LEGAL AGRICULTURAL USE DETERMINATION FOR METOLACHLOR/S-METOLACHLOR DEGRADATE DETECTIONS IN CALIFORNIA

Rick Bergin
Environmental Scientist

California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring Branch
P.O. Box 4015
Sacramento, California 95812-4015

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ABSTRACT

Metolachlor, a preemergent herbicide, was registered in California in 1977. It is primarily used in the production of corn (human consumption and forage), beans (dry and succulent), cotton, and processing tomatoes. In 2000, S-metolachlor, a purified version of metolachlor, was registered. S-metolachlor currently accounts for 70% of the combined total metolachlor/S-metolachlor use. Metolachlor and S-metolachlor's physical and chemical properties indicate that they are persistent and mobile. Persistent and mobile pesticides are placed on the California Department of Pesticide Regulation's (DPR) Groundwater Protection List (GWPL) for future ground water monitoring, as required by Title 3 California Code of Regulations section 6800(b). DPR has currently analyzed 433 samples from 282 wells for the presence of metolachlor. While DPR has not detected either metolachlor or S-metolachlor in ground water, DPR has detected their ethanesulfonic and oxanilic acid degradates, MESA and MOXA, respectively. These residues range in concentrations from 0.05 to 20.2 parts per billion (ppb) in 62 wells. DPR's monitoring results for metolachlor, MESA, and MOXA are consistent with detection patterns nationwide.

There have been eight groups of adjacent detections located in San Joaquin, Solano, and Stanislaus Counties. Metolachlor/S-metolachlor has been used in the vicinity of these adjacent detections. These detections are likely due to legal agricultural use of metolachlor/S-metolachlor.

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INTRODUCTION

Metolachlor and S-metolachlor are two related herbicides. Metolachlor is a racemic mixture composed of equal parts of two R- and two S-stereoisomers. S-metolachlor is a resolved isomer mix composed mainly of the S-isomers (an 88:12 isomer mix). The S-isomers have the majority of the herbicidal activity (Muller et al., 2001). Thus, metolachlor and S-metolachlor are composed of the same isomers, just in different proportions.

Pesticide Use Profile

Metolachlor and S-metolachlor are preemergent, chloroacetamide herbicides that control a wide variety of broadleaf and annual grass species in agricultural settings. Preemergent herbicides are typically applied directly to the soil before seed germination. In California, from 1990 to 2014, metolachlor/S-metolachlor was used on over 80 different crops. The top five crops with the highest reported use in that time period were (in descending order): processing tomatoes, corn (all), cotton, and beans (all) (Table 1). Those four crops comprise about 89% of total metolachlor/S-metolachlor use.

Historically, metolachlor was primarily used on corn, beans, and cotton, although this use pattern has changed with the registration of S-metolachlor. Metolachlor use declined year-over-year by 13% in 2000 and 20% in 2001 due to the shift from metolachlor to S-metolachlor (CDPR, 2016a). After 2000, metolachlor/S-metolachlor use rebounded due to increasing use of S-metolachlor on processing tomatoes (Figure 1). S-metolachlor is one of the top pesticides, by the number of acres treated, used on processing tomatoes in California (CDPR, 2016b). However, since 2008, metolachlor use has been increasing with the registration of generic metolachlor products by other manufacturers (Figure 2); the original registrant cancelled their metolachlor products in 1999 during the switch to S-metolachlor. In 2014, S-metolachlor accounted for 70% of the combined total metolachlor/S-metolachlor use (CDPR, 2016b).

Aside from the metolachlor/S-metolachlor change, some decreases of metolachlor/S-metolachlor use can be attributed to the cultural and economic characteristics of its main crops: corn, beans, and cotton. Metolachlor/S-metolachlor use on these crops correlates with acres planted; fewer acres planted leads to less pesticide use (CDPR, 2016b). In corn and cotton, growers have moved away from preemergent herbicides like metolachlor to postemergent herbicides like glyphosate due to increased use of Roundup Ready™ corn and cotton (Lanini et al., 2006; CDPR, 2016b).

Environmental Fate

DPR's Environmental Fate Review indicates that metolachlor/S-metolachlor has physical-chemical characteristics that facilitate its potential downward movement to ground water (Rivard, 2003). Metolachlor is moderately persistent with a field dissipation half-life of 114 days and a hydrolysis half-life >200 days. Metolachlor is mobile with a high water solubility (530 ppm) and a low soil adsorption coefficient (K_{oc}= 200 cm^3/g). The principal routes of metolachlor degradation are photolysis and microbial soil metabolism.

Metolachlor and S-metolachlor break down, mainly via soil microbial metabolism through different enzymatic pathways, into ethanesulfonic and oxanilic acid degradates (Rivard, 2003).

During the breakdown process, the removal and substitution of the chlorine atom in metolachlor/S-metolachlor increases degradate polarity and water solubility (Thurman et al., 1996). The two major degradation products of metolachlor and S-metolachlor, MESA and MOXA, can persist in agricultural soils for at least three years after a metolachlor/S-metolachlor application (Phillips et al., 1999). MESA/MOXA are also more likely to be found in ground water than the parent compounds (Barbash, 1999). This demonstrates their mobility and persistence in the environment.

Title 3 of the California Code of Regulations section 6800(b) places pesticides on the GWPL if they have the potential to pollute ground water. This pollution potential is determined by specific numerical values (SNVs). SNVs indicate the relative risk of ground water contamination posed by agricultural use pesticides. DPR created SNVs for water solubility, soil adsorption, hydrolysis half-life, aerobic soil metabolism half-life, and anaerobic soil metabolism half-life. Metolachlor and S-metolachlor exceed all SNVs except for anaerobic soil metabolism half-life, hence their inclusion on the GWPL for monitoring.

Detections Reported by Other Agencies

Ground water monitoring for metolachlor and metolachlor degradates has occurred in many states, including Iowa, Georgia, Wisconsin, and Minnesota (Table 2). Metolachlor degradates, MESA and MOXA, are detected more frequently in ground water than metolachlor itself. MESA is detected at the highest frequency followed by MOXA and metolachlor.

From 2004 through 2010, the State Water Resources Control Board (SWRCB), in conjunction with the U.S. Geological Survey (USGS), sampled 1845 wells in 54 counties for metolachlor as part of their Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project. The GAMA Priority Basin Project was implemented to assess ground water quality in basins that account for over 90% of all ground water used to supply drinking water in California. Prioritized basins were monitored for many chemicals, often at very low detection limits, in order to fully characterize and identify the extent of ground water contamination. In this project, metolachlor was detected in 43 wells in 18 counties at concentrations ranging from 0.002 to 0.16 ppb (SWRCB, 2015). The USGS did not analyze for metolachlor degradates in this study. DPR conducted sampling to confirm GAMA detections but did not detect the parent compounds (Nordmark, 2015).

