Study GW 09: Ground Water Protection List Monitoring for Metolachlor and Alachlor

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ABSTRACT

Metolachlor, primarily used on beans, corn, cotton, and processing tomatoes, is a preemergent herbicide on the Department of Pesticide Regulation's (DPR's) Ground Water Protection List (GWPL). Pesticides on the GWPL have the potential to contaminate ground water based on their physical-chemical properties and application methods. DPR annually monitors for pesticides on the GWPL to determine if they have migrated to ground water; metolachlor's increased, heavy use on processing tomatoes since 2000, in the form of s-metolachlor, made it a candidate for monitoring. Alachlor was also included for monitoring due to previous detections of its degradates in Californian ground water.

From April to December 2009, DPR sampled sixty-eight wells in Kings, Sacramento, San Joaquin, Solano, Stanislaus, and Yolo counties for metolachlor, alachlor, and their respective ethanesulfonic acid and oxanilic acid degradates. Metolachlor and alachlor were not detected in any sample. Metolachlor ethanesulfonic acid (MESA) and metolachlor oxanilic acid (MOXA) were detected in 33 wells (49%) and 12 wells (18%), respectively. MESA concentrations ranged from 0.05 to 2.84 parts per billion (ppb), and MOXA concentrations ranged from 0.05 to 0.53 ppb. Alachlor ethanesulfonic acid (AESA) and alachlor oxanilic acid (AOXA) were detected in 16 wells (23%) and 1 well (2%). Most of the AESA detections occurred in the same wells as the MESA detections. Concentrations of AESA ranged from 0.05 to 1.04 ppb, and the one AOXA detection was 0.06 ppb. While detections of the alachlor and metolachlor degradates continue, the amounts detected are low and, based on current information, do not constitute a significant human health risk from drinking water intake.

Metolachlor and alachlor are mainly used in crop production; the subsequent detection of their degradates in ground water are likely from agricultural use. Metolachlor use shifted from corn, cotton, and beans to processing tomatoes when it was supplanted by s-metolachlor, a resolved isomer mix of metolachlor. Alachlor use has decreased due to the increased planting of Roundup Ready™ corn and large decreases in planted bean acreage. Downward movement of metolachlor and alachlor compounds to ground water might be mitigated by future changes in use patterns and irrigation methods.

As part of our continuous evaluation of registered pesticide products, ground water samples were also analyzed for atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, simazine, tebuthiuron, and several of their degradates. Continued monitoring for these pesticides allows DPR to assess the effectiveness of our ground water protection program, identify new ground water protection areas (GWPAs), and determine if further regulatory action is needed. These pesticides or their degradates were found in 14 wells (20%), with concentrations ranging from 0.052 ppb to 0.302 ppb. Residues of atrazine, simazine, diuron, hexazinone, tebuthiuron metabolite 104, desmethylnorflurazon (DSMN), deethylatrazine (DEA), deisopropylatrazine (ACET), and didealkylated triazine (DACT) were detected. Eight of the fourteen wells were located outside of a GWPA; DPR is evaluating this data and is considering adding these sections to the list of GWPAs.

INTRODUCTION

Selecting Pesticides for Monitoring

DPR monitors for pesticides on the GWPL (Title 3, California Code of Regulations (3 CCR) section 6800[b]) in areas where they are used to determine if their agricultural use is causing them to migrate to ground water (Food and Agricultural Code [FAC] section 13148). Pesticides are placed on the GWPL if they are mobile, persistent, and are applied directly to soil or require rain or irrigation soon after application. DPR uses mobility, persistence and application data to rank each GWPL pesticide's relative threat to ground water and uses this ranking system to prioritize monitoring activities. Since 1990, DPR has sampled over 1200 unique wells for more than 80 pesticides and pesticide breakdown products as part of GWPL monitoring.

Metolachlor was selected for monitoring during fiscal year 2008─2009 partially based on its historical use on corn and beans and its increasing use in processing tomatoes. Metolachlor is a preemergent, chloroacetamide herbicide that controls 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 1991 to 2010, metolachlor was used on 80 different crops; the top five crops with the highest reported use in that time period were (in descending order): processing tomatoes, cotton, corn, beans, and safflower (Table 1). Since 2000, with the introduction of the resolved isomer mix called s-metolachlor, metolachlor/ s-metolachlor use increased to an all-time high in 2004; this post-2000 increase is driven mainly by s-metolachlor use on processing tomatoes (Figure 1). Currently, s-metolachlor is one of the top pesticides, by the number of acres treated, used on processing tomatoes in California (CDPR, 2012a).

Metolachlor and s-metolachlor are two related active ingredients (A.I.s). Metolachlor is a racemic mixture composed of equal parts of two R- and two S-stereoisomers. The S-isomers have the majority of the herbicidal activity (Muller et al., 2001). Starting in 1999, the registrant released s-metolachlor into the market, supplanting their metolachlor products. S-metolachlor is a resolved isomer mix composed of mainly the S-isomers. Thus, metolachlor and s-metolachlor are composed of the same isomers, just in different proportions. Both metolachlor and s-metolachlor are on the GWPL. In this study, metolachlor and s-metolachlor are used interchangeably and synonymously as they have similar environmental fates, use patterns, and are indistinguishable from each other in our analytical method. S-metolachlor is mainly discussed in the context of use patterns as it drives most of the metolachlor/s-metolachlor use after 2000.

Besides its heavy use, metolachlor also has physical-chemical characteristics that facilitate its potential downward movement to ground water (Rivard, 2003), hence its classification as a GWPL pesticide. Metolachlor is moderately persistent with a field dissipation half-life of 114 days and a hydrolysis half-life >200 days. Metolachlor is potentially mobile: it has high water solubility (530 ppm) and low soil adsorption (K_{oc}= 200 cm^3/g). The principal routes of metolachlor degradation are photolysis and microbial soil metabolism. The two major degradation products of metolachlor, MESA and MOXA, can persist in agricultural soils for at least three years after a metolachlor application (Phillips et al., 1999).

Alachlor was also monitored in this study because it is analytically similar to metolachlor and is used on some of the same crops as metolachlor. Alachlor is a preemergent, chloroacetamide herbicide that controls a wide variety of broadleaf and annual grass species in agricultural crops. In California, from 1991 to 2010, although alachlor was used on 33 different crops, corn and beans accounted for ~95% of the total reported use (Table 1). Alachlor use has been declining over the years (Figure 2) and did not play a role in sample site selection. However, like metolachlor, alachlor is a GWPL pesticide that has the potential to contaminate ground water.

The U.S. Environmental Protection Agency's(U.S. EPA's) Registration 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." Like metolachlor, the ethanesulfonic and oxanilic acid degradates are the principal breakdown products and are more persistent in soil than alachlor itself (U.S. EPA, 1998).

The selected wells were also sampled for atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, simazine, tebuthiuron, and several of their degradates, including DEA, ACET, DACT, DSMN, and tebuthiuron metabolites 104, 106, 107, and 108. DPR monitors for these pesticides to better understand their behavior in the environment and to determine if they are polluting ground water due to their legal agricultural uses. DPR regulates the use of atrazine, bromacil, diuron, norflurazon, prometon and simazine in areas classified as GWPAs. GWPAs are considered to be vulnerable to ground water contamination by pesticides due to soil conditions, shallow depths to ground water (less than 70 feet), and/or the presence of verified pesticide detections in ground water (Troiano et al., 2000). In 2011, due to previous detections of hexazinone in ground water, DPR's Director, in concurrence with the findings of the Subcommittee of the Pesticide Registration and Evaluation Committee, committed to further monitoring of hexazinone as an appropriate approach to protect against pollution of the ground waters of the state (Reardon, 2011). Similarly, tebuthiuron has also been detected to ground water by DPR. However, more monitoring is necessary to determine if tebuthiuron detections arise from legal agricultural use (Dias, 2011). Continued monitoring for these pesticides allows DPR to assess the effectiveness of our ground water protection program, identify new GWPAs, and determine if additional regulatory action is needed.

Prior Metolachlor/Alachlor Monitoring Studies

Ground water contamination by metolachlor and alachlor has been investigated in many states, including Iowa, Georgia, Wisconsin, Nebraska, and Minnesota. In Iowan ground water, metolachlor and alachlor had detection frequencies of 8% and 1%, respectively, while MESA, MOXA, AESA, and AOXA had detection frequencies of 60%, 25%, 50% and 20%, respectively (Kalkhoff et al., 1998). The Georgia investigation detected metolachlor and alachlor in 7% and 0% of the wells sampled, respectively, while their degradates were found in two-thirds of all wells sampled (Pittman, 2003). Wisconsin sampling of private, municipal, and monitoring wells

detected metolachlor and alachlor in 15% and 0% of the wells sampled, respectively, whereas AESA and MESA were detected in approximately 80% of the wells (Rheineck, 2001). Researchers in Nebraska detected metolachlor, MESA and MOXA in 57%, 99% and 35% of the samples, respectively (Spalding et al., 2003). The concentrations of MESA were generally higher than either MOXA or metolachlor. A similar pattern in detection frequencies and concentrations was observed with alachlor and alachlor degradates in the same Nebraska study. In 2010, the Minnesota Department of Agriculture (MDA), as part of their annual ground water monitoring, has reported detection frequencies for metolachlor, alachlor, MESA, MOXA, AESA, and AOXA as 14%, 1%, 84%, 40%, 46%, and 2%, respectively (MDA, 2010). Overall, these studies show that metolachlor and alachlor degradates, especially the ethanesulfonic acid degradates, are detected at higher frequencies and concentrations than their respective parent compounds.

Metolachlor and alachlor have also been monitored in Californian ground water in prior years. In 2001, DPR monitored for alachlor, metolachlor and the ethanesulfonic and oxanilic acid degradates of each using the same analytical method as in this study (Weaver, 2002). Although DPR did not detect the parent pesticides, MESA, MOXA, AESA, and AOXA were detected in 32%, 11%, 19%, and 1% of the sampled wells, respectively, with concentrations that ranged from 0.051 ppb to 24 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 metolachlor and 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, metolachlor was detected in 38 wells in 18 counties and alachlor was detected in only one well (SWRCB, 2012). The samples had concentrations of metolachlor ranging from 0.002 to 0.16 ppb and an alachlor concentration of 0.004 ppb. The USGS did not sample for metolachlor or alachlor degradates in this study. DPR is evaluating the GAMA data to determine if follow-up ground water monitoring for metolachlor is needed.

Although these studies throughout the U.S. cannot be compared directly due to different reporting limits (Barbash et al., 2001), they all generally indicate that metolachlor and alachlor degradates are detected more frequently and at higher concentrations than their respective parent pesticides. These detections of metolachlor, alachlor, and their degradates contributed to DPR's decision to monitor again for metolachlor and alachlor in ground water.

MATERIALS AND METHODS

Well Selection

DPR chose sampling locations based on the pounds of metolachlor/s-metolachlor applied in one-square mile areas referred to as "sections" in the Public Lands Survey System (CDPR, 2012a), soil vulnerability, depth to ground water, and well availability. Pesticide use reporting data from 1996 to 2003 was used because the median ground water recharge time in coarse soils is estimated to be six to seven years (Spurlock et. al., 2000). This time interval also captures both

metolachlor and s-metolachlor use patterns as it spans the transition period between the two related A.I.s. Sections assigned the highest sampling priority were located in counties with high cumulative metolachlor/s-metolachlor use (Table 2), were classified as GWPAs, and had wells available for sampling. High-use sections that were located outside of GWPAs were prioritized based on depth to ground water: those with shallowest ground water were assigned the highest sampling priority.

