LEGAL AGRICULTURAL USE DETERMINATION FOR ALACHLOR DEGRADATE DETECTIONS IN CALIFORNIA

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ABSTRACT

Alachlor, a preemergent herbicide, was registered in California in 1977. It is primarily used in the production of corn (human consumption and forage) and beans (dry and succulent). Alachlor's physical and chemical properties indicated that it was persistent and mobile so it was placed on the California Department of Pesticide Regulation's (DPR) Groundwater Protection List as required by Title 3, California Code of Regulations section 6800(b). DPR has currently analyzed 406 samples from 253 wells for the presence of alachlor. While alachlor has not been detected in ground water, its ethanesulfonic and oxanilic acid degradates (AESA and AOXA, respectively) have been detected. These residues range in concentrations from 0.05 to 1.38 parts per billion (ppb) in 29 wells. DPR's monitoring results for alachlor, AESA, and AOXA are consistent with detection patterns nationwide.

There have been four groups of adjacent detections located in San Joaquin, Solano, and Stanislaus Counties in areas of either corn or bean production. Alachlor has been used in the vicinity of these adjacent detections. These detections are likely due to legal agricultural use of alachlor.

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INTRODUCTION

Pesticide Use Profile

Alachlor is a preemergent chloroacetamide herbicide that has been registered for use in California since 1977. Alachlor controls a wide variety of broadleaf and annual grass species. In California, from 1990 to 2013, corn and beans accounted for 93% of the total reported alachlor use (Table 1). Alachlor use has been steadily declining over the years (Figure 1). In California, alachlor use trends are tied to the cultural and economic characteristics of its two main crops: beans and corn. Decreases of alachlor use may be attributed to a decline in acres planted and a shift to postemergence weed control. The amount of beans planted in California has been declining over the years (USDA, 2010), facilitating the similar decreases in alachlor use, most notably in 1993 (Figure 1). In corn, growers have moved from preemergent herbicides like alachlor to postemergent herbicides like glyphosate due to increased Roundup Ready™ corn use (Lanini et al., 2006).

Environmental Fate

The U.S. Environmental Protection Agency's (U.S. EPA's) Reregistration Eligibility Decision (RED) document (1998) indicates that alachlor is highly mobile in soil (K_{oc} = 190 cm^3/g, water solubility = 242 ppm) and is stable to abiotic breakdown processes such as hydrolysis and photolysis. Dissipation of alachlor in the environment occurs mainly through aerobic soil metabolism (half-life = 2-3 weeks) and leaching through the soil. The RED also states that "the persistence and mobility of the chemical [alachlor] may increase as it reaches deeper soil horizons which have lower organic matter content and decreased biological activity, thus increasing its potential to leach into groundwater." The ethanesulfonic and oxanilic acid degradates are the principal breakdown products of alachlor and are more persistent in soil than alachlor itself (U.S. EPA, 1998).

Alachlor degradates have greater mobility than their parents; the removal and substitution of the chlorine atom increases the degradate's polarity and hence their water solubility (Thurman et al., 1996). One study suggests that AESA is the dominate alachlor degradate and resides in ground water for years even when alachlor use has discontinued (Steele et al., 2008). Alachlor degradates are more likely to be found in ground water than the parent compound.

Title 3 of the California Code of Regulations section 6800(b) places pesticides on the Groundwater Protection List if they have the potential to pollute groundwater. This pollution potential is determined by specific numerical values (SNVs). SNVs indicate the relative risk of groundwater 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. Alachlor exceeds all SNVs except for aerobic and anaerobic soil metabolism half-life, hence its inclusion on the Groundwater Protection List for monitoring.