Drinking Water Quality Standards

The California Department of Public Health (CDPH) sets Maximum Contaminant Levels (MCLs). MCLs are the highest level of a contaminant allowed in drinking water. There is no MCL set for metolachlor or S-metolachlor. However, the U.S. EPA has established a lifetime Health Advisory (HA) and a Drinking Water Equivalent Level (DWEL) for metolachlor. The lifetime HA is the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure. The DWEL is a drinking water lifetime exposure level, assuming 100% exposure from drinking water only, at which adverse noncarcinogenic health effects would not be expected to occur. Metolachlor's lifetime HA is 700 ppb and its DWEL is 3,500 ppb. MESA and MOXA have no set water quality standards however there is no indication that they are more toxic than metolachlor itself (CDPR, 2015c).

RESULTS

DPR Sampling

Since the late 1980s, DPR has analyzed 433 samples from 282 wells for metolachlor. Metolachlor was not detected in any of these samples. Starting in 2001, DPR added two metolachlor/S-metolachlor degradates to the analytical screen, MESA and MOXA, in response to ground water detections in other states. In 2001, DPR monitored 88 wells for metolachlor, MESA, and MOXA; metolachlor was not detected. However, MESA and MOXA were detected in 23% and 10% of the sampled wells, respectively, at concentrations ranging from 0.059 ppb to 20.2 ppb (Weaver, 2002). Another metolachlor monitoring study yielded similar results in 2009. Once again metolachlor was not detected in the 68 wells sampled. However, MESA and MOXA were detected in 49% and 18% of the sampled wells, respectively, at concentrations ranging from 0.05 ppb to 2.835 ppb (Bergin, 2012). In 2004, DPR conducted two detection response studies ("z-studies") for metolachlor and detected only MESA and MOXA in 50% and 8% of the sampled wells, respectively, at concentrations ranging from 0.091 ppb to 1.1 ppb (Rollins, 2005a; Rollins, 2005b). In 2015, DPR initiated another "z-study" for metolachlor and detected MESA and MOXA in 67% and 33% of the sampled wells, respectively, at concentrations ranging from 0.05 ppb to 1.67 ppb (Nordmark, 2015). In all DPR sampling, metolachlor and S-metolachlor are indistinguishable and cannot be differentiated from each other.

In total, DPR has detected MESA/MOXA in 62 wells with concentrations ranging from 0.05 to 20.2 ppb. All MOXA detections had a corresponding MESA detection in the same well. All MESA/MOXA detections reported in this document pre-2015 were analyzed using an unequivocal method as required by California Food and Agricultural Code (FAC) section 13149(d) (Spurlock, 2001). All 2015 sampling was analyzed under a different unequivocal method (Aggarwal, 2016).

Nineteen of the 62 positive wells are isolated from other MESA/MOXA detections because they are not adjacent to, or within the same section as another positive detection. These isolated detections have occurred in Kings, Sacramento, San Joaquin (04N07E03, 01N05E23, 01N08E30, 02S06E27, 03S05E03, and 03S06E08), Solano (06N01E08 and 07N02E14), Stanislaus (02S08E25, 05S09E14, 05S09E36, 06S09E29), Tulare, and Yolo Counties. The remaining 43 positive wells are located in eight groups in San Joaquin, Solano, and Stanislaus Counties:

1. San Joaquin/East of Tracy (Figure 3): Two wells tested positive in adjacent sections (02S06E19 and 30) in 2009. A previous legal agricultural use determination for hexazinone found no evidence of point source contamination in the area (Nordmark, 2010).

2. San Joaquin/West of Woodbridge (Figure 4): Two wells tested positive in adjacent sections (04N05E35 and 36) in 2009.

3. San Joaquin/Northwest of Escalon (Figure 5): Two wells tested positive in the same section (01S08E14). One well was sampled in 2001 and the other in 2009.

4. Solano/Southeast of Dixon (Figure 6): Five wells tested positive in five separate sections (07N01E25, 07N02E16, 07N02E20, 07N02E28, and 07N02E30) in 2009.

5. Stanislaus/North of Newman (Figure 7): In 2001, ten wells tested positive in eight sections (06S08E25, 06S08E36, 06S08E31, 07S08E02, 07S08E12, 07S08E14, 07S09E06, and 07S09E18). In 2009, 5 wells tested positive in 5 sections (06S08E25, 06S08E36, 07S08E02, 07S08E01, and 07S09E18). The same well in 07S08E02 tested positive for metolachlor degradates during both sampling events.

6. Stanislaus/North of Patterson (Figure 7): In 2001, three wells tested positive in two sections (05S07E24 and 05S08E19). In 2009, six wells tested positive in five sections (05S07E12, 05S08E08, 05S07E13, 05S08E18, and 05S07E24). The well in section 05S07E13 has been sampled both in 2001 and 2009 and was only positive for metolachlor degradates in 2009.

7. Stanislaus/South of Patterson (Figure 7): In 2015, four wells tested positive in three sections (06S08E03, 06S08E04, and 06S08E09).

8. Stanislaus/North of Denair (Figure 8): In 2004, five wells tested positive in three sections (04S11E29, 04S11E30, and 04S11E31).

Reported Pesticide Use

The total reported use of metolachlor/S-metolachlor in the area surrounding the 62 positive wells varies from thousands to tens of thousands of pounds for the 10 to 24 year period prior to detection (Table 3). The three counties with adjacent detections, San Joaquin, Solano, and Stanislaus, have a history of nearby metolachlor/S-metolachlor use. Around the San Joaquin County detections, metolachlor/S-metolachlor use is evenly split between corn, beans, and processing tomatoes. Around the Solano County detections, over half of the metolachlor/S-metolachlor use is on corn. Around the Stanislaus County detections, two-thirds of the metolachlor/S-metolachlor use is on beans.

DISCUSSION

Historically, pesticide degradate detections only entered the review process outlined in FAC sections 13149 and 13150 if their detected concentrations surpassed water quality standards. Detections of parent pesticide compounds did not have this additional criterion. In 2014, the law was changed to require pesticide degradates to undergo the same review process as parent compounds before conducting a human health risk assessment. When a pesticide or pesticide degradate is found in the ground water of the state, DPR is required by FAC section 13149 to make a determination as to whether those residues resulted from legal agricultural use, in accordance with state and federal laws and regulations, and must state in writing the reasons for the determination. Detections of a pesticide or pesticide degradate in ground water is a result of legal agricultural use if the following is true:

1. The pesticide or pesticide degradate is detected in two or more wells in the same or adjacent one-square mile section of land (Goh, 1992).

2. The pesticide has reported use in the vicinity of the detections or there are sites within the section where the pesticide might be used (Oshima, 1987).