It is DPR's standard procedure to sample at least one well in each selected section, according to procedures in SOP FSWA006.01 (Nordmark, 2008). Shallow domestic wells were targeted for sampling because they are assumed to have the highest potential for contamination by anthropogenic sources, including agricultural pesticide applications (Troiano et. al., 2001) If there were no suitable wells available in the target section, as per SOP FSWA006.01, a well within approximately 0.2 miles of the section could be sampled. Samples were collected using the methods described in SOP FSWA001.02 (Nordmark, 2011). If available, DPR obtained information regarding the well construction and depth from the well owner.

Analytical Methods and Quality Control

The California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry analyzed two primary samples from each well. One primary sample was analyzed for metolachlor, alachlor, and their respective ethanesulfonic acid and oxanilic acid degradates (CDFA, 2001). Metolachlor and s-metolachlor are analytically indistinguishable using the CDFA method; any detected residues are reported as metolachlor. The other primary sample was analyzed for atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, simazine, tebuthiuron, and several of their degradates, including DEA, ACET, DACT, DSMN, and tebuthiuron metabolites 104, 106, 107, and 108. (CDFA, 2009). Both of these methods are considered unequivocal and valid as per FAC section 13149(d) (Spurlock, 2001 and Fattah, 2008). Pesticide detections in ground water are only considered valid for the purposes of GWPL monitoring if the analytical method unequivocally identifies the pesticide or if the detection is verified by a second laboratory or method.

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 de-ionized water (field blanks) were collected at the same time as the field samples and were analyzed, as necessary, to confirm the validity of positive results. The reporting limit for all analytes is 0.05 ppb. The reporting limit is the smallest amount that can be reliably detected and is set by the testing laboratory for each analyte.

RESULTS

A total of 68 wells were sampled in 64 sections in Kings, Sacramento, San Joaquin, Solano, Stanislaus, and Yolo counties (Table 3). Although Fresno County had the highest overall use of metolachlor/s-metolachlor (Table 2), DPR did not sample in this county because the sections with metolachlor/s-metolachlor use were clustered in a portion of the county with a lack of available wells. The majority of sampled sections with high metolachlor/s-metolachlor use were located outside of GWPAs; only 11 of the 64 sampled sections were classified as GWPAs. The average depth to ground water in the sampled sections was 40 feet and the average

metolachlor/s-metolachlor use was 1300 pounds (Table 3). Metolachlor/s-metolachlor was applied chiefly to corn, beans, and processing tomatoes in the sampled sections. Alachlor use was very low in the sampled sections and was not used as a factor in site selection; only 3 sections had any alachlor use since 1996 (Table 3). All submitted field blanks resulted in nondetects, indicating no contamination during the sampling process.

Metolachlor Analytical Results

Figures 3 to 6 show that 81% of sampled wells are outside of GWPAs but in fine textured, runoff-prone soils (Troiano et al., 2000 and Table 3). Metolachlor was not detected in any sampled well (Appendices I and II). MESA and MOXA were detected in 33 wells (49%) and 12 wells (18%), respectively (Table 4). MESA ranged from 0.05 to 2.84 ppb, and MOXA ranged from 0.05 to 0.53 ppb (Table 4). MOXA detections always had a corresponding MESA detection.

Alachlor Analytical Results

Figures 7 to 10 show that 95% of the sampled sections had no alachlor use since 1996. Alachlor was not detected in any sampled well (Appendices I and II). AESA and AOXA were detected in 16 wells (23%) and 1 well (2%), respectively (Table 4). Fourteen out of the sixteen AESA detections occurred in the same wells as the MESA detections. Concentrations of AESA ranged from 0.05 to 1.04 ppb; the one AOXA detection was 0.06 ppb (Table 4).

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

Fourteen wells (20%) sampled positive for previously detected pesticides (Table 4). Residues of atrazine, simazine, diuron, hexazinone, tebuthiuron metabolite 104, DSMN, DEA, ACET, and DACT were found in these wells, with DACT being detected the most in 7 of the 14 wells (Table 5). Eight of the fourteen wells were located outside of a GWPA; DPR is evaluating this data and is considering adding these sections to the list of GWPAs. These detections ranged from 0.052 ppb (Diuron) to 0.302 ppb (ACET) (Appendix I). Six of these fourteen wells had no corresponding metolachlor degradate detection.

Metolachlor/S-metolachlor Use Patterns

Metolachlor use declined year-over-year by 13% in 2000 and 20% in 2001 due to a shift from racemic metolachlor (a 50:50 mix of both R- and S-isomers) to a new A.I. called s-metolachlor (an 88:12 isomer mix favoring the S-isomer) (CDPR, 2012a). S-metolachlor is considered a "reduced-risk pesticide" by the U.S. EPA because it is efficacious at lower rates than the previously registered formulation. Following the first applications of s-metolachlor in 1999, average application rates of metolachlor/s-metolachlor decreased from 2.0 pounds/acre to 1.5 pounds /acre (CDPR, 2012a). Since 2007, however, metolachlor use has been increasing with the registration of generic metolachlor products by other manufacturers; the original registrant cancelled their metolachlor products in 1999 during the switch to s-metolachlor.

Historically, metolachlor was primarily used on corn, beans, and cotton, although this use pattern has changed since the registration of s-metolachlor. When s-metolachlor, the successor to metolachlor, was first registered in 1998, processing tomatoes were added to the label as a Section 18 emergency exemption for nutsedge control (CDPR, 2012b). Emergency exemptions are granted by the U.S. EPA to prevent catastrophic crop loss. S-metolachlor suppresses yellow

nutsedge and nightshade, difficult weeds to control in tomato fields (UCIPM, 2010). Since processing tomatoes were added to the label, s-metolachlor use on processing tomatoes is higher than the traditional high-use crops like beans, corn, and cotton (Figure 1). This use is expected to be sustained as processing tomatoes are an important crop; California accounts for 90% and 35% of processing tomato production in the U.S. and the world, respectively (Hartz, 2008).

The decreases of metolachlor/s-metolachlor use in corn, beans, and cotton can be attributed to factors such as a decline in acres planted and a shift to postemergence weed control. Cotton herbicide use in general has declined as a consequence of fewer acres of cotton being planted; 667,000 acres were planted in 2005, as opposed to 190,000 acres planted in 2009 (CCGGA, 2012). Herbicide use on beans follows a similar trend when, in 2001, there was a 25% decrease of acres planted for beans that has been sustained ever since (USDA, 2010). Metolachlor/ s-metolachlor decreases in corn are due to the statewide trend toward postemergence weed control from increased Roundup Ready™ corn use (Lanini et al., 2006). As a result, the number one herbicide on corn, in terms of the amount used, is glyphosate, the A.I. in Roundup™ products (CDPR, 2012a).

Alachlor Use Patterns

Alachlor use has been steadily declining over the years in California and nationally (Figure 2; USDA, 2010). National declines in alachlor are partially as a result of its replacement by acetochlor, another chloroacetamide herbicide (Rheineck, 2001). However, acetochlor has not been registered for use in California. In California, alachlor use trends are tied to the cultural and economic characteristics of its two main crops: corn and beans. As noted in the metolachlor/ s-metolachlor use section above, corn growers have moved away from preemergent herbicides like alachlor to postemergent herbicides like glyphosate. Unlike metolachlor/s-metolachlor, 44% of alachlor is applied to beans versus metolachlor/s-metolachlor's 18% on beans (Table 1). If bean production shifts, then one would expect alachlor use patterns to shift as well. The amount of beans planted in California has been declining over the years (USDA, 2010), facilitating the similar decreases in the alachlor use, most notably in 1993 (Figure 2).

DISCUSSION

Pesticide Use and Ground Water Detection Frequencies

In this study, metolachlor degradates were detected in ground water in areas where metolachlor/s-metolachlor has been used to produce agricultural crops. Only three sections had no reported metolachlor/s-metolachlor use from 1996 to 2008 (Table 3); they were chosen because of well availability and proximity to sections with metolachlor/s-metolachlor use (Figures 3-6). Overall, metolachlor degradates were detected in areas of high use at a 49% detection frequency.

Other studies have reported a link between metolachlor use and its detection in ground water. Barbash et al. (1999), in a review of national ground water studies, stated that "the spatial patterns of metolachlor detection across the Nation during the NAWQA studies align relatively closely with the geographic distribution of its agricultural use, consistent with the highly significant correlation noted earlier between its detection frequency and the intensity of its application in agricultural areas". Eckhardt et al. (2001) noticed a similar link between land use

and metolachlor detections in ground water: the more agricultural land surrounding a well, the higher the concentrations of metolachlor detected. The extremely high use of metolachlor/ s-metolachlor in the Midwest might explain the increased detection frequencies of metolachlor and its degradates in that area when compared to California.

Metolachlor/s-metolachlor is heavily used in the Midwest, particularly on corn, which may be driving metolachlor detections in that region. States like Nebraska, Iowa, Illinois, Indiana, Minnesota and Ohio produce nearly 70% of the corn grown in the U.S. (Pearson, 2011). In 2010, 19.1 million pounds of s-metolachlor was applied to ***corn only*** in the Midwest, with 2.4 million pounds applied in Iowa alone (USDA, 2010). In contrast, 314,000 pounds of metolachlor/s-metolachlor was applied to ***all crops*** in California in 2010 (CDPR, 2012a). Figure 11 illustrates the average annual use rate of s-metolachlor in the United States (USGS, 2002). Consistent with the cumulative use totals, much more s-metolachlor is being applied in the Midwest than in California. However, if metolachlor/s-metolachlor use increases, or becomes more widespread, additional monitoring is recommended. Alachlor does not pose a similar problem as its use is extremely low and declining; 95% of the sampled wells had no alachlor applications in their sections since 1996 (Table 3; Figure 2).

Detection Limits and Ground Water Detection Frequencies

Analytical reporting limits can influence pesticide detection frequencies. Detection frequency is inversely related to reporting limits. Studies with lower reporting limits often have greater detection frequencies than studies with higher reporting limits (Barbash et al., 2001). This issue of analytical sensitivity may partially explain the lack of metolachlor and alachlor detections in this study. In California, the GAMA Priority Basin Project has detected both metolachlor and alachlor at very low concentrations. The GAMA reporting limits for metolachlor vary between 0.006 ppb and 0.013 ppb, while the alachlor analysis has a reporting limit of 0.008 ppb (SWRCB, 2012). On the other hand, DPR has a reporting limit of 0.05 ppb for both pesticides. Consequently, the detection frequencies of DPR and the GAMA program cannot be meaningfully compared without taking into account their different reporting limits.

A common method to adjust for differing report limits is to censor the data from all the studies with a common value (Barbash et al., 2001). When applying a reporting limit of 0.05 ppb, the reporting limit for this study, to the GAMA data, the detection frequencies of metolachlor and alachlor change. Under the new report limit, there are no alachlor detections and only one metolachlor detection, at 0.16 ppb, located in San Bernardino County. San Bernardino County was not targeted in this study due to low cumulative use in that county; San Bernardino was ranked number 30 according to cumulative use (Table 2). DPR is evaluating the GAMA monitoring data to determine if follow-up ground water sampling for metolachlor in this county in needed. Even though DPR's and GAMA's ground water monitoring programs are different, the results of both programs show that metolachlor, alachlor, and their degradates appear to be behaving similarly in California as elsewhere in the U.S.

Mobility and Persistence of Metolachlor/Alachlor Degradates

Metolachlor and alachlor break down, mainly via soil microbial metabolism through different enzymatic pathways, into ethanesulfonic and oxanilic acid degradates (Rivard, 2003; U.S. EPA, 1998). These degradates are more likely to be found in ground water than their parent

compounds. This discrepancy in detection frequencies between parent and degradate may be partially attributed to chemistry. The metolachlor and alachlor degradates have greater mobility than their parents; the removal and substitution of the chlorine atom increases the polarity of the degradates and hence their water solubility (Thurman et al., 1996). The high detection frequencies of the ethanesulfonic acid degradates may be attributed to their dissipation rates. MOXA degrades twice as fast when compared to MESA degradation rates (Hancock et al., 2008) and this may explain why MESA is detected more frequently than MOXA. Another study has suggested that AESA is the dominate alachlor degradate and resides in ground water for years even when alachlor use has discontinued (Steele et al., 2008). The persistence and mobility of metolachlor and alachlor degradates contributes to their high detection frequencies in ground water.