Detections Reported by Other Agencies

Ground water monitoring for alachlor and alachlor degradates has occurred in many states, including Iowa, Georgia, Wisconsin, and Minnesota. In Iowa, 88 municipal wells were tested for alachlor, AESA, and AOXA with detection frequencies of 1%, 50%, and 20%, respectively, with concentrations ranging from 25 ppb to 0.2 ppb (Kalkhoff et al., 1998). The Georgia investigation did not detect alachlor out of 28 wells sampled; however, AESA and AOXA were found in 48% and 18% of the wells, respectively, with a max concentrations ranging from 5.86 ppb to 1.18 ppb (Pittman, 2003). In 2000, the Wisconsin Department of Agriculture sampled 27 monitoring wells, 22 private drinking water wells, and 23 municipal wells (Rheineck, 2001). In the monitoring wells, alachlor, AESA, and AOXA were detected 0%, 81%, and 41%, respectively, with the highest concentrations ranging from 33 ppb to 15 ppb. In the private drinking water wells, alachlor, AESA, and AOXA were detected 14%, 91%, and 73%, respectively, with the highest concentrations ranging from 34 ppb to 0.28 ppb. In the municipal wells, alachlor, AESA, and AOXA were detected 4%, 48%, and 17%, respectively, with the highest concentrations ranging from 4.4 ppb to 0.67 ppb. In 2010, the Minnesota Department of Agriculture, as part of their annual ground water monitoring, reported detection frequencies for alachlor, AESA, and AOXA as 1%, 46%, and 2%, respectively, out of 259 samples taken from monitoring wells throughout the state (MDA, 2010). Maximum concentrations of the detected analytes ranged from10.3 ppb to 0.44 ppb.

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 alachlor 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, alachlor was detected in only one well at 0.004 ppb (SWRCB, 2015). The USGS did not sample for alachlor degradates in this study.

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. The California Office of Environmental Health Hazard Assessment (OEHHA) establishes Public Health Goals (PHGs). PHGs are concentrations of drinking water contaminants that pose no significant health risk if consumed for a lifetime, based on current risk assessment principles, practices, and methods. The CDPH MCL for alachlor is 2 ppb. The OEHHA PHG for alachlor is 4 ppb. AESA and AOXA have no set water quality standards but AESA has been determined to be less toxic than alachlor (U.S. EPA, 1998).

RESULTS

DPR Sampling

Since the late 1980s, DPR has analyzed 406 samples from 253 wells for alachlor. Alachlor was not detected in any of these samples. Starting in 2001, DPR added two degradates to the alachlor analytical screen, AESA and AOXA, in response to ground water detections in other states. In 2001, DPR monitored 88 wells for alachlor, AESA, and AOXA; alachlor was not detected. However, AESA and AOXA were detected in 15% and 1% of the sampled wells, respectively, with concentrations ranging from 0.05 ppb to 1.38 ppb (Weaver, 2002). Another alachlor monitoring study, in 2009, yielded similar results. Once again alachlor was not detected in the 68 wells sampled, but AESA and AOXA were detected in 23% and 2% of the sampled wells, respectively, with concentrations ranging from 0.05 ppb to 1.04 ppb (Bergin, 2012). All AOXA detections had a corresponding AESA detection in the same well. All alachlor degradate detections reported in this document were analyzed using an unequivocal method as required by California Food and Agricultural Code (FAC) section 13149(d) (Spurlock, 2001).

Nine of the 29 positive wells are isolated from other alachlor degradate 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 (01N08E30), Solano (06N01E17 and 07N01E25), Stanislaus (06S09E29, 05S09E36, and 04S11E29), and Yolo Counties. The remaining 20 positive wells are located in four groups in San Joaquin, Solano, and Stanislaus Counties:

1. San Joaquin/East of Tracy (Figure 2): Two wells with alachlor degradate residues were found in two sections (02S06E19 and 30) in the 2009 ground water monitoring study. A previous legal agricultural use determination for hexazinone found no evidence of point source contamination in the area (Nordmark, 2010).

2. Solano/Southeast of Dixon (Figure 3): Two wells with alachlor degradate residues were found in two sections (07N02E20 and 28) in the 2009 ground water monitoring study.

3. Stanislaus/North of Newman (Figure 4): Five wells with alachlor degradate residues were found in four sections (06S08E26, 06S08E36, 07S08E12, and 07S08E14) in the 2001 ground water monitoring study. An additional positive well was found in section 06S08E36 in the 2009 ground water monitoring study.

4. Stanislaus/North of Patterson (Figure 5): In 2001, five wells with alachlor degradate residues were found in three sections (05S07E13, 05S07E24, and 05S08E18). In 2009, six wells with alachlor degradate residues were found in five sections (05S07E12, 05S08E08, 05S07E13, 05S08E18, and 05S07E24). The well in section 05S07E13 has been sampled both in 2001 and 2009 and was positive for alachlor degradates each time.