DPR has detected MESA/MOXA residues in 62 wells in seven counties (Table 3). Forty-three of these detections meet the adjacent section criteria. All but four of these wells are located in sections with metolachlor/S-metolachlor use; however, all detections are surrounded by sections with some metolachlor/S-metolachlor use. Therefore, these detections are a result of the legal agricultural use of metolachlor/S-metolachlor. Other factors that contribute to the likelihood that these residues are from legal agricultural use are:

1. DPR's ground water monitoring results for metolachlor, MESA, and MOXA mirror ground water monitoring studies across the nation. In other states where metolachlor/S-metolachlor is used, MESA and MOXA are often found at higher frequencies than metolachlor in ground water. MESA/MOXA are mobile and persistent which allows them to leach into ground water at higher rates than the parent compounds.

2. DPR sampled the same areas in 2001 and 2009 and found similar results in terms of frequency and magnitude. If residues were temporary or transient, then one would expect different outcomes between the two sampling events. Reoccurring residues suggest contamination by either long-lived compounds or continued pesticide loading into the well.

3. The two wells located near Tracy have been previously evaluated for signs of point source contamination. No evidence of point source contamination was found during that investigation. This indicates that the pesticide residues found in these wells are likely to be from legal agricultural use.

CONCLUSIONS

Current and historical monitoring data strongly suggest that the agricultural use of metolachlor/S-metolachlor results in MESA and MOXA migrating to ground water in California. This is similar to other areas of the country where metolachlor/S-metolachlor is used; MESA/MOXA, more than the parent compounds, are frequently detected in ground water.

Detections in 2001, 2004, 2009, and 2015 in San Joaquin, Solano, and Stanislaus Counties meet DPR's legal agricultural use criteria: detections in two or more wells in the same or adjacent one-square mile section of land and reported use of metolachlor/S-metolachlor in the vicinity of the detections. These detections indicate that MESA/MOXA are reaching ground water due to legal agricultural use of metolachlor/S-metolachlor.

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FIGURES

Figure 1. Metolachlor/S-metolachlor use on beans, corn, cotton, and processing tomatoes from 1990 to 2014 (CDPR, 2016a)

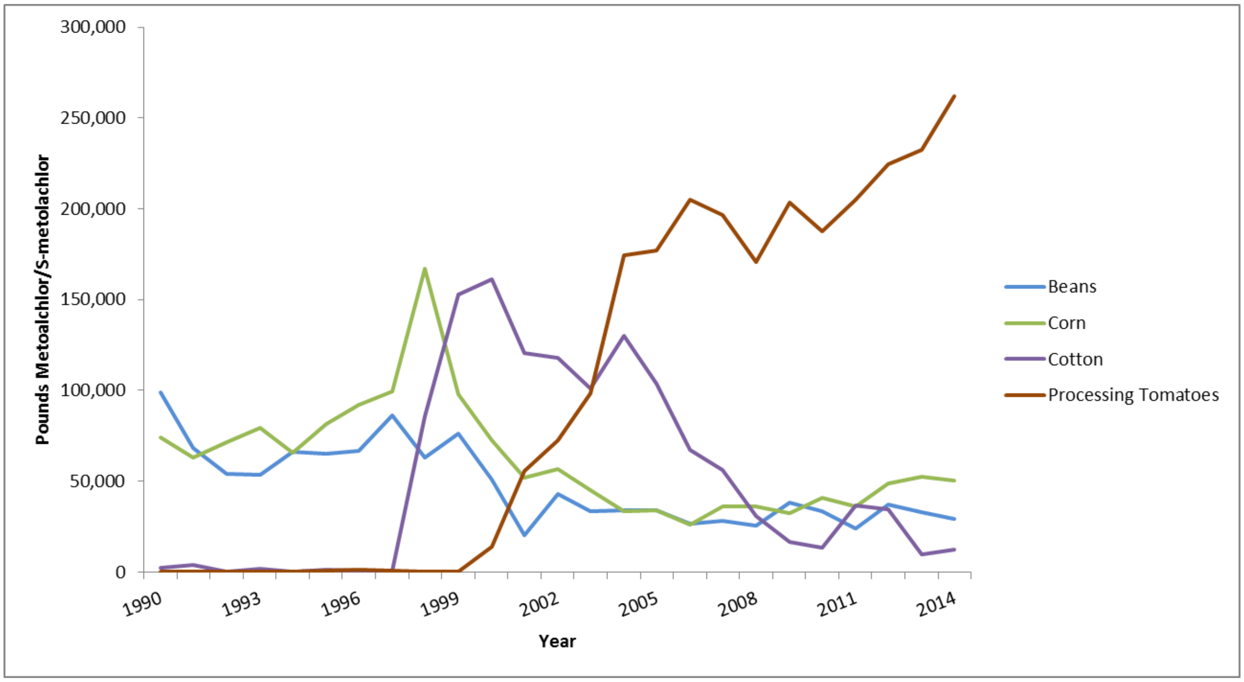


Figure 2. Metolachlor and S-metolachlor use, all crops, from 1990 to 2014 (CDPR, 2016a)