Irrigation Influencing Pesticide Movement to Ground Water

In order to contaminate ground water, pesticides must be applied in a way that facilitates off-site movement in the form of surface run-off or leaching. Often, certain irrigation practices can lead to this off-site movement. Metolachlor/s-metolachlor and alachlor have been used extensively in agriculture, mostly in beans and corn. These two crops are primarily irrigated through furrow irrigation (Long, 2010; Frate, 2008). When irrigation water is applied to fields, especially by furrow irrigation, percolating water can be created and downward movement of pesticides can occur (Troiano et al., 1993). Metolachlor/s-metolachlor and alachlor, when used on a furrow irrigated crop, may have opportunity to reach ground water supplies. If pesticides are applied to crops with irrigation systems that generate little percolating or run-off water, then ground water contamination may be reduced.

Mitigating Movement of Metolachlor Residues to Ground Water

S-metolachlor's emergent and sustained use on tomatoes, and the potential impact to ground water that may result, might be mitigated by the use of drip irrigation. Drip irrigation produces less deep percolation than furrow irrigation (Burt, 2006), and less deep percolation means less water available for pesticide leaching. Generally, the longer a pesticide is kept in the microbially active root zone the more time it has to degrade; a pesticide degrades slowly when it moves past the root zone (van Es, 1990). Drip irrigation is attractive in processing tomatoes because it generally increases yields and facilitates efficient water use (Hartz, 2008). The prevalence of drip irrigation on processing tomatoes is greater than 20% and increasing each year (Hartz, 2008). S-metolachlor use on tomatoes may not impact ground water resources if metolachlor residues are not permitted to leach due to a reduction or lack of water drainage.

Limiting percolating water generated by furrow irrigation in beans and corn is possible but not without its challenges, especially in clayey soils. Wider furrow beds, shorter field lengths, alternate row irrigation, and conversion to sprinkler irrigation have all been advanced as methods to increase water use efficiency in beans and corn (Long, 2010; Frate, 2008). Wider furrow beds and alternate row irrigation have issues in heavy soil; it is often difficult to adequately irrigate without waterlogging part of the field or create cracking across the beds. Shortening field lengths also carry the disadvantage of potentially increasing surface runoff and creating another avenue for pesticide off-site movement. Switching to sprinklers can be problematic due to increased production costs and foliar disease pressures. Modifying furrow irrigation for increased water

use efficiency must be tailored to site-specific characteristics, like soil type, and the economic factors of crop production.

Metolachlor/Alachlor Degradate Toxicity

The detected metolachlor and alachlor degradates do not constitute a significant human health risk at the concentrations measured (Appendix III). The degradate concentrations are below the toxicity benchmarks for their respective parent compounds and the data suggest they are 5 to10 times less toxic (Appendix III). Unless the metolachlor and alachlor degradates are detected at higher concentrations, it may be difficult to assert that they pose a threat to public health given the current toxicological information on these compounds.

CONCLUSION

Metolachlor, alachlor, and their degradates are mobile and persistent compounds that have been found in ground water, particularly in the Mid-Western U.S., in areas of high use. Metolachlor and alachlor were selected for well monitoring as part of DPR's continuing evaluation of pesticide's ability to contaminate ground water. From April to December 2009, DPR sampled sixty-eight wells in Kings, Sacramento, San Joaquin, Solano, Stanislaus, and Yolo counties for metolachlor, alachlor and other herbicides previously detected in ground water. Metolachlor or alachlor were not found in any sample. However, 49% and 23% of the sampled wells in areas of high metolachlor/s-metolachlor use had detections of metolachlor and alachlor degradates, respectively. These results are similar to detections reported in other monitoring studies throughout the U.S. and California: metolachlor and alachlor degradates are found more frequently than their parent compounds. The agricultural use of metolachlor and alachlor likely resulted in the migration of their degradates to ground water. Downward movement of metolachlor and alachlor compounds to ground water might be mitigated by future changes in use patterns and irrigation methods. While detections of the alachlor and metolachlor degradates continue, the amounts detected are low and, based on current information, do not constitute a significant human health risk from drinking water intake.

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TABLES

Table 1. Top twenty sites, by pounds applied, of metolachlor/s-metolachlor and alachlor for the reporting years of 1991-2010 (CDPR, 2012a). Other sites were omitted for clarity; their combined use represented less than 0.5% of the total use for their respective pesticide.

Site	Pounds Metolachlor/S-metolachlor Applied	Site	Pounds Alachlor Applied
PROCESSING TOMATOES	1,554,710	CORN	342,032
CORN	1,194,502	BEANS	295,113
COTTON	1,165,127	SUNFLOWER	20,001
BEANS	955,869	COTTON	14,981
SAFFLOWER	161,968	OUTDOOR TRANSPLANT	912
POTATO	73,569	CELERY	891
TOMATO	70,501	RIGHTS OF WAY	789
OUTDOOR CUT FLOWER	25,542	SOIL APPLICATION	485
SUNFLOWER	25,287	CANTALOUPE	449
SORGHUM	23,738	PISTACHIO	348
PEPPERS	23,706	SORGHUM	310
SOIL APPLICATION	22,095	PEAS	235
LANDSCAPE MAINTENANCE	14,540	VERTEBRATE PEST CONTROL	209
PEAS	11,536	LIME	155
RIGHTS OF WAY	11,456	PEPPERS	138
WHEAT	10,557	SOYBEANS	87
OUTDOOR CONTAINER	8,667	SPINACH	60
SUGARBEET	6,074	LANDSCAPE MAINTENANCE	51
UNCULTIVATED AG	5,021	OUTDOOR CUT FLOWER	19
ALMOND	2,932	VEGETABLES	9

Table 2. Counties with the highest cumulative use of metolachlor/s-metolachlor for the reporting years of 1996–2003 (CDPR, 2012a). Sampled counties indicated with an asterisk.

County	Pounds Metolachlor/S-metolachlor Applied	County	Pounds Metolachlor/S-metolachlor Applied
Fresno	572,190	Contra Costa	13,285
Kings*	373,273	Riverside	12,863
San Joaquin*	240,546	San Luis Obispo	6,589
Stanislaus*	187,657	Placer	4,023
Merced	124,112	Tehama	3,168
Kern	87,328	Orange	2,321
Tulare	87,195	Imperial	1,828
Sacramento*	72,713	Santa Clara	1,825
Yolo*	71,882	San Diego	1,760
Glenn	60,581	San Benito	1,519
Solano*	57,066	Humboldt	1,422
Colusa	50,649	Yuba	1,004
Sutter	28,933	Ventura	985
Monterey	28,828	Los Angeles	835
Santa Barbara	18,860	San Bernardino	832
Madera	16,905	Del Norte	797
Butte	14,085	Amador	582

Table 3. Sections containing wells sampled during 2009 GWPL monitoring. Pounds of metolachlor/s-metolachlor and alachlor applied in each section are given for reporting years 1996–2003 (CDPR, 2012a). Depth to ground water and soil texture are from Troiano et al. (2000). GWPL detections are for any detected degradate of metolachlor or alachlor.

County	Section	Soil Texture	Depth to ground water (ft)	Pounds of Metolachlor/S-metolachlor applied	Pounds of Alachlor applied	Metolachlor Degradate Detection?	Alachlor Degradate Detection?
Kings	16M18S20E27	Medium Textured	52	1265	0		
Kings	16M18S20E29	Medium Textured	65	1561	0		
Kings	16M18S22E13	Coarse + Pan	73	635	0		
Kings	16M18S22E33	Medium Textured	88	588	0	YES	
Kings	16M19S19E24	Fine + Water Table	27	106	0		
Kings	16M19S21E13	Medium Textured	80	937	0		
Kings	16M19S21E27	Coarse Textured	61	1445	0		
Kings	16M19S22E30	Medium Textured	76	1040	0		YES
Kings	16M19S23E04	Medium Textured	87	0	0		
Sacramento	34M05N05E03[a]	Medium + Pan	58	2650	0		
Sacramento	34M05N06E02	Medium + Pan	88	3583	0		
Sacramento	34M06N05E28	Medium + Pan	73	1673	0		
Sacramento	34M07N07E22	Medium + Pan	115	3393	0		
San Joaquin	39M01N08E30	Fine + Pan	103	719	0	YES	YES
San Joaquin	39M01S05E34	Fine + Water Table	48	845	0		
San Joaquin	39M01S07E07[b]	Coarse Textured	28	5938	0		
San Joaquin	39M01S08E14	Coarse + Pan	92	813	0	YES	
San Joaquin	39M02S05E02[c]	Fine + Water Table	38	1544	0		
San Joaquin	39M02S05E11	Fine + Water Table	25	1851	0		
San Joaquin	39M02S05E25	Fine Textured	28	1275	0		
San Joaquin	39M02S06E19[a]	Fine Textured	31	244	0	YES	YES
San Joaquin	39M02S06E27	Fine + Water Table	10	1821	0	YES	
San Joaquin	39M02S06E30	Fine Textured	31	2687	0	YES	YES
San Joaquin	39M03S05E03	Fine Textured	42	0	0	YES	
San Joaquin	39M03S05E11	Fine Textured	42	708	0		

County	Section	Soil Texture	Depth to ground water (ft)	Pounds of Metolachlor/S-metolachlor applied	Pounds of Alachlor applied	Metolachlor Degradate Detection?	Alachlor Degradate Detection?
San Joaquin	39M03S05E14	Fine Textured	53	1413	0		
San Joaquin	39M03S06E06	Fine + Water Table	24	1610	0		
San Joaquin	39M03S06E08	Fine + Water Table	30	2029	0	YES	
San Joaquin	39M04N05E05	Fine + Water Table	4	259	0		
San Joaquin	39M04N05E35	Medium + Pan	9	2432	0	YES	
San Joaquin	39M04N05E36[b c]	Coarse + Pan	13	952	0	YES	
San Joaquin	39M04N07E03	Medium + Pan	112	1467	0	YES	
San Joaquin	39M04N07E05	Medium + Pan	99	2267	0		
Solano	48M06N01E17	Fine Textured	8	1885	269		YES
Solano	48M06N01E18	Fine Textured	5	1531	0		
Solano	48M07N01E25	Fine Textured	20	418	1559	YES	
Solano	48M07N02E14	Fine Textured	24	548	0	YES	
Solano	48M07N02E16	Fine Textured	27	0	0	YES	
Solano	48M07N02E20	Fine Textured	23	307	0	YES	YES
Solano	48M07N02E28	Fine Textured	26	833	0	YES	YES
Solano	48M07N02E30	Fine Textured	22	1399	0	YES	
Stanislaus	50M02S08E25[b]	Coarse Textured	37	3390	0	YES	
Stanislaus	50M02S08E26[b]	Coarse Textured	36	2447	0		
Stanislaus	50M05S07E12	Medium Textured	59	272	0	YES	YES
Stanislaus	50M05S07E13	Medium Textured	72	407	0	YES	YES
Stanislaus	50M05S07E24[c]	Fine Textured	80	2718	0	YES	YES
Stanislaus	50M05S08E08	Fine Textured	19	754	0	YES	YES
Stanislaus	50M05S08E18	Fine Textured	44	760	0	YES	YES
Stanislaus	50M05S09E14[b]	Very Coarse	14	711	0	YES	
Stanislaus	50M05S09E20[b c]	Coarse Textured	12	723	0		
Stanislaus	50M05S09E36[b]	Very Coarse	9	422	0	YES	YES
Stanislaus	50M05S10E31[b]	Coarse Textured	9	137	0		
Stanislaus	50M06S08E01	Fine + Water Table	12	118	0		

County	Section	Soil Texture	Depth to ground water (ft)	Pounds of Metolachlor/S-metolachlor applied	Pounds of Alachlor applied	Metolachlor Degradate Detection?	Alachlor Degradate Detection?
Stanislaus	50M06S08E15	Fine + Water Table	17	2318	0		
Stanislaus	50M06S08E25	Medium Textured	18	3376	0	YES	
Stanislaus	50M06S08E26	Medium Textured	19	462	0		
Stanislaus	50M06S08E36	Fine Textured	24	3014	0	YES	YES
Stanislaus	50M06S09E29	Fine Textured	16	2546	0	YES	YES
Stanislaus	50M07S08E01	Fine Textured	29	361	0	YES	
Stanislaus	50M07S08E02	Medium Textured	29	76	0	YES	
Stanislaus	50M07S09E18	Fine Textured	29	371	0	YES	
Yolo	57M10N02E04	Fine Textured	24	488	0		
Yolo	57M10N02E08	Medium Textured	40	428	0		
Yolo	57M10N02E12[b]	Coarse Textured	13	219	459	YES	

a. Section is a Runoff GWPA.
b. Section is a Leaching GWPA
c. Section contains two wells. All other sections have one well.

