ALS inhibitor. Can be applied directly into water.	Herbicide. Phased out from 2005-2009 due to health/wildlife concerns. Was applied directly into water.	Herbicide. ALS inhibitor. Can be applied directly into water.	Herbicide. ALS inhibitor. Can be applied directly into water.	Herbicide. Controls resistant weeds that survived earlier herbicides. Foliar only.	Fungicide. Controls aggregate sheath spot. Foliar only.	Herbicide. Decline due to resistance/ long post-application water holding times. Foliar/water.	Herbicide. Controls ricefield bulrush and redstem. Foliar only.

Table 2. Summary of Well Sampling for Selected Pesticides (USGS, 2013; CDPR, 2013b).

Pesticide	Wells with Detection / Total Wells Sampled					
	NAWQA-National Sampling	**NAWQA Detection Comments**	**Other Agencies-California Sampling**	**Other Agencies Detection Comments**	**DPR Sampling**	**DPR Detection Comments**
2, 4-D	**37 / 4938**	0.007 - 14.8 ug/L in 19 states; none in CA.	**17 / 7579**	0.3 - 46 ug/L in Butte, Colusa, Del Norte, Los Angeles, Modoc, Sacramento, San Diego, San Joaquin, San Mateo, Santa Clara, Sonoma, and Yuba Co. [a]	**0 / 88**	Surveyed counties include Butte, Colusa, Glenn, Sacramento, Yolo, and Yuba.
Azoxystrobin	No Data		No Data		**0 / 124**	Acid degradate found in 3 wells in Glenn County (Dias, 2010).
Bensulfuron-methyl	**4 / 2094**	0.018 ug/L - 0.093 ug/L in OH and WA; none CA.	**1 / 753**	SWRCB found one detection at 0.01 ug/L in Butte Co.	No Data	
Bispyribac-sodium	No Data		No Data		No Data	
Clomazone	No Data		No Data		No Data	
Halosulfuron-methyl	No Data		No Data		No Data	
Molinate	**31 / 7290**	0.001 ug/L - 0.11 ug/L in 13 states; 12 detects in Colusa, Glenn, Orange, Riverside, Sutter, and Yolo Co.	**17 / 7866**	0.002 ug/L - 10 ug/L in Butte, Colusa, Fresno, Glenn, Sacramento, Sutter, Yolo, and Yuba Co.	**4 / 304**	Investigation revealed detections were a result of poor well construction (Schuette et al., 2003).
Orthosulfamuron	No Data		No Data		No Data	
Penoxsulam	No Data		No Data		No Data	
Propanil	**23 / 7264**	0.001 ug/L - 0.021 ug/L in 12 states; three detections in Riverside and Sutter Co.	**2 / 736**	Detected by SWRCB in Butte and Sutter Counties at 0.097 ug/L and 0.006 ug/L, respectively.	No Data	
Propiconazole	**5 / 2110**	0.002 ug/L - 0.045 ug/L in five states; one detection in Fresno Co.	**1 / 971**	SWRCB detected both cis- and trans-propiconazole (isomers of propiconazole) in one well at 0.001 ug/L and 0.01 ug/L, respectively, in Glenn Co.	No Data	
Thiobencarb	**7 / 7276**	0.003 ug/L - 0.028 ug/L in five states; two detections in Colusa and Glenn Counties.	**9 / 8047**	0.006 ug/L - 8.7 ug/L in Colusa, Fresno, Glenn, Los Angeles, Riverside, and San Bernardino Co. [a]	**0 / 257**	Surveyed counties include Butte, Colusa, Glenn, Placer, Sacramento, Sutter, Yolo, and Yuba.
Triclopyr	**6 / 5061**	0.007 ug/L - 1.129 ug/L in six states; one detection in Sacramento Co.	**1 / 806**	SWRCB detected at 0.12ug/L in Butte Co.	No Data	

a. Detections were attributed to one of three factors:
- The detections were located in shallow monitoring wells,
- The detections were from a point source, or
- The detection was an isolated occurrence given the history of repeated sampling in that well.