Reported Pesticide Use

The total reported use of alachlor in the area surrounding the 29 positive wells varies from zero to thousands of pounds for the 10 to 18 year period prior to detection (Table 2). The three counties with adjacent detections, San Joaquin, Solano, and Stanislaus, have a history of nearby alachlor use. Around the San Joaquin and Stanislaus County detections, alachlor use is predominantly on beans. Around the Solano County detections, alachlor use is split between both corn and 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 without pre-judging toxicity. When a pesticide or pesticide degradate is found in the ground water of the state, DPR is required by the 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. To determine that a pesticide degradate meets the conditions of FAC section 13149 (a) as a result of legal agricultural use, DPR reviews the facts of each case, including whether:

1. The pesticide ingredient is verified in a second well in the same or adjacent one-square mile section of land. This was originally stated as a second well within one-half mile (Oshima, 1987) but was subsequently revised to two wells within a four-section area (Goh, 1992).

2. The pesticide has been reported used in the vicinity or there are sites within the section where the pesticide ingredient might have been used (Oshima, 1987).

DPR has detected alachlor degradate residues in 29 wells in six counties (Table 2). Twenty of these detections meet the adjacent section criteria. All but one of these adjacent wells is located in areas near alachlor use. Other factors contribute to the likelihood that these residues are from legal agricultural use are:

1. DPR's ground water monitoring results for alachlor, AESA, and AOXA mirror ground water monitoring studies across the nation. In other states where alachlor is used, AESA and AOXA are often found in ground water while alachlor is not. Alachlor degradates are mobile and persistent which allows them to leach into ground water at higher rates than their parent.

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 alachlor results in AESA and AOXA migrating to ground water in California. This is similar to other areas of the country where alachlor is used; alachlor degradates, not the parent, are frequently detected in ground water.

Detections from 2001 and 2009 in San Joaquin, Solano, and Stanislaus Counties meet DPR's current legal agricultural use determination policy of two or more detections within the same or adjacent one-square mile sections of land and reported use of alachlor in the section and the surrounding area. These detections indicate that alachlor degradates are reaching ground water due to legal agricultural use of alachlor.

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FIGURES

Figure 1. Alachlor use on beans, corn, and all sites from 1990 to 2013 (CDPR, 2015)