Table 4. Summary results of GW 09 sampling.

	Analyte				
	Metolachlor Degradates		Alachlor Degradates		CDFA Method EM 62.9 Pesticides and Selected Degradates
	MESA	MOXA	AESA	AOXA	
# Positive Wells	33	12	16	1	14
Detection Frequency %	49	18	24	1	21
Maximum Detected Concentration (ppb)	2.84	0.53	1.04	0.06	0.302 (ACET)
Minimum Detected Concentration (ppb)	0.05	0.05	0.05	0.06	0.052(DIURON)

Table 5. Wells with detections of MESA, MOXA, AESA, AOXA and previously detected pesticides summarized by county and analyte. Only detections are reported.

County	Wells Sampled	Wells With Detections												
		MESA	MOXA	AESA	AOXA	Atrazine	Simazine	Hexazinone	Diuron	Tebuthiuron	M104	DSMN	DEA	DACT	ACET
Kings	9	1	1	1	0	1	1	0	2	0	0	0	2	2
Sacramento	4	0	0	0	0	0	0	0	0	0	0	0	0	0
San Joaquin	22	10	3	3	1	0	1	2	0	1	1	2	2	0
Solano	8	6	0	3	0	0	0	0	0	0	0	1	0	0
Stanislaus	22	15	8	9	0	0	1	0	0	0	0	0	3	0
Yolo	3	1	0	0	0	0	0	0	0	0	0	0	0	0
TOTAL	68	33	12	16	1	1	3	2	2	1	1	3	7	2

FIGURES

Figure 1. Combined metolachlor and s-metolachlor use by the top five crops from 1991 to 2010 (CDPR, 2012a).

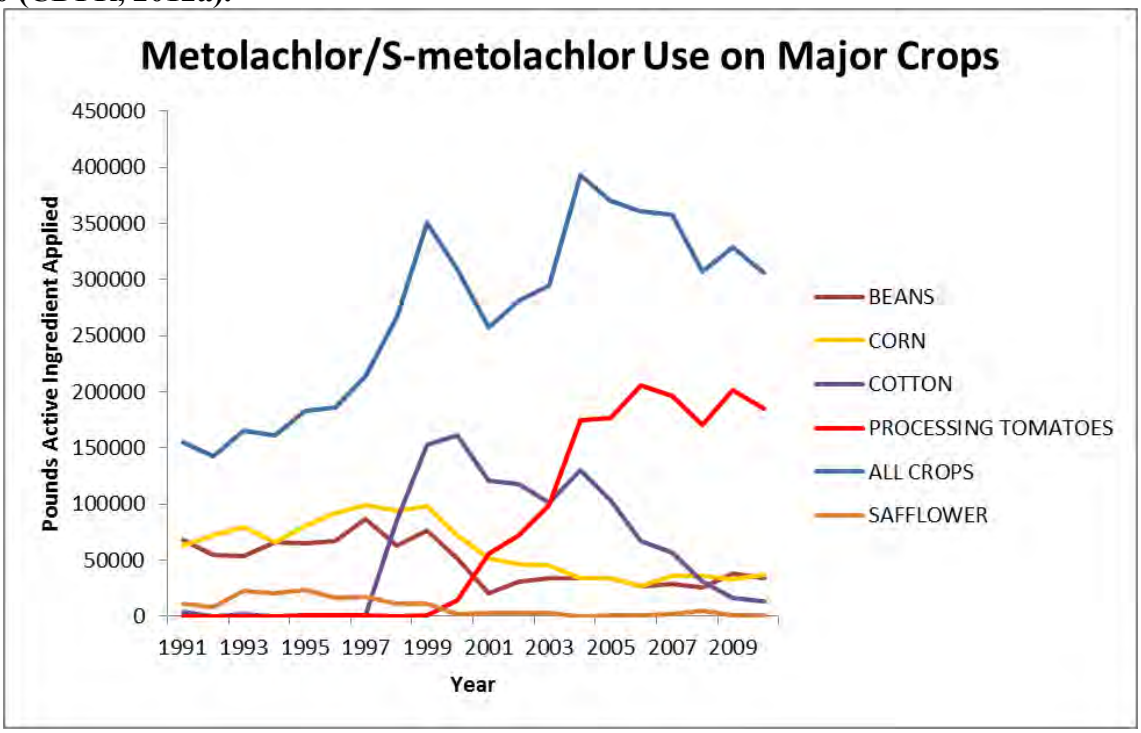


Figure 2. Alachlor use on beans, corn, and all sites from 1991 to 2010 (CDPR, 2012a). Use on corn and beans accounts for > 90% of total use since 1993.

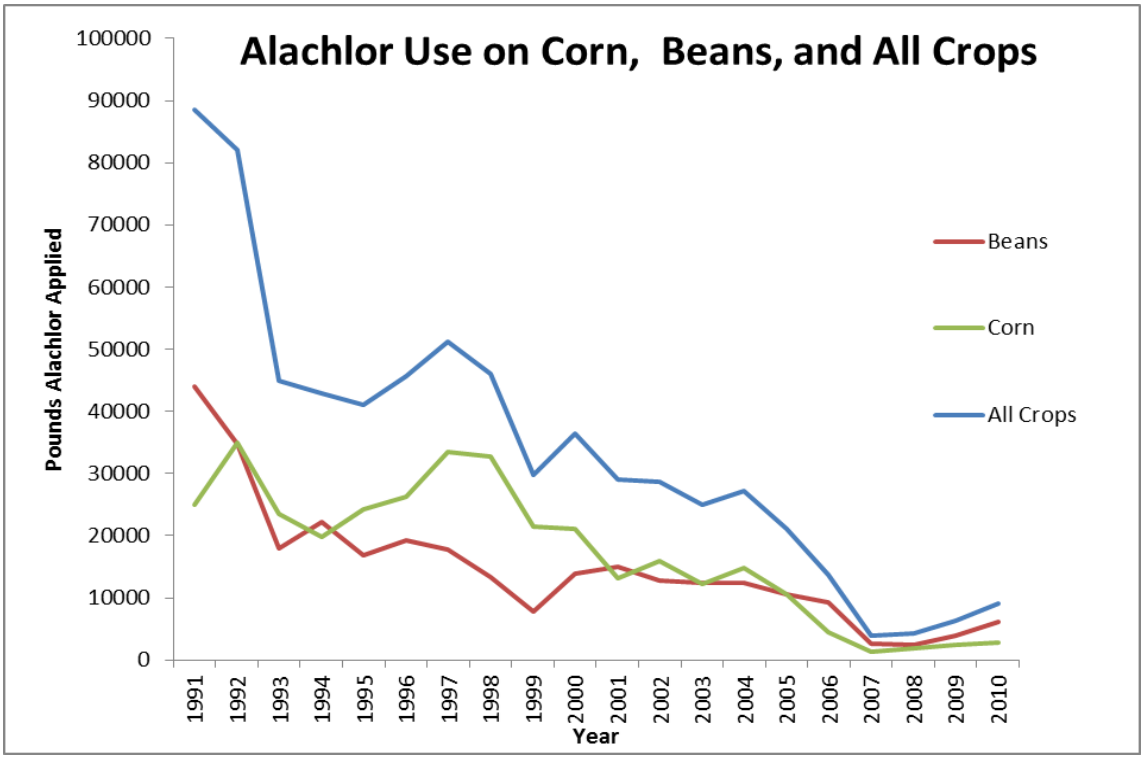


Figure 3. Metolachlor/s-metolachlor use (1996-2003), GWPAs, and sampled well locations in Southern San Joaquin County.

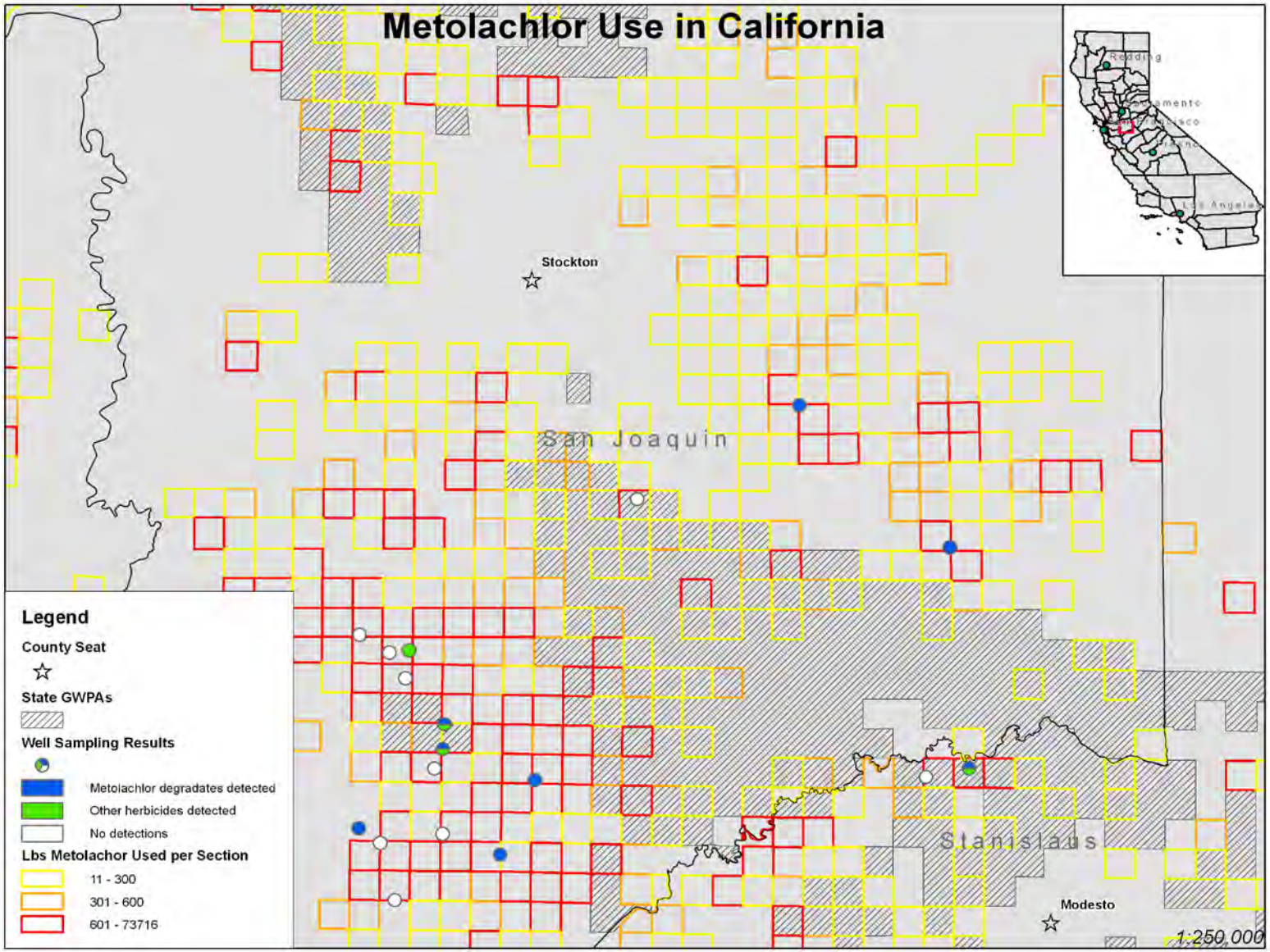


Figure 4. Metolachlor/s-metolachlor use (1996-2003), GWPAs, and sampled well locations in Sacramento, Solano, and Northern San Joaquin Counties.