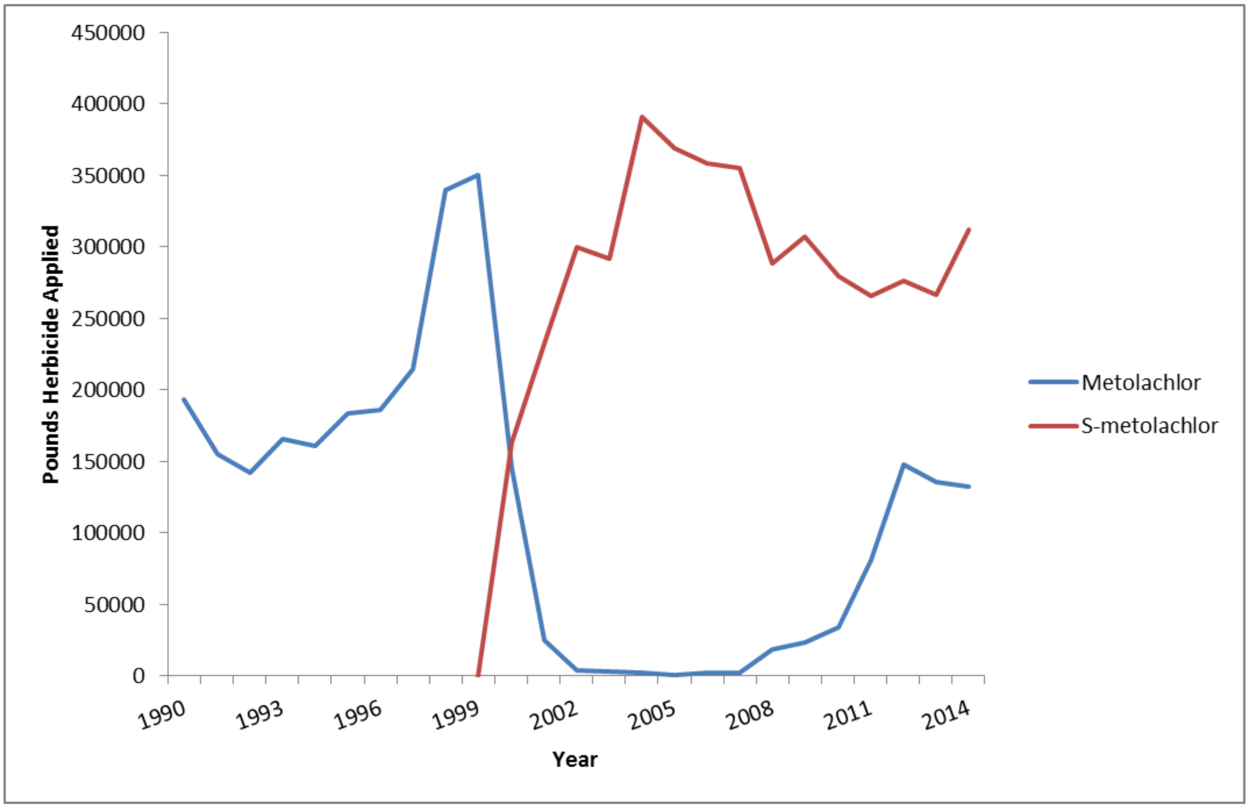


Figure 3. Metolachlor/S-metolachlor use and DPR sampled well locations in San Joaquin County and east of Tracy

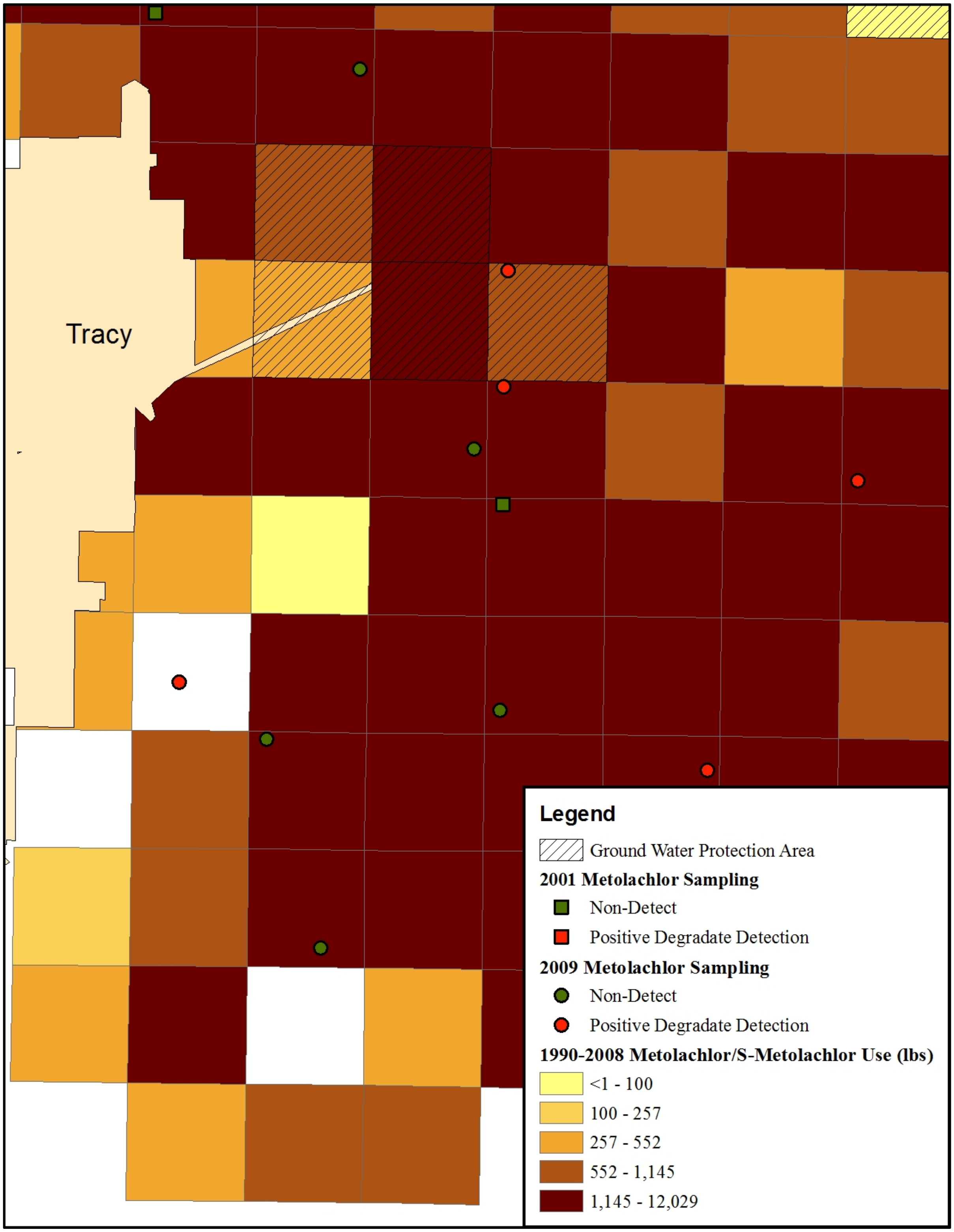


Figure 4. Metolachlor/S-metolachlor use and DPR sampled well locations in San Joaquin County and west of Woodbridge