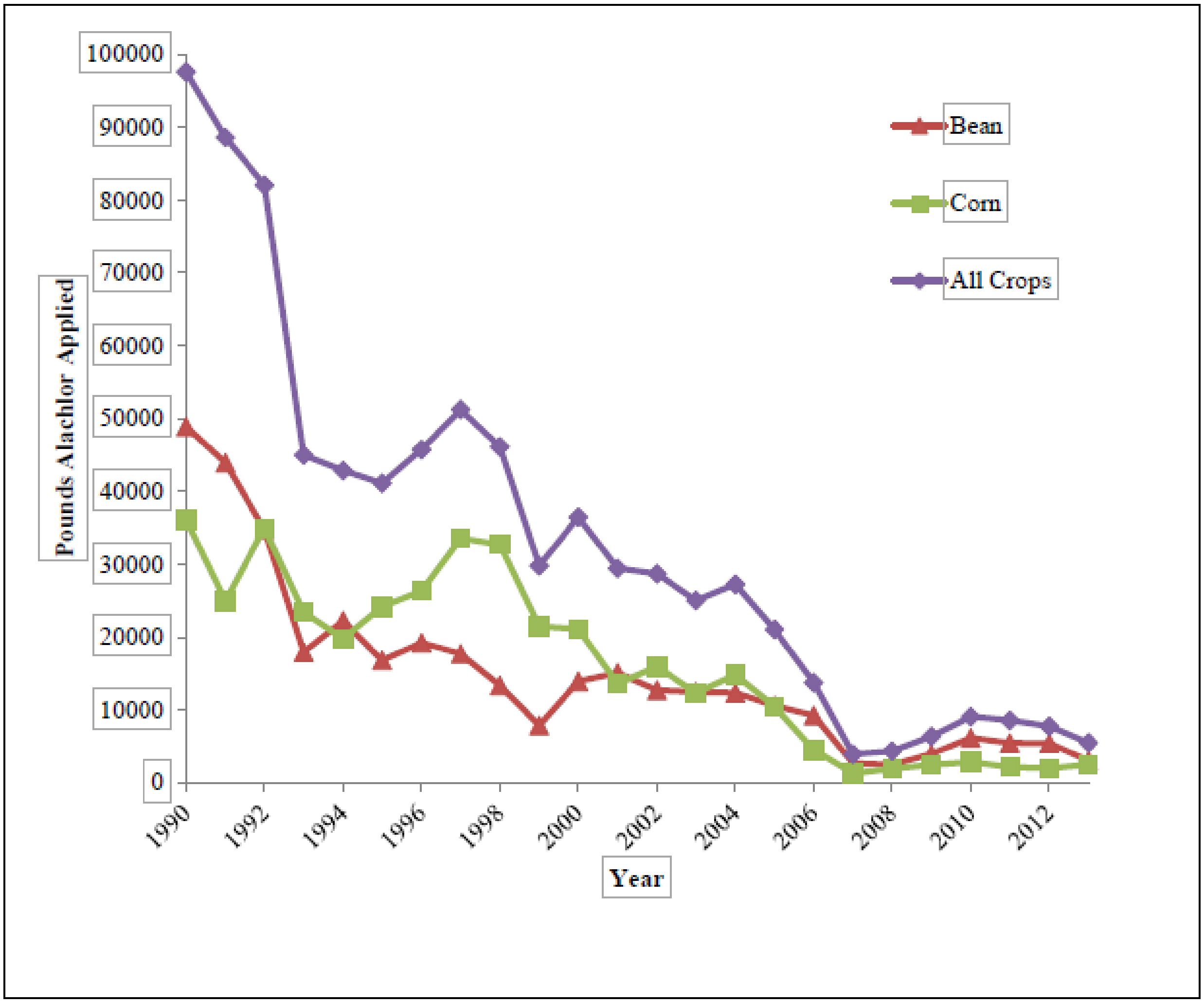


Figure 2. Alachlor use and DPR sampled well locations in San Joaquin County and east of Tracy