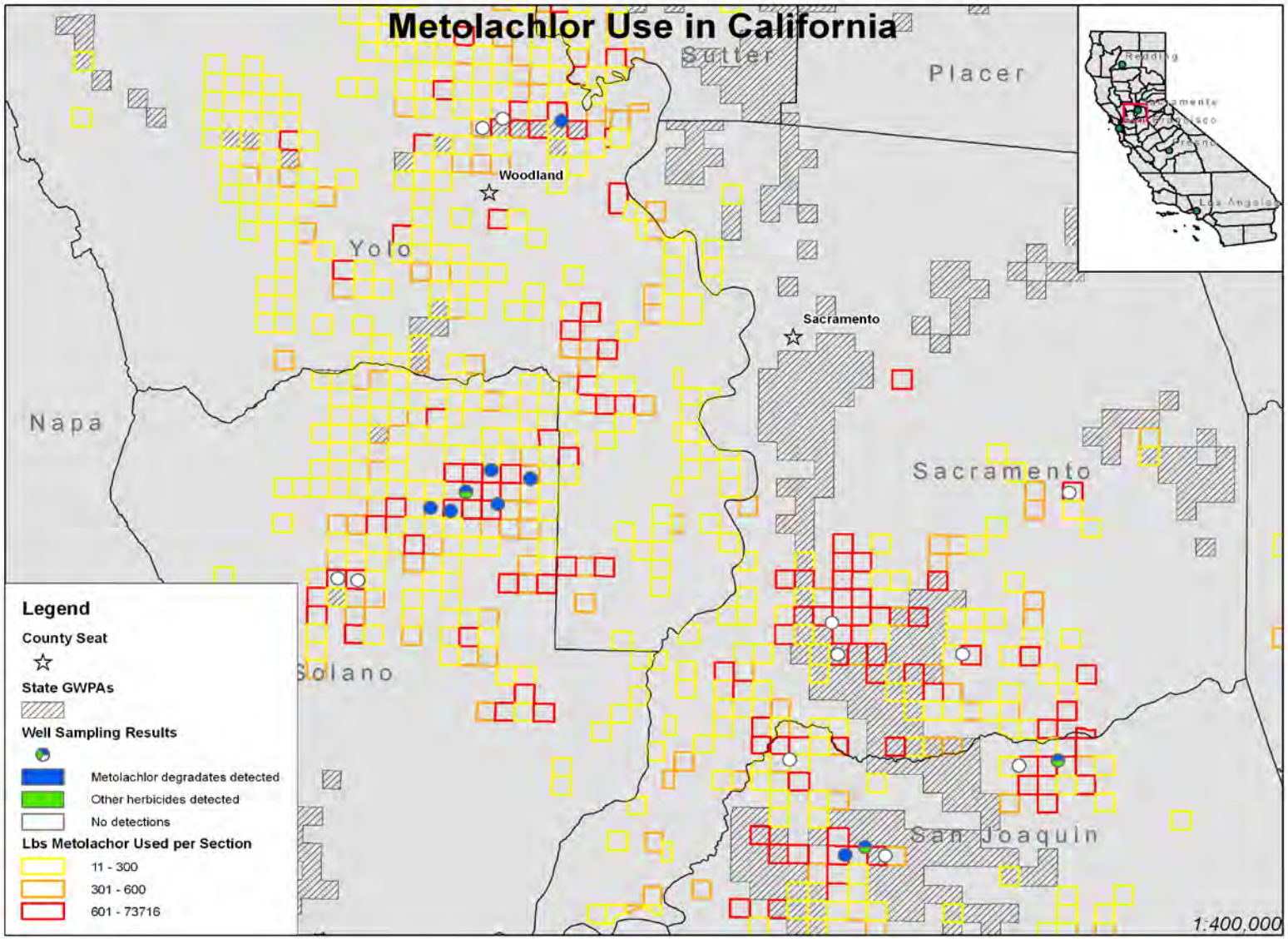


Figure 5. Metolachlor/s-metolachlor use (1996-2003), GWPAs, and sampled well locations in Central Stanislaus County.

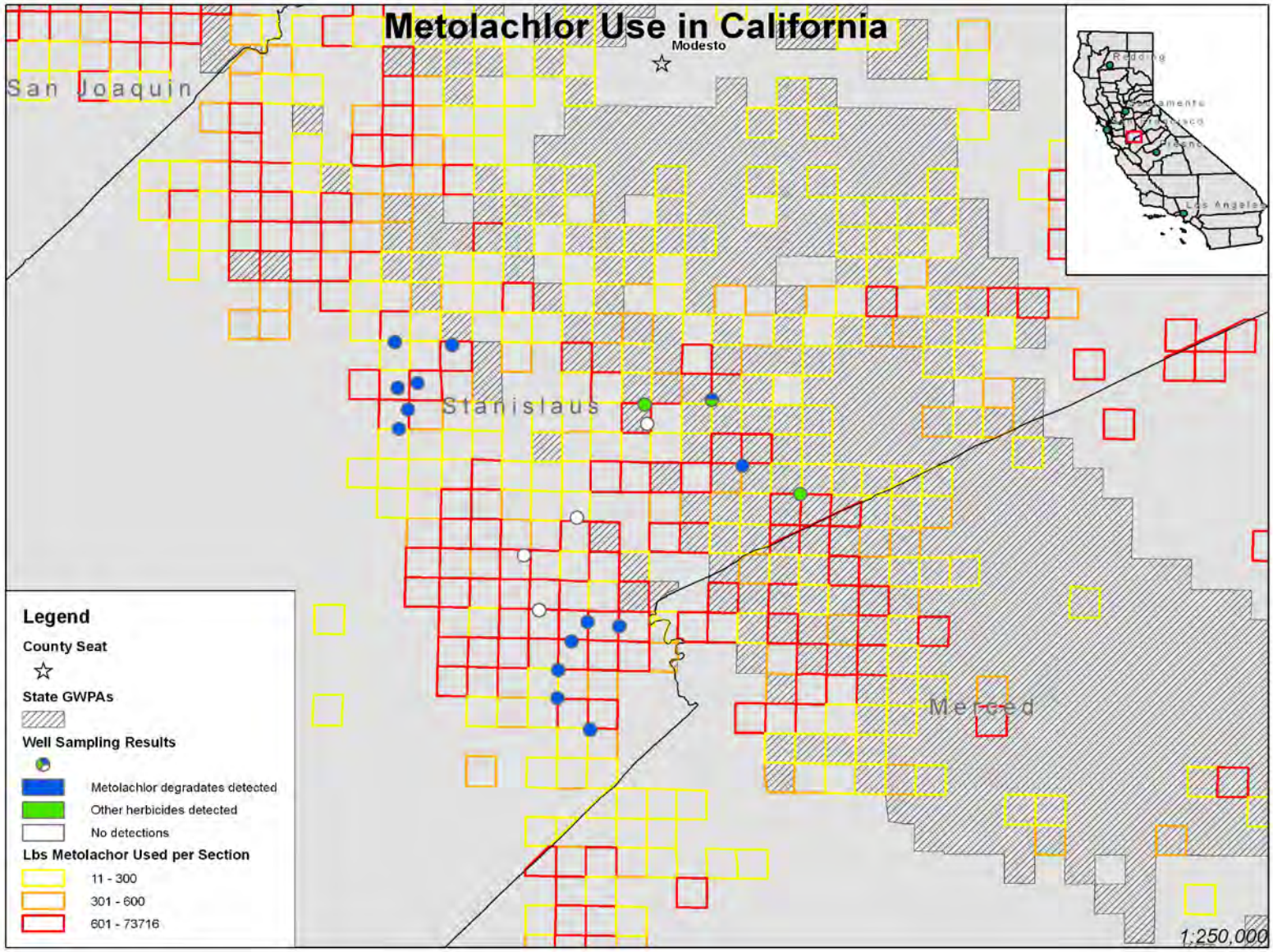


Figure 6. Metolachlor/s-metolachlor use (1996-2003), GWPAs, and sampled well locations in Kings County.

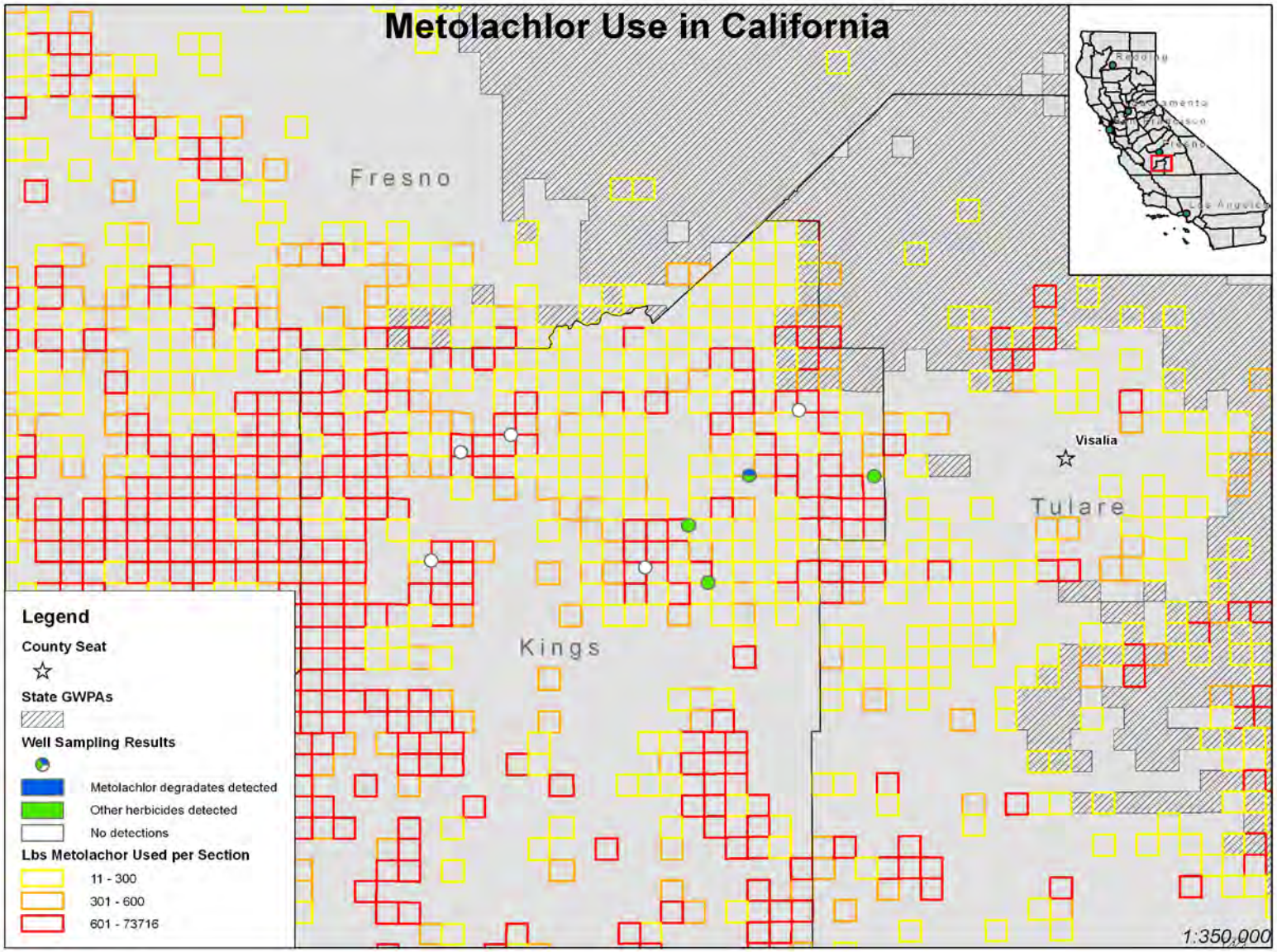


Figure 7. Alachlor use (1996-2003), GWPAs, and sampled well locations in Southern San Joaquin County.