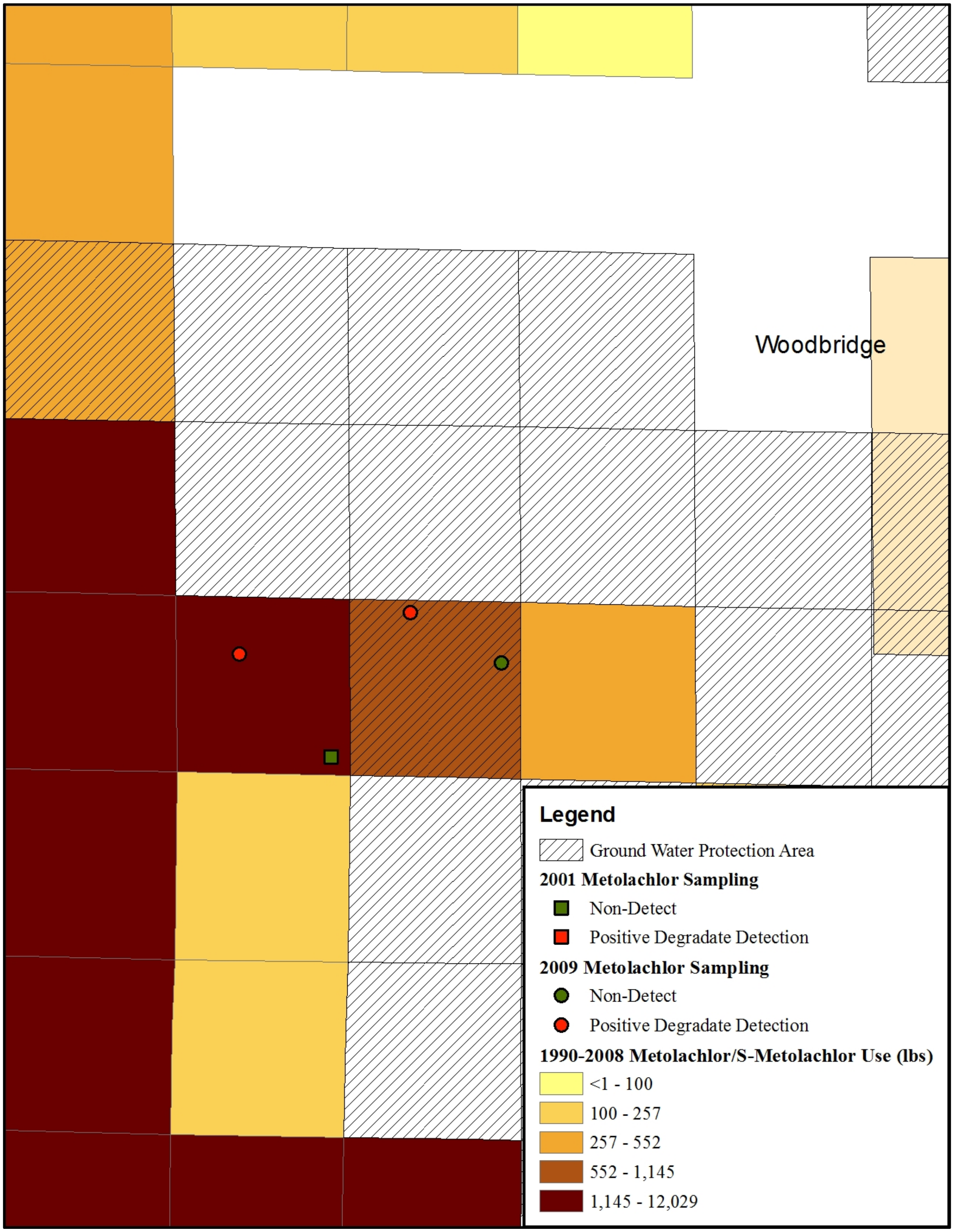


Figure 5. Metolachlor/S-metolachlor use and DPR sampled well locations in San Joaquin County and northwest of Escalon

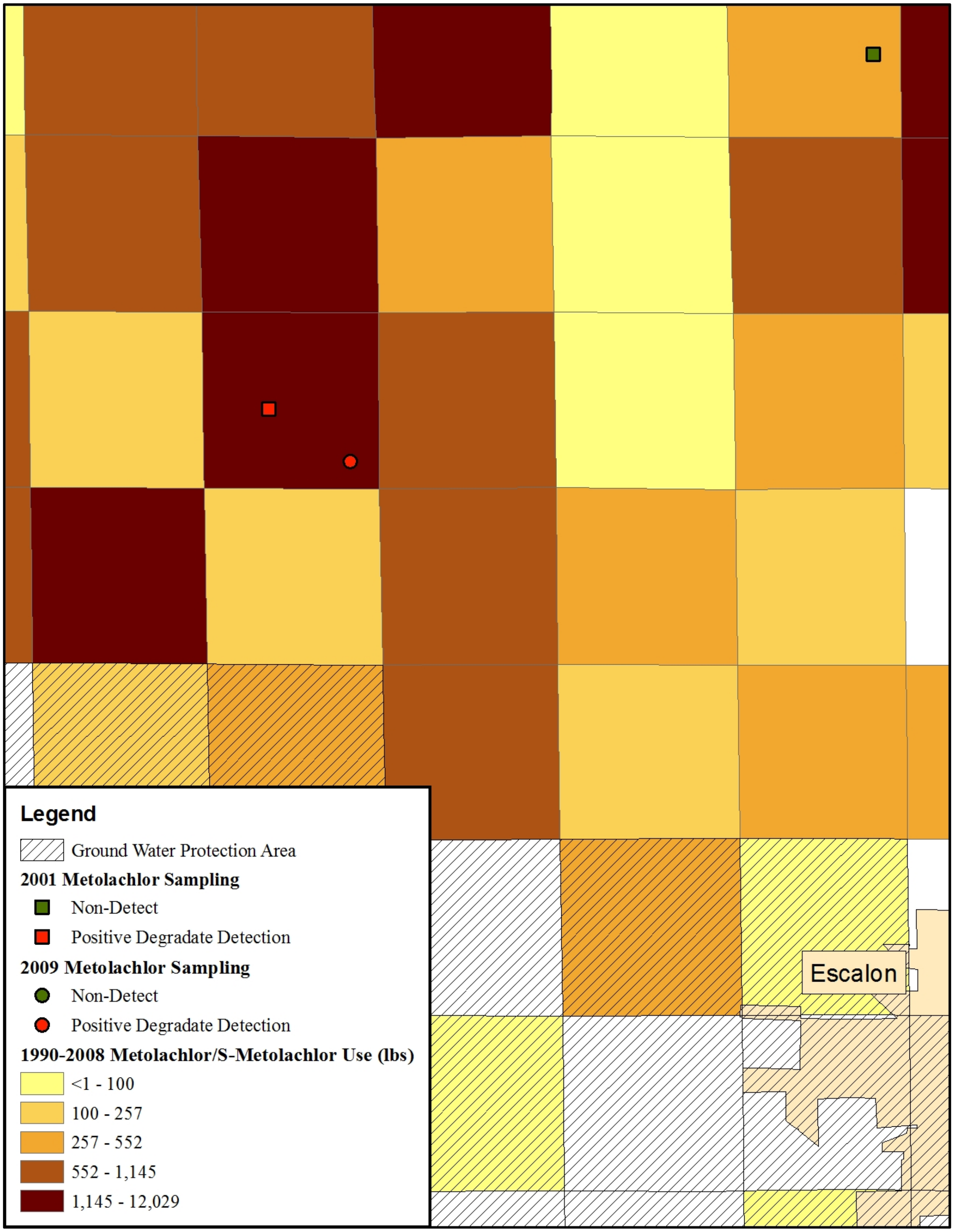


Figure 6. Metolachlor/S-metolachlor use and DPR sampled well locations in Solano County and southeast of Dixon