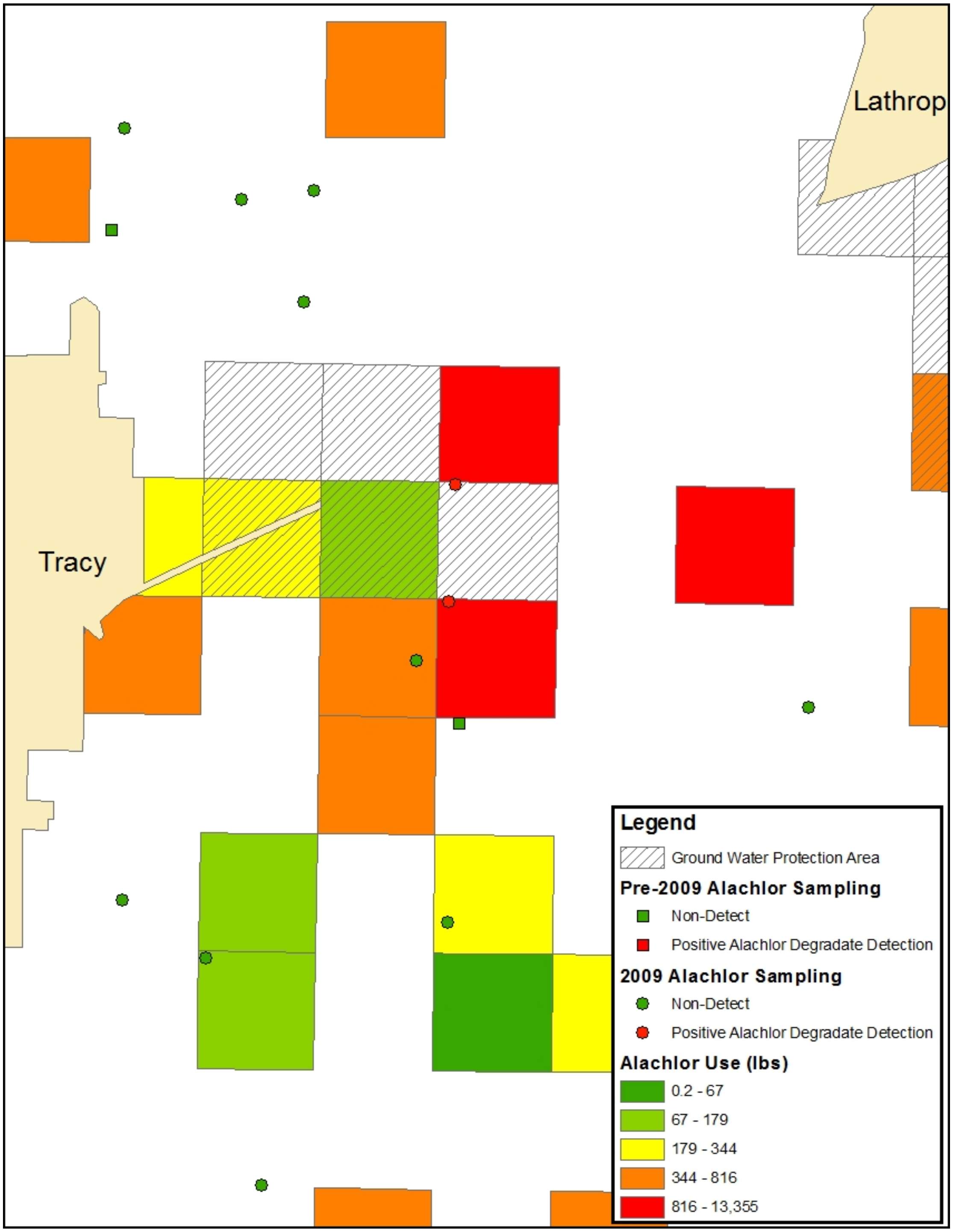


Figure 3. Alachlor use and DPR sampled well locations in Solano County and southeast of Dixon