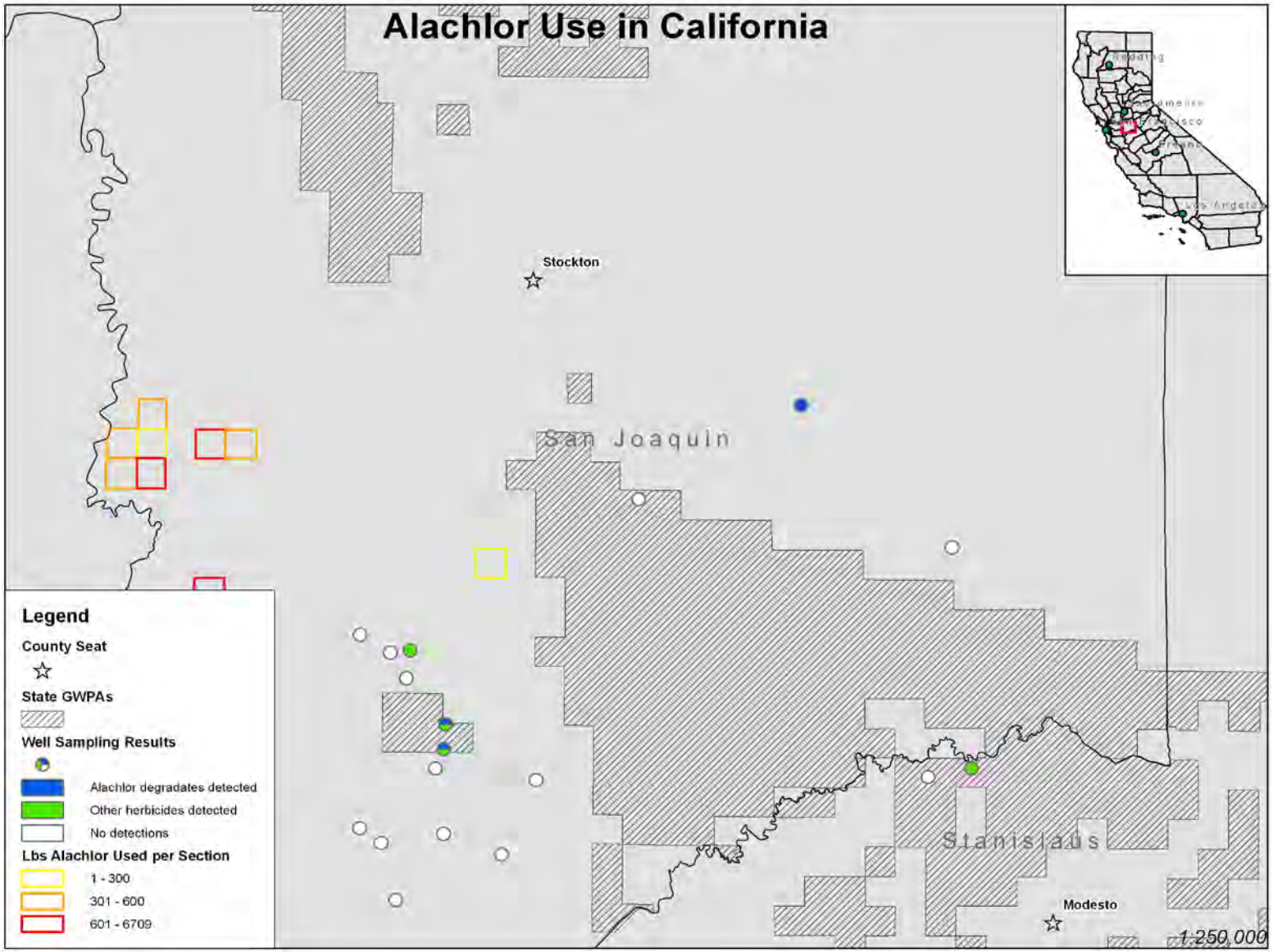


Figure 8. Alachlor use (1996-2003), GWPAs, and sampled well locations in Sacramento, Solano, and Northern San Joaquin Counties.

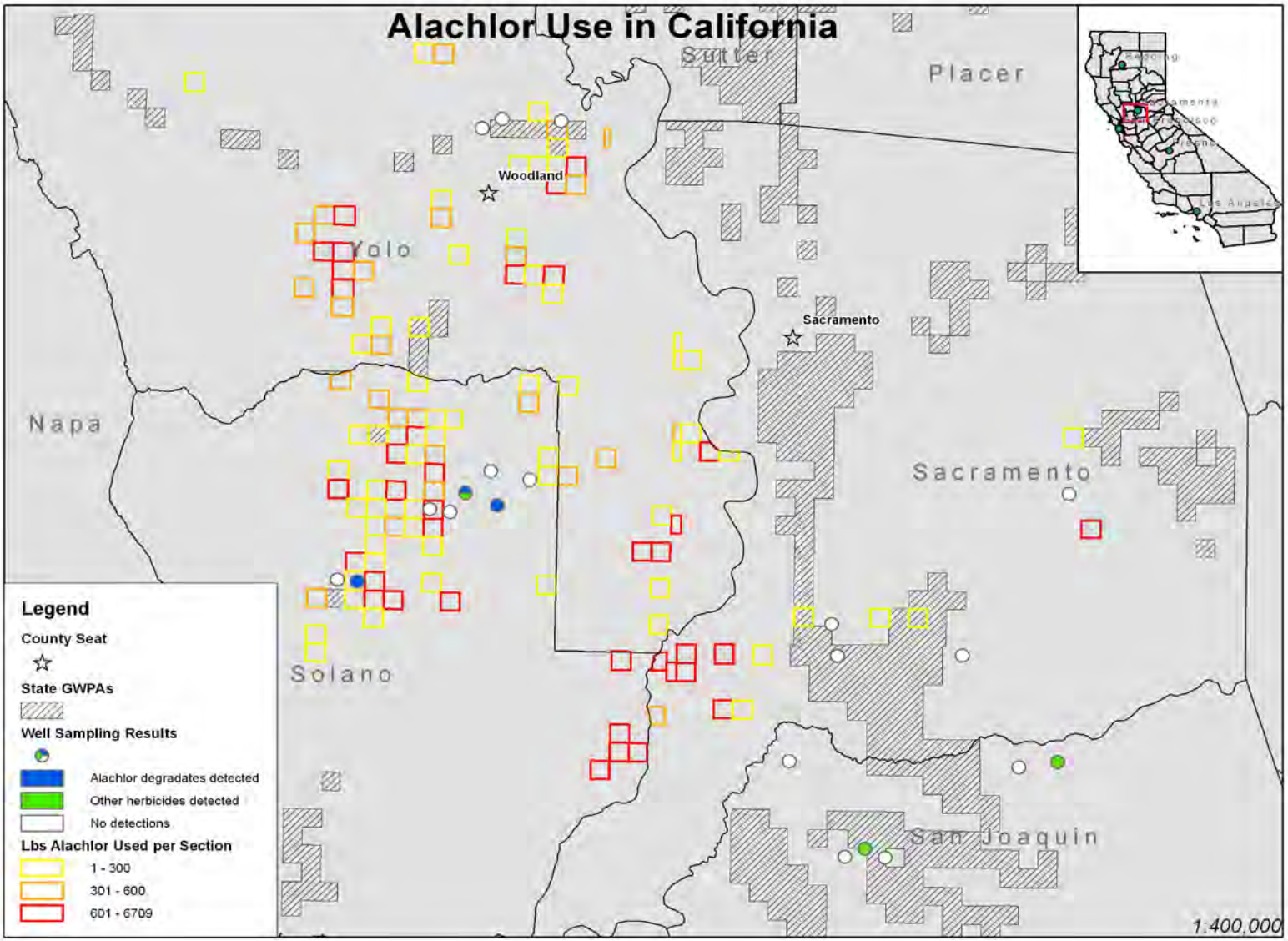


Figure 9. Alachlor use (1996-2003), GWPAs, and sampled well locations in Central Stanislaus County.

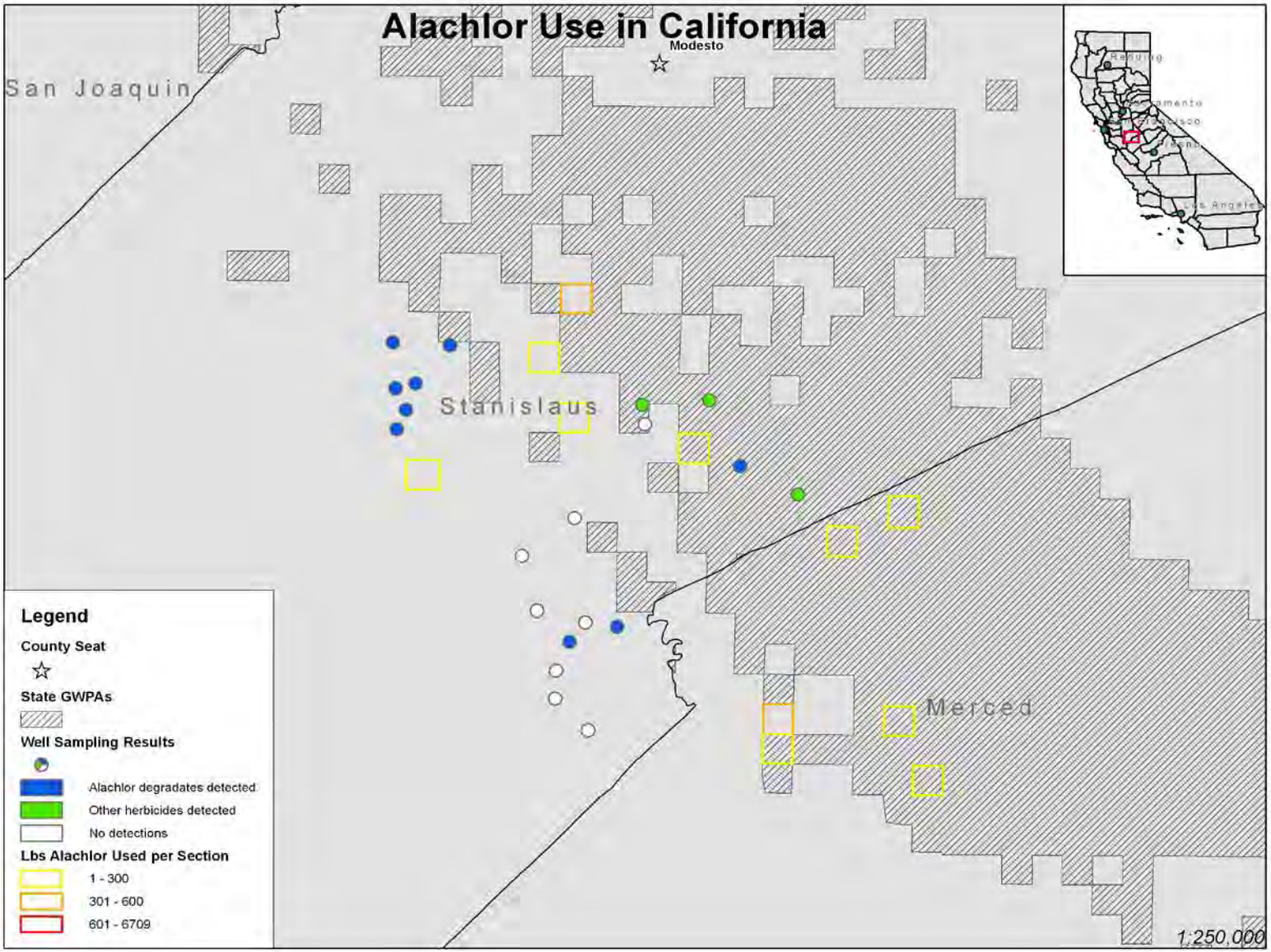


Figure 10. Alachlor use (1996-2003), GWPAs, and sampled well locations in Kings County.