Table 3. Environmental Fate Characteristics of Bentazon and the Selected Pesticides (CDPR, 2013c).

Pesticide	Water Solubility (mg/L)	Soil Adsorption (Koc)	Aerobic Metabolism Half-life (days)	Anaerobic Metabolism Half-life (days)	Hydrolysis Half-life (days)	Notes
Bentazon	530	116	40	Stable	Stable	Degradation in aqueous environment is dependent on photolysis.
2,4-D, Dimethylamine salt	657,000	46	33	333	Stable	Dissipation via aerobic metabolism and photolysis. Rapidly turns into 2,4-D acid.
Azoxystrobin	6	581	112	119	Stable	Dissipation via photolysis and aerobic metabolism. Acid degradate more mobile.
Bensulfuron methyl	281	332	75	168	103	Breaks down via aqueous photolysis rapidly.
Bispyribac-sodium	73,000	272	50	101	Stable	Stable to aqueous photolysis; breaks down viable microbial processes.
Clomazone	1,100	244	66	19	Stable	Degrades quickly in aquatic field dissipation studies.
Halosulfuron methyl	1,650	124	51	23	14	Hydrolytically unstable.
Molinate	970	199	41	105	Stable	Stable to photolysis.
Orthosulfamuron	629	538	25	58	24	Hydrolysis is pH dependent; faster degradation under acidic conditions.
Penoxsulam	470	119	57	8	Stable	Rapid aqueous photolysis.
Propanil	152	518	2	3	Stable	Stable to abiotic processes only.
Propiconazole	100	656	72	211	Stable	Aqueous photolysis is main degradation pathway.
Thiobencarb	28	530	37	306	Stable	Aqueous photolysis is a key breakdown process.
Triclopyr, triethylamine salt	234,000	62	13	Stable	Stable	Rapidly breaks down into triclopyr acid. Undergoes rapid photolysis.

Table 4. Bentazon Sampling in the Sacramento Valley by DPR (Spurlock, 1995).

Hydrogeologic Area	Wells Sampled	Positive	Negative
I. Stony Creek Alluvial Fan and Colusa Basin Transition Zone	42	16	26
II. River Lands	63	32	31
III. Upper Northeast Butte Basin	12	8	4
IV. Colusa Basin/Western Alluvial Plain	12	0	12
V. American Basin/Eastern Alluvial Plain	16	1	15

Table 5. Combined Use of the Selected Pesticides on Rice, in the Top Thirteen Counties, from 1990 to 2010 (CDPR, 2013a). Counties with an asterisk are targeted for sampling.

County	Total Pounds of Selected Rice Pesticides Applied
Colusa*	12,397,822
Sutter*	9,769,886
Butte*	9,496,484
Glenn*	8,415,520
Yolo*	2,821,432
Yuba*	2,622,764
Placer*	1,321,544
Sacramento*	1,062,046
San Joaquin	480,871
Merced	352,971
Fresno	228,025
Stanislaus	203,887
Tehama	44,203

Table 6. Method Detection and Reporting Limits for Selected Pesticides (CDFA, 2008; CDFA, 2010).

Pesticide	Method Detection Limit (ug/L)	Reporting Limit (ug/L)
2, 4-D	0.015	0.05
Azoxystrobin	0.017	0.05
Azoxystrobin acid	0.030	0.05
Azoxystrobin Z-metabolite	0.019	0.05
Bensulfuron-methyl	0.0006	0.05
Bispyribac-sodium	0.0002	0.05
Clomazone	0.0002	0.05
Halosulfuron-methyl	0.0011	0.05
Molinate	0.0012	0.05
Orthosulfamuron	0.0118	0.10
Penoxsulam	0.0009	0.05
Propanil	0.0004	0.05
Propiconazole	0.0005	0.05
Thiobencarb	0.0005	0.05
Triclopyr	0.0011	0.05