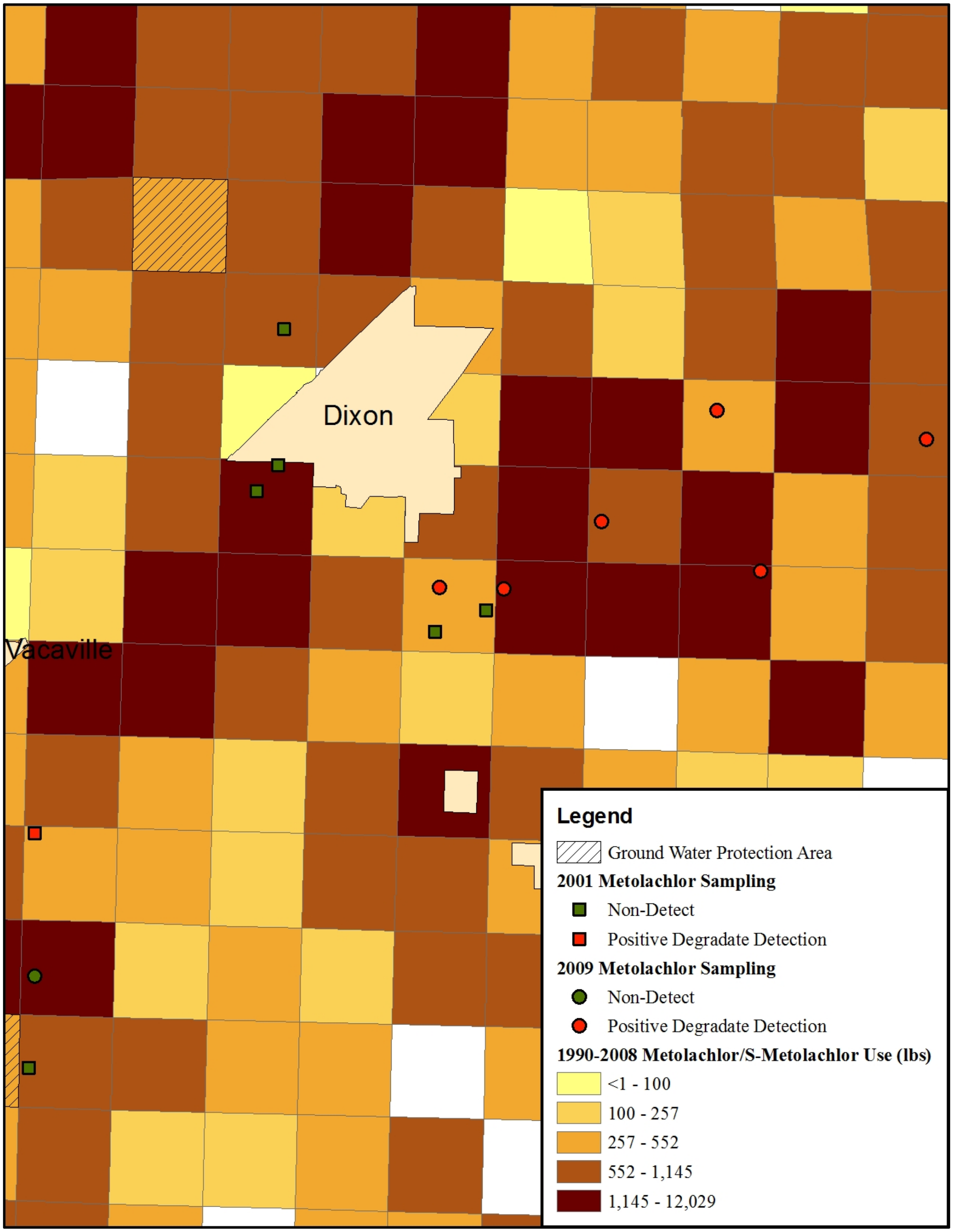


Figure 7. Metolachlor/S-metolachor use and DPR sampled well locations in Stanislaus County from Patterson to Newman