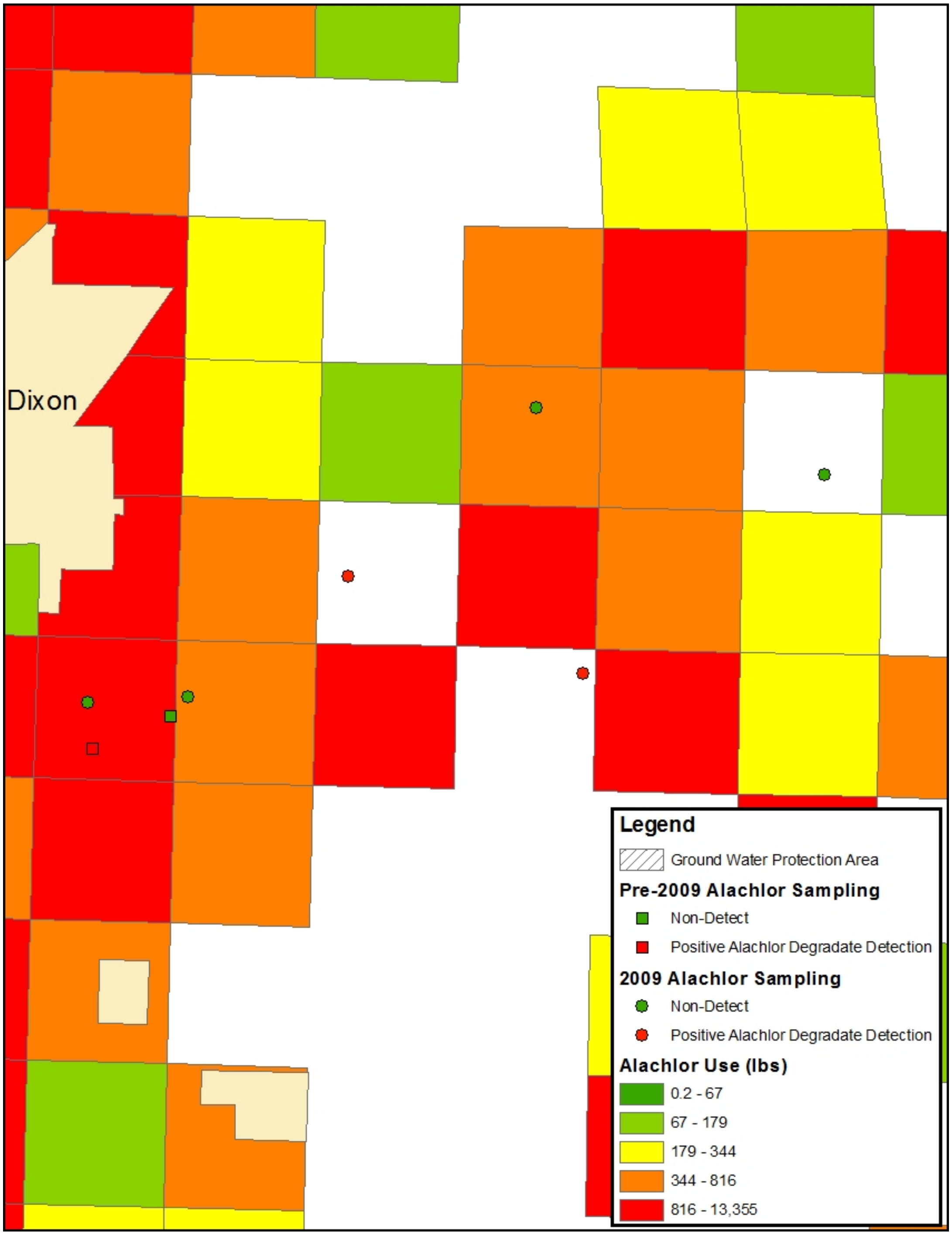


Figure 4. Alachlor use and DPR sampled well locations in Stanislaus County and north of Newman