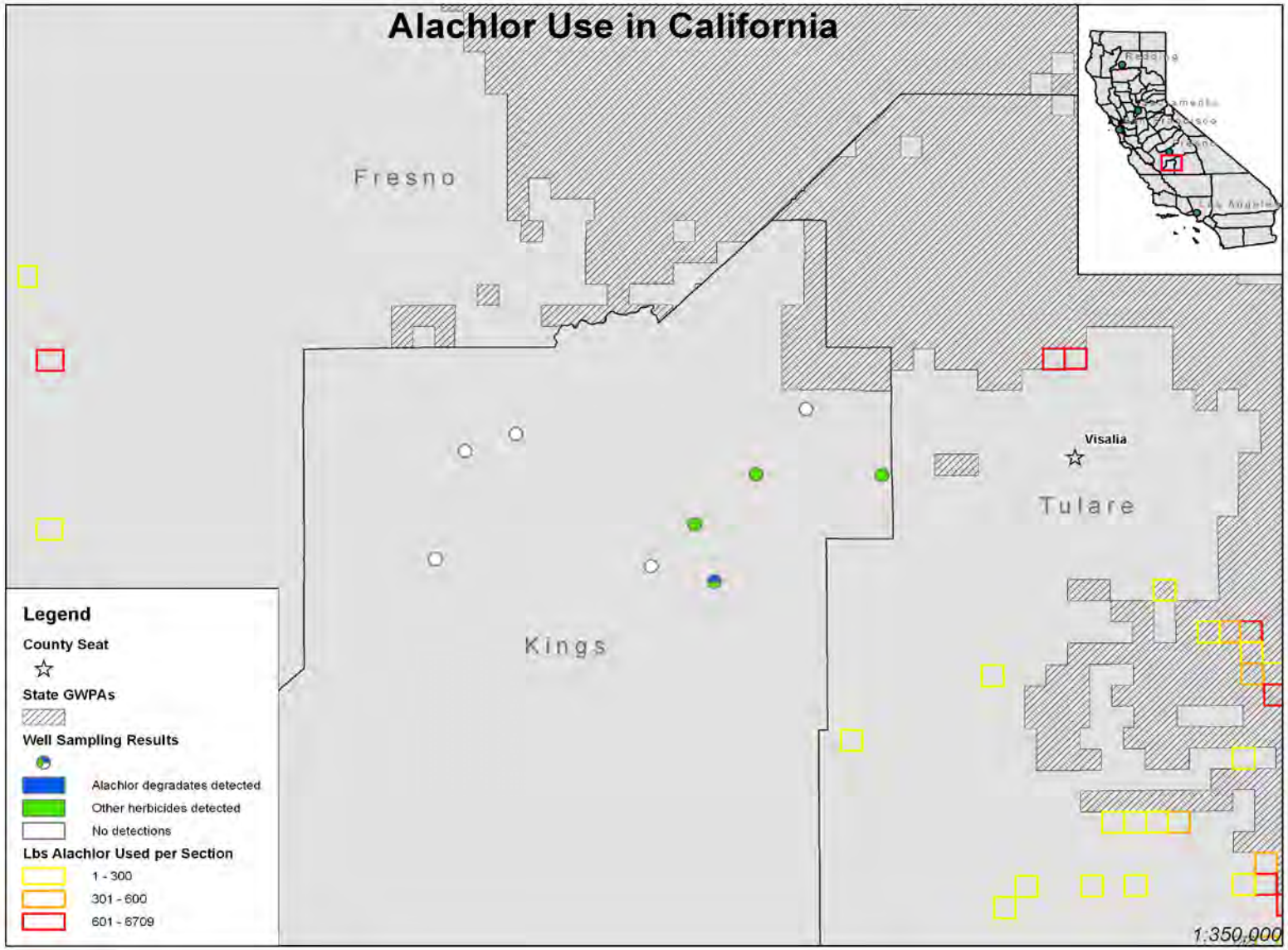
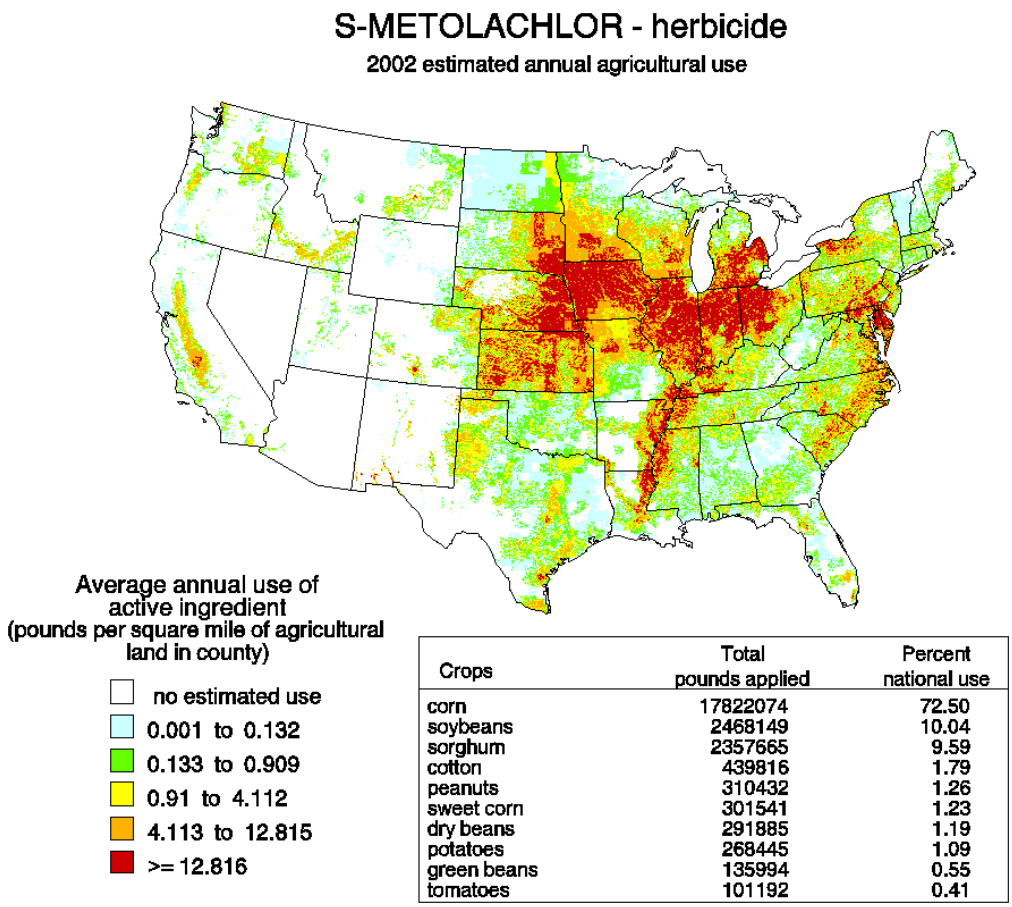


Figure 11. 2002 s-metolachlor pesticide use map. Map indicates average estimated use intensity of s-metolachlor from 1999 to 2004. The use intensities depicted here are based on statewide averages of both application rates for a s-metolachlor applied to a crop and the average percentage of a crop's area treated with s-metolachlor; therefore, the data do not yield precise estimates of pesticide use at the county level. S-metolachlor use map courtesy of the U.S. Geological Survey (2002).



Crops	Total pounds applied	Percent national use
corn	17822074	72.50
soybeans	2468149	10.04
sorghum	2357665	9.59
cotton	439816	1.79
peanuts	310432	1.26
sweet corn	301541	1.23
dry beans	291885	1.19
potatoes	268445	1.09
green beans	135994	0.55
tomatoes	101192	0.41

APPENDIX I

Table 1. Sampling results for GW09 in ppb.

Well Location Information		GW 09-Specific Pesticides						CDFA Method EM 62.9 Pesticides and Their Degradation Products															
County	Township/ Range-Section	**Metolachlor**	**MESA**	**MOXA**	**Alachlor**	**AESA**	**AOXA**	**Atrazine**	**Simazine**	**Diuron**	**Prometon**	**Bromacil**	**Hexazinone**	**Tebuthiuron**	**Norflurazon**	**Tebuthiuron Metabolite 104**	**Tebuthiuron Metabolite 106**	**Tebuthiuron Metabolite 107**	**Tebuthiuron Metabolite 108**	**DSMN**	**DEA**	**ACET**	**DACT**
Kings	19S/23E-04	ND[a]	ND	ND	ND	ND	ND	ND	**0.08**	**0.052**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.226**	**0.243**
Kings	19S/21E-13	ND	ND	ND	ND	ND	ND	ND	ND	**0.098**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Kings	19S/22E-30	ND	ND	ND	ND	**0.053**	ND	**0.06**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Kings	19S/21E-27	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Kings	18S/22E-33	ND	**1.2**	**0.534**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.302**	**0.152**
Kings	18S/22E-13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Kings	18S/20E-27	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Kings	18S/20E-29	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Kings	19S/19E-24	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sacramento	07N/07E-22	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sacramento	05N/06E-02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sacramento	05N/05E-03[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sacramento	06N/05E-28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	04N/05E-05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	04N/05E-35	ND	**0.051**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	04N/05E-36[c]	ND	**0.33**	ND	ND	ND	ND	ND	**0.06**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.123**	**0.141**	ND	**0.245**
San Joaquin	02S/06E-30	ND	**2.15**	**0.183**	ND	**0.726**	ND	ND	ND	ND	ND	ND	**0.093**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	03S/06E-06	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	03S/05E-11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	03S/05E-14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	03S/06E-08	ND	**0.128**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	03S/05E-03	ND	**0.13**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	02S/06E-27	ND	**0.065**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	02S/06E-19[b]	ND	**1.453**	**0.251**	ND	**0.867**	ND	ND	ND	ND	ND	ND	**0.072**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	02S/05E-25	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Well Location Information		GW 09-Specific Pesticides						CDFA Method EM 62.9 Pesticides and Their Degradation Products															
County	Township/ Range-Section	**Metolachlor**	**MESA**	**MOXA**	**Alachlor**	**AESA**	**AOXA**	**Atrazine**	**Simazine**	**Diuron**	**Prometon**	**Bromacil**	**Hexazinone**	**Tebuthiuron**	**Norflurazon**	**Tebuthiuron Metabolite 104**	**Tebuthiuron Metabolite 106**	**Tebuthiuron Metabolite 107**	**Tebuthiuron Metabolite 108**	**DSMN**	**DEA**	**ACET**	**DACT**
San Joaquin	02S/05E-11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	02S/05E-02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.058**	ND	ND	ND	ND	ND	ND	ND
San Joaquin	01S/07E-07[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	02S/05E-02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	01S/05E-34	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	01S/08E-14	ND	**0.838**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	01N/08E-30	ND	**0.384**	**0.156**	ND	**0.764**	**0.058**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	04N/05E-36[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	04N/07E-05	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	04N/07E-03	ND	**0.183**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.231**	ND	**0.114**
Solano	06N/01E-17	ND	ND	ND	ND	**1.0**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Solano	06N/01E-18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Solano	07N/02E-28	ND	**0.087**	ND	ND	**0.39**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Solano	07N/02E-30	ND	**0.102**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Solano	07N/02E-14	ND	**0.081**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Solano	07N/01E-25	ND	**0.233**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Solano	07N/02E-16	ND	**0.689**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Solano	07N/02E-20	ND	**0.078**	ND	ND	**0.129**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.071**	ND	ND
Stanislaus	05S/07E-24	ND	**0.21**	**0.082**	ND	**0.624**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/07E-13	ND	**0.086**	ND	ND	**0.648**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/08E-18	ND	**1.472**	ND	ND	**0.514**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/08E-08	ND	**0.635**	ND	ND	**0.2**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/10E-31[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.061**
Stanislaus	05S/07E-24	ND	**0.176**	ND	ND	**1.037**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/07E-12	ND	**0.799**	**0.206**	ND	**0.09**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/09E-20[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/09E-20[c]	ND	ND	ND	ND	ND	ND	ND	**0.082**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	05S/09E-14[c]	ND	**1.155**	**0.121**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.058**