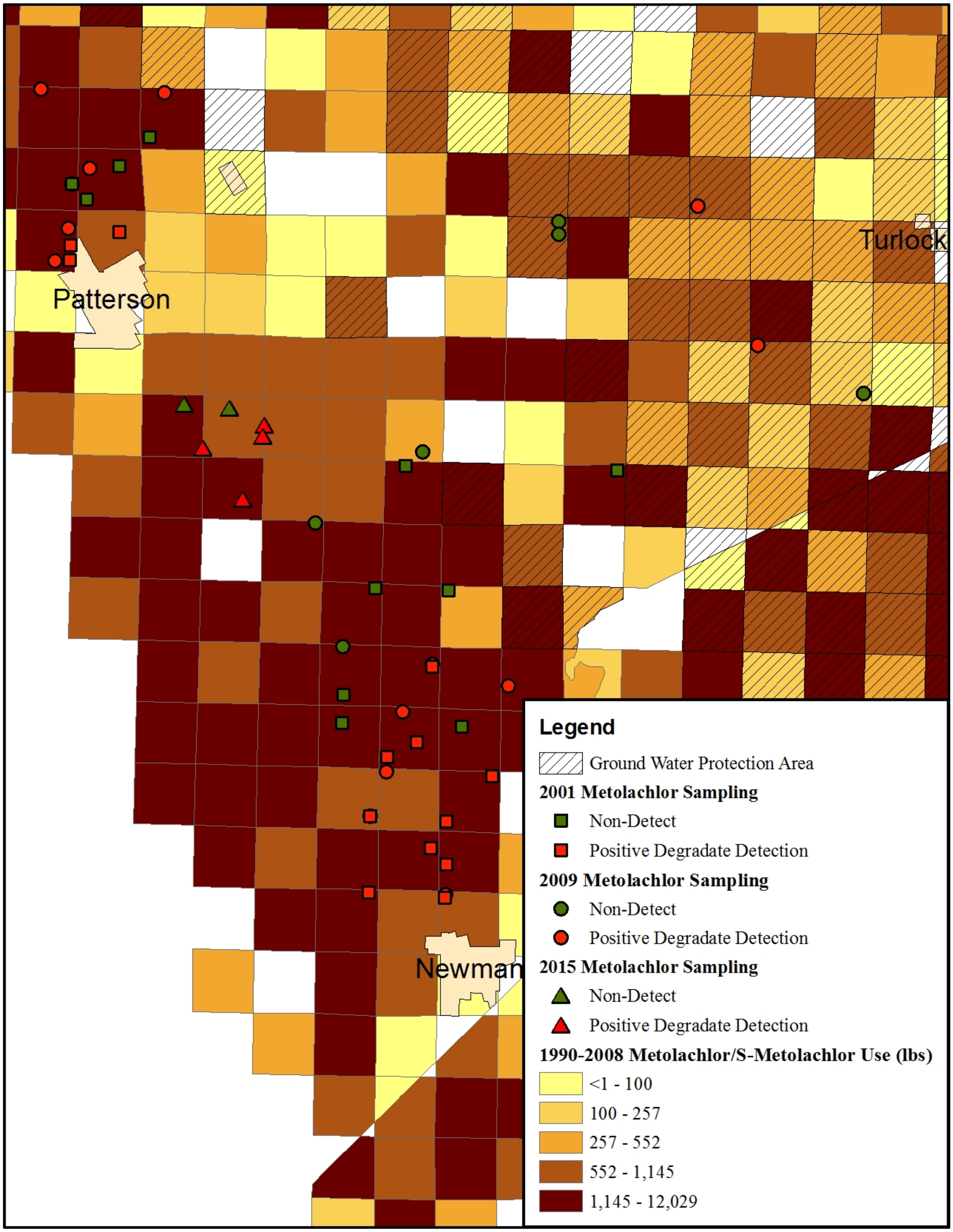
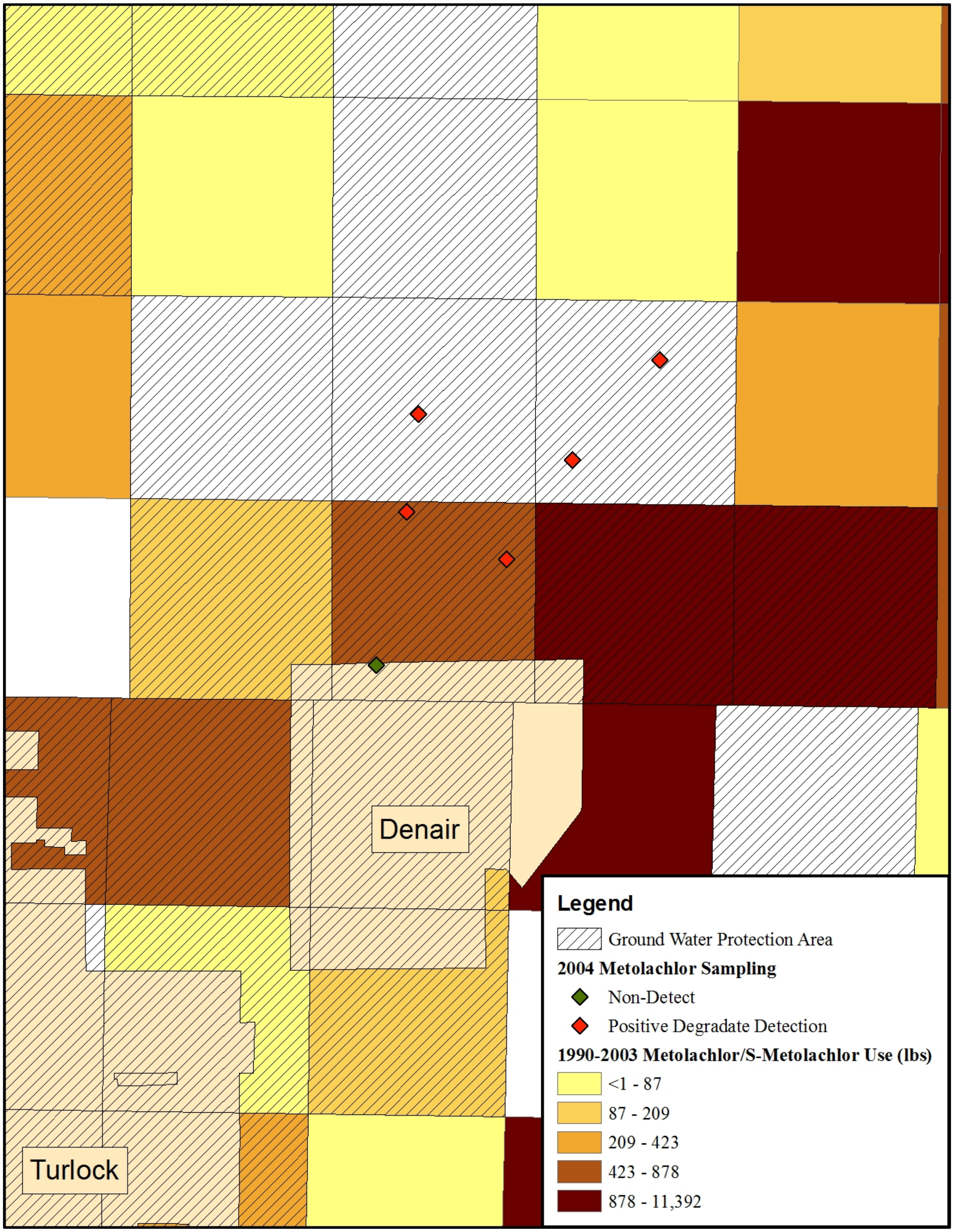


Figure 8. Metolachlor/S-metolachlor use and DPR sampled well locations in Stanislaus County and north of Denair



TABLES

Table 1. Top counties of metolachlor use/S-metolachlor use and metolachlor sampling results

Total Lbs Applied By Location[a]			Total Lbs Applied by Crop				DPR Sampling	
			Corn (all)	Beans (all)	Cotton	Processing tomatoes	Number of Wells	Confirmed Degradate Detections
Statewide		7,305,442	1,546,585	1,191,183	1,261,491	2,482,924	282	62
County	**Rank[b]**							
Fresno[c]	1	1,673,164	108,629	50,199	684,734	778,181	39	0
San Joaquin	2	909,816	250,466	231,792	188	302,884	33	12
Kings	3	771,790	153,760	19,771	365,525	211,039	17	1
Stanislaus	4	652,433	251,588	318,172	0	71,575	60	36
Yolo	5	559,311	57,784	9,615	3,724	438,045	14	1
Merced[d]	6	541,896	141,047	60,584	82,084	218,363	30	0
Kern	7	440,486	55,666	55,684	77,454	44,821	0	0
Sacramento	8	276,241	206,242	17,232	119	25,987	14	1
Colusa	9	256,659	15,438	50,752	13,929	155,595	0	0
Solano	10	245,435	50,922	32,389	0	109,222	23	7
Tulare	11	209,951	106,358	75,873	10,387	0	17	4

a. Use aggregated from 1990 to 2014; Pesticide Use Report Data (CDPR, 2016a).
b. County ranks based on total metolachlor/S-metolachlor usage statewide.
c. Majority of sampling did not include degradates.
d. Sampling occurred in late 1980s before degradates were added to the analytical method.