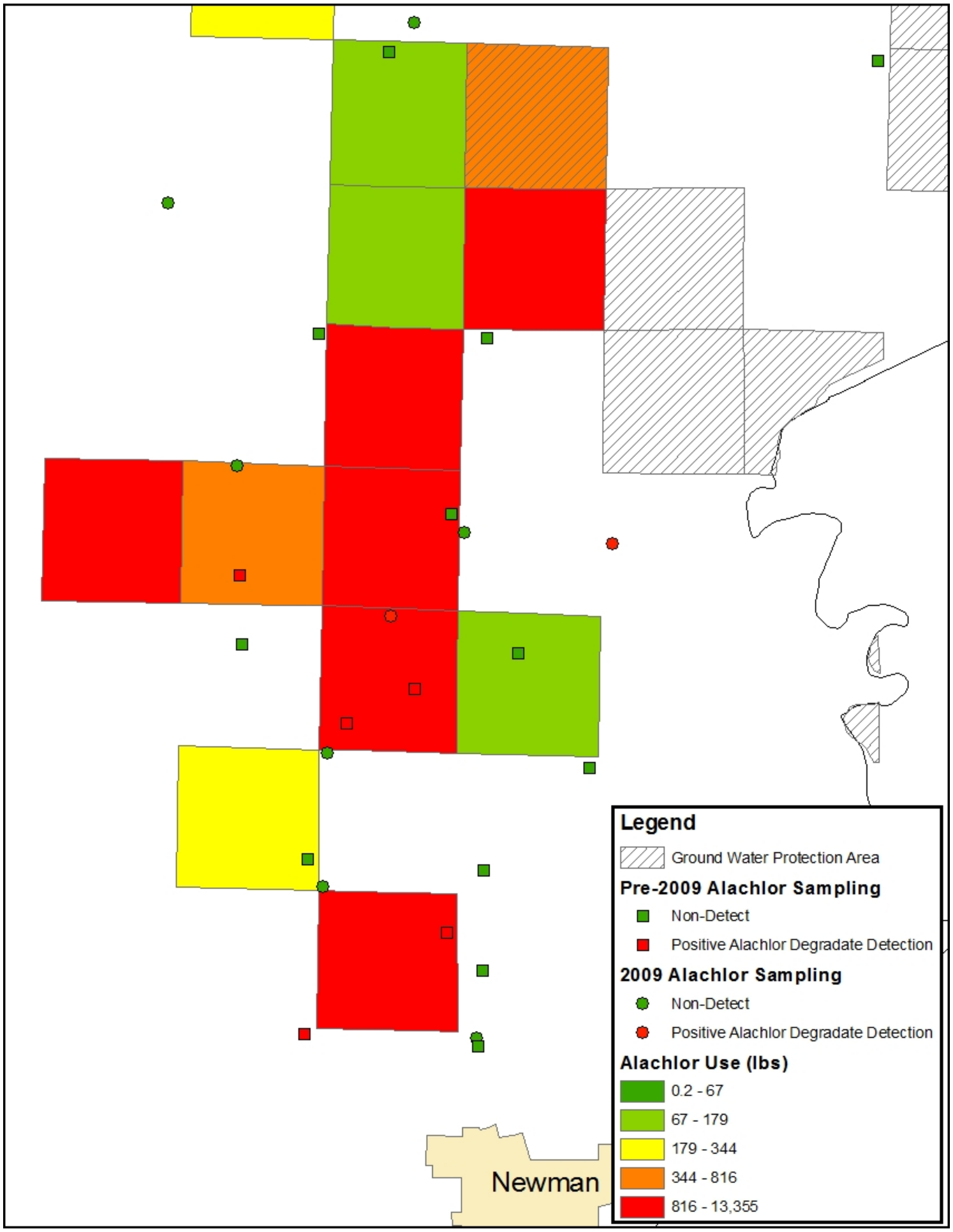
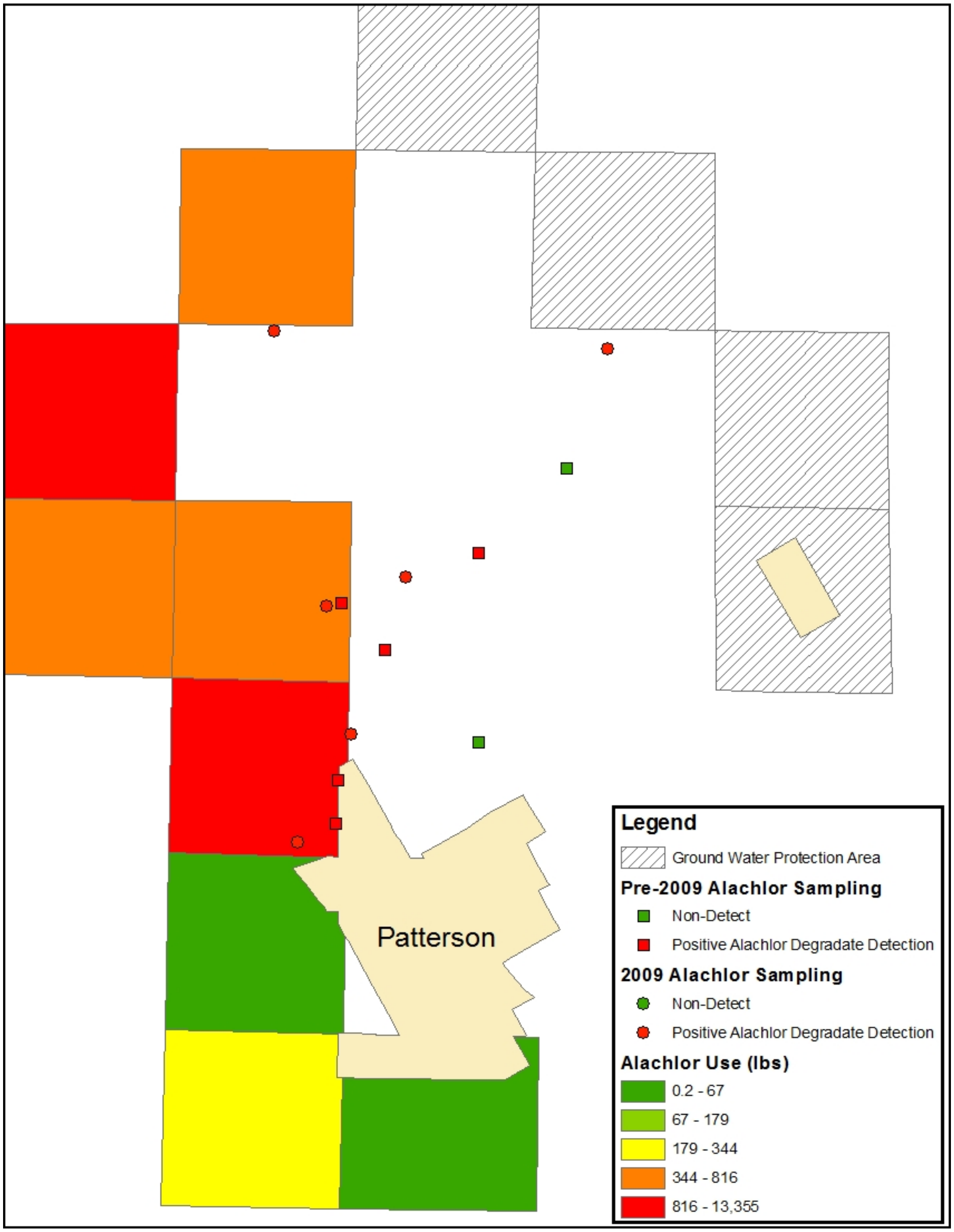