Well Location Information		GW 09-Specific Pesticides						CDFA Method EM 62.9 Pesticides and Their Degradation Products															
County	Township/ Range-Section	**Metolachlor**	**MESA**	**MOXA**	**Alachlor**	**AESA**	**AOXA**	**Atrazine**	**Simazine**	**Diuron**	**Prometon**	**Bromacil**	**Hexazinone**	**Tebuthiuron**	**Norflurazon**	**Tebuthiuron Metabolite 104**	**Tebuthiuron Metabolite 106**	**Tebuthiuron Metabolite 107**	**Tebuthiuron Metabolite 108**	**DSMN**	**DEA**	**ACET**	**DACT**
Stanislaus	05S/09E-36[c]	ND	**0.553**	**0.086**	ND	**0.91**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	07S/08E-01	ND	**0.879**	**0.077**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	06S/08E-25	ND	**0.279**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	06S/08E-36	ND	**1.138**	**0.05**	ND	**0.062**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	07S/08E-02	ND	**0.599**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	07S/09E-18	ND	**0.341**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	06S/09E-29	ND	**2.835**	**0.128**	ND	**0.78**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	06S/08E-26	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	06S/08E-01	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	06S/08E-15	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	02S/08E-25[c]	ND	**0.567**	**0.072**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.196**
Stanislaus	02S/08E-26[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Yolo	10N/02E-12[c]	ND	**0.185**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Yolo	10N/02E-08	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Yolo	10N/02E-04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

a. ND = None Detected

b. Section is a Runoff GWPA

c. Section is a Leaching GWPA

APPENDIX II

Table 1. Quality Control for GW 09: Summary for Metolachlor/Alachlor Analysis

Analyte	Percent Recovery						
	Average Recovery	Standard Deviation	CV	Upper Control Limit	Upper Warning Limit	Lower Warning Limit	Lower Control Limit
Metolachlor	95.7	9.3	9.8	113	102	80.6	69.8
Metolachlor ESA	94	8.7	9.3	114	105	87.4	78.6
Metolachlor OXA	88.6	11.2	13	114	103	79.1	67.3
Alachlor	91.5	10.7	12	108	96	72.3	60.5
Alachlor ESA	100.2	11.6	12	112	103	84.7	75.4
Alachlor OXA	85.4	10.2	12	122	107	76.8	61.6

Table 2. Quality Control for GW 09: Summary for CDFA Method EM 62.9 Analysis

Analyte	Percent Recovery						
	Average Recovery	Standard Deviation	CV	Upper Control Limit	Upper Warning Limit	Lower Warning Limit	Lower Control Limit
DACT	87.7	7.4	8.4	130	117.1	64.7	51.6
ACET	97	12.3	12.7	120	110.9	73.5	64.2
Teb M-108	85	11.6	13.6	111	102	66.3	57.4
Teb M-106	98.6	11.4	11.6	119	111	78.4	70.3
Teb M-104	108.7	8.6	7.9	140	126	70.2	56.3
DEA	93.9	6.7	7.1	112	103.6	71	62.9
Teb M-107	94.7	7.9	8.4	126	115	69	57.6
Hexazinone	96.4	7.9	8.2	112	106	84	78.4
Tebuthiuron	95	8.1	8.5	129	118	74.6	63.6
Simazine	91.2	10	11	111	101.3	64.5	55.3
Bromacil	99.2	10	10.1	126	117.1	79.5	70.2
Prometon	91.2	7.7	8.4	107	98.4	62.8	53.9
Atrazine	90.3	8.9	9.9	100.7	93.7	65.5	58.5
DSMN	97.1	9.9	10.2	118	111	84.7	78
Norflurazon	97	10.5	10.9	111	104.3	76.3	69.3
Diuron	93.4	8.4	8.9	117	107.6	69.2	59.6
Propazine	88.8	8.9	10	104	97.4	69.4	62.4

Table 3. Quality Control for GW 09: Blind Spike Analysis

Sample #	Extraction Date	Analysis	Analyte	Spike Level (ppb)	Result (ppb)	Percent Recovery	Control limit exceeded
124	5/1/2008	Teb	Teb M-104	0.3	0.252	84.0	no
121	5/1/2008	Teb	Teb M-106	0.2	0.158	79.0	no
			Teb M-108	0.25	0.222	88.8	no
127	5/1/2008	Teb	tebuthiuron	0.2	0.157	78.5	no
586	5/21/2008	Tri	simazine	0.2	0.159	79.5	no
549	5/21/2008	Tri	norflurazon	0.2	0.187	93.5	no
528	5/21/2008	Tri	DSMN	0.25	0.197	78.8	no
			DEA	0.15	0.124	82.7	no
122	5/28/2008	Teb	tebuthiuron	0.15	0.117	78.0	no
130	5/28/2008	Teb	Teb M-106	0.15	0.12	80.0	no
			Teb M-107	0.2	0.181	90.5	no
128	5/28/2008	Teb	tebuthiuron	0.25	0.226	90.4	no
738	4/3/2009	Tri	simazine	0.15	0.131	87.3	
			norflurazon	0.12	0.129	107.5	no
356	7/28/2009	Teb	Teb M-108	0.15	0.166	110.7	no
			Teb M-106	0.15	0.339	226.0	yes
355	9/15/2009	Metolachlor	metolachlor OXA	0.25	0.201	80.4	no
			alachlor OXA	0.3	0.209	69.66667	no
451	9/29/2009	Metolachlor	metolachlor ESA	0.15	0.153	102	no
325	1/7/2010	Metolachlor	metolachlor OXA	0.25	0.219	87.6	no
			alachlor OXA	0.15	0.122	81.33333	no
517	1/7/2010	Metolachlor	metolachlor OXA	0.25	0.218	87.2	no
			alachlor OXA	0.15	0.147	98	no
326	12/28/2009	Tri	DACT	0.1	0.119	119	no
			Diuron	0.25	0.291	116.4	no
518	12/28/2009	Tri	DACT	0.1	0.132	132	yes
			Diuron	0.25	0.329	131.6	yes

APPENDIX III

DPR Medical Toxicology Branch Determination of Metolachlor/Alachlor Degradate Toxicity

Mary-Ann Warmerdam
Director

Department of Pesticide Regulation

Arnold Schwarzenegger
Governor

MEMORANDUM

TO: John S. Sanders, Ph.D.
Environmental Program Manager II
Environmental Monitoring Branch

FROM: Jay Schreider, Ph.D.
Primary State Toxicologist
916-445-4241

DATE: January 14, 2010

SUBJECT: POTENTIAL HEALTH EFFECTS OF ALACHLOR AND METOLACHLOR DEGRADATES IN WELL WATER

This memorandum is in response to your recent request that the Medical Toxicology Branch determine whether the well-water detections of metolachlor and alachlor degradates pose a threat to public health. A threat to public health from exposure to a chemical in drinking water might be better characterized in toxicological terms as a significant risk to human health.

Alachlor and its degradates

There is an extensive toxicity database for alachlor at DPR and at USEPA. The toxicity database on alachlor ESA is limited; however, the studies that do exist indicate that in the same study type, alachlor ESA is 5 – 10 less toxic that the alachlor parent. In setting alachlor food tolerances, USEPA grouped alachlor and alachlor degradates together, with the implicit assumption that the degradates were not more toxic than the parent. This indicates that health based drinking water standards for alachlor can be used as a health protective means for evaluating drinking water levels of the degradates. The USEPA Maximum Contaminant Level (MCL) for alachlor is 2 ppb. The Office of Environmental Health Hazard Assessment (OEHHA) established an alachlor Public Health Goal (PHG) of 4 ppb. These values are based on chronic effects. There were no detections of the alachlor parent; the primary detection was for alachlor ESA; and all of the detections were below the 2 ppb or 4 ppb values. Since the detections of alachlor ESA were below the health based MCL and PHG for alachlor, and the available data indicate that alachlor ESA is less toxic than alachlor, the concentrations detected in the well water in 2001 and 2009 do not appear to constitute a significant human health risk.

Metolachlor and its degradates

As is the case for alachlor, there is an extensive toxicity database for metolachlor at DPR and at USEPA, with limited data available for metolachlor ESA. In subchronic dog studies, the NOEL for metolachlor ESA is over 10 times larger that the NOEL for metolachlor. In setting metolachlor/S-metolachlor food tolerances, USEPA grouped metolachlor/S-metolachlor and its metabolites together, with the implicit assumption that the degradates were not more toxic than the parent. Further, USEPA has made the determination that "ESA and OXA metabolites appear

to be less toxic than the parent metolachlor/S-metolachlor." As with alachlor, this indicates that health based drinking water guidance levels for metolachlor can be used as a health protective means for evaluating drinking water levels of the degradates. An MCL has not been established for metolachlor; however, USEPA has established a lifetime Health Advisory (HA) of 700 ppb (often becomes the MCL and is the concentration in drinking water that is not expected to have adverse effects for a lifetime of exposure) and a Drinking Water Equivalent Level (DWEL) of 3,500 ppb (the DWEL assumes lifetime exposure with all exposure coming from drinking water). There were no detections of the metolachlor parent; the primary detection was for metolachlor ESA; and all of the detections were orders of magnitude below the HA and DWEL. Since the detections of metolachlor ESA were well below the health based HA and DWEL for metolachlor, and the available information indicate that metolachlor ESA is less toxic than metolachlor, the concentrations detected in the well water in 2001 and 2009 do not appear to constitute a significant human health risk.

While detections of the alachlor and metolachlor degradates continue, the amounts detected are low and, based on current information, do not constitute a significant human health risk from drinking water intake.

I hope this information addresses your request. If you need more information or have any questions, please do not hesitate to contact me.

cc: Gary Patterson
Lisa Ross