Table 2. Ground water monitoring for metolachlor and its degradates in selected states

State	Number of Samples	Analyte		
		Metolachlor (% detection/max concentration[a])	**MESA[b] (% detection/max concentration)**	**MOXA[c] (% detection/max concentration)**
Georgia[d]	28	7 / 0.13	67 / 19	33 / 4.42
Iowa[e]	88	8 / 10	60 / 8	25 / 15
Minnesota[f]	22	14 / 4.25	84 / 24.3	40 / 12.6
Wisconsin[g]	259	36 / 5.9	91 / 18	86 / 23

a. Concentration in parts per billion (ppb).
b. Metolachlor ethanesulfonic acid
c. Metolachlor oxanilic acid
d. Pittman, 2003
e. Kalkhoff et al., 1998
f. MDA, 2010
g. Rheineck, 2001

Table 3. Metolachlor degradate sampling results and pesticide use information for areas where verified metolachlor degradate residues have been detected

County	Location[a]	Number of Wells Sampled	Metolachlor Degradate Positive Wells[b]				Metolachlor/ S-metolachlor Use (lbs)[c]	
			Number of Positive Wells	Highest Conc (ppb)	First Year Detected	Last Year Section Sampled	In Section	9 Section[d]
Kings	M18S22E33	1	1	1.2	2009	2009	588	4,624
Sacramento	M05N05E01	1	1	0.716	2001	2001	3,523	8,671
San Joaquin	M01N05E23	1	1	0.196	2001	2001	378	4,299
San Joaquin	M01N08E30	1	1	0.384	2009	2009	2,311	14,222
San Joaquin	M01S08E14	2	2	0.838	2001	2009	2,703	8,351
San Joaquin	M02S06E19	1	1	1.453	2009	2009	707	23,678
San Joaquin	M02S06E27	1	1	0.065	2009	2009	2,462	15,261
San Joaquin	M02S06E30	1	1	2.15	2009	2009	4,106	24,535
San Joaquin	M03S05E03	1	1	0.13	2009	2009	0	7,579
San Joaquin	M03S06E08	1	1	0.128	2009	2009	4,920	28,710
San Joaquin	M04N05E35	2	1	0.051	2009	2009	2,522	14,168
San Joaquin	M04N05E36	2	1	0.33	2009	2009	952	3,932
San Joaquin	M04N07E03	1	1	0.183	2009	2009	3,773	13,470
Solano	M06N01E08	1	1	1.05	2001	2001	199	5,717
Solano	M07N01E25	3	1	0.233	2009	2009	418	6,811
Solano	M07N02E14	1	1	0.081	2009	2009	736	7,844
Solano	M07N02E16	1	1	0.689	2009	2009	369	9,060
Solano	M07N02E20	1	1	0.078	2009	2009	560	11,732
Solano	M07N02E28	1	1	0.087	2009	2009	1,386	7,329

County	Location[a]	Number of Wells Sampled	Metolachlor Degradate Positive Wells[b]				Metolachlor/ S-metolachlor Use (lbs)[c]	
			Number of Positive Wells	Highest Conc (ppb)	First Year Detected	Last Year Section Sampled	In Section	9 Section[d]
Solano	M07N02E30	1	1	0.102	2009	2009	2,158	7,072
Stanislaus	M02S08E25	2	1	0.567	2009	2009	3,827	8,765
Stanislaus	M04S11E29	2	2	0.981	2004	2004	0	6,059
Stanislaus	M04S11E30	1	1	0.102	2004	2004	0	3,131
Stanislaus	M04S11E31	3	2	1.1	2004	2004	655	4,639
Stanislaus	M05S07E12	1	1	0.799	2009	2009	1,205	14,263
Stanislaus	M05S07E13[e]	1	1	0.086	2009	2009	1,333	15,115
Stanislaus	M05S07E24	4	4	0.75	2001	2009	1,365	5,897
Stanislaus	M05S08E08	2	1	0.635	2009	2009	1,502	7,479
Stanislaus	M05S08E18	3	1	1.472	2009	2009	3,054	14,731
Stanislaus	M05S08E19	1	1	0.06	2001	2001	475	5,206
Stanislaus	M05S09E14	1	1	1.155	2009	2009	1,132	7,270
Stanislaus	M05S09E36	1	1	0.553	2009	2009	642	5,031
Stanislaus	M06S08E03	1	1	0.639	2015	2015	1,150	10,872
Stanislaus	M06S08E04	3	2	1.67	2015	2015	1,447	15,689
Stanislaus	M06S08E09	1	1	0.119	2015	2015	1,951	21,231
Stanislaus	M06S08E25	2	2	0.279	2001	2009	4,345	19,641
Stanislaus	M06S08E36	3	3	1.98	2001	2009	3,622	17,044
Stanislaus	M06S09E29	1	1	2.835	2009	2009	4,290	16,863
Stanislaus	M07S08E01	1	1	0.879	2009	2009	708	31,179
Stanislaus	M07S08E02[f]	1	1	0.599	2001	2009	0	15,443
Stanislaus	M07S08E12	1	1	4.02	2001	2001	7,282	14,020
Stanislaus	M07S08E14	1	1	20.2	2001	2001	3,247	15,083

County	Location[a]	Number of Wells Sampled	Metolachlor Degradate Positive Wells[b]				Metolachlor/ S-metolachlor Use (lbs)[c]	
			Number of Positive Wells	Highest Conc (ppb)	First Year Detected	Last Year Section Sampled	In Section	9 Section[d]
Stanislaus	M07S09E06	2	2	0.279	2001	2001	910	18,082
Stanislaus	M07S09E07	1	1	10.03	2001	2001	762	10,080
Stanislaus	M07S09E18	2	2	0.341	2001	2009	569	9,492
Tulare	M17S24E23	1	1	1.15	2001	2001	6,166	6,166
Tulare	M17S24E35	1	1	1.1	2001	2001	1,710	6,615
Tulare	M21S26E06	2	1	0.091	2004	2004	435	4,720
Tulare	M21S27E07	1	1	0.194	2001	2001	1,566	4,118
Yolo	M10N02E12	1	1	0.185	2009	2009	1,073	12,809

a. Township, range, and section of the well(s). A section is approximately one square mile.
b. Data in these columns apply only to wells that have had at least one sample with a metolachlor degradate concentration above the reporting limit.
c. Metolachlor/S-metolachlor use totals are given for one of three periods, 1990-2000, 1990-2003, 1990-2008, and 1990-2014 based on the year of the first detection in the section. The period used was selected to represent the metolachlor/S-metolachlor use prior to the first reported metolachlor degradate detection. Rights-of-way use is reported at the county level and is not included.
d. Total metolachlor/S-metolachlor use in the section where the positive well is located and the surrounding 8 sections.
e. Same well sampled in both 2001 and 2009; only positive for metolachlor degradates in 2009 sampling event.
f. Same well sampled in both 2001 and 2009; positive for metolachlor degradates in both sampling events.