Figure 5. Alachlor use and DPR sampled well locations in Stanislaus County and north of Patterson



TABLES

Table 1. Total pounds of alachlor used from 1990 to 2013 and alachlor sampling results statewide and top ten counties

Total Lbs Applied By Location[a]			Total Lbs Applied by Crop		DPR Sampling	
			Corn (all)	Beans (all)	Number of Wells	Confirmed Degradate Detections
Statewide		797,205	385,085	358,189	253	29
County	**Rank[b]**					
Ventura	1	133,298	20,061	110,536	2	0
Fresno	2	130,878	118,439	11,298	9	0
Santa Barbara	3	106,021	16,074	88,141	0	0
Solano	4	96,434	52,838	32,523	24	4
Yolo	5	59,207	47,631	3,291	7	1
San Joaquin	6	37,954	20,096	17,498	36	3
Glenn[c]	7	32,517	18,929	7,376	33	0
Stanislaus	8	29,056	797	28,259	54	19
Sacramento	9	27,665	27,518	0	14	1
Monterey	10	27,045	4,447	22,561	0	0
Kings[d]	23	2,736	0	60	17	1

a. Pesticide Use Report Data (CDPR, 2015).
b. County ranks based on total alachlor usage statewide.
c. Sampling occurred in late 1980s before degradates were added to the analytical method.
d. Majority of use on cotton.

Table 2. Alachlor degradate sampling results and pesticide use information for areas where verified alachlor degradate residues has been detected

County	Location[a]	Number of Wells Sampled	Alachlor Degradate Positive Wells[b]				Alachlor Use (lbs)[c]	
			Number of Positive Wells	Highest Conc (ppb)	First Year Detected	Last Year Section Sampled	In Section	9 Section[d]
Kings	M19S22E30	1	1	0.053	2009	2009	0	201
Sacramento	M05N05E01	1	1	0.058	2001	2001	0	0
San Joaquin	M01N08E30	1	1	0.764	2009	2009	0	283
San Joaquin	M02S06E19	1	1	0.867	2009	2009	0	2,572
San Joaquin	M02S06E30	1	1	0.726	2009	2009	958	2,280
Solano	M06N01E17	1	1	1.0	2009	2009	2,265	8,251
Solano	M07N01E25	3	1	0.29	2001	2009	1,559	7,464
Solano	M07N02E20	1	1	0.129	2009	2009	0	4,905
Solano	M07N02E28	1	1	0.39	2009	2009	0	4,747
Stanislaus	M04S11E29	2	1	0.077	2004	2004	0	0
Stanislaus	M05S07E12	1	1	0.09	2009	2009	0	2,369
Stanislaus	M05S07E13[e]	1	1	0.648	2001	2009	371	3,917
Stanislaus	M05S07E24	4	4	1.31	2001	2009	1,987	2,757
Stanislaus	M05S08E08	2	1	0.2	2009	2009	0	0
Stanislaus	M05S08E18	3	3	0.688	2001	2009	0	2,358
Stanislaus	M05S09E36	1	1	0.91	2009	2009	0	0
Stanislaus	M06S08E26	2	1	0.05	2001	2009	494	4,677
Stanislaus	M06S08E36	3	3	0.621	2001	2009	1,089	2,972
Stanislaus	M06S09E29	1	1	0.78	2009	2009	0	179
Stanislaus	M07S08E12	1	1	0.051	2001	2001	1,009	1,222
Stanislaus	M07S08E14	1	1	0.479	2001	2001	0	1,009
Yolo	M09N01E17	1	1	0.05	2001	2001	0	5,237

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 an alachlor degradate concentration above the reporting limit.
c. Alachlor use totals are given for one of three periods, 1990-2000, 1990-2003 and 1990-2008, based on the year of the first detection in the section. The period used was selected to represent the alachlor use prior to the first reported alachlor degradate detection. Rights-of-way use is reported at the county level and is not included here.
d. Total alachlor use in the section where the positive well is located and the surrounding 8 sections.
e. Same well sampled in both 2001 and 2009; positive for alachlor degradates in both sampling events.