SURVEY FOR HERBICIDES IN WELL WATER

IN TULARE COUNTY

January, 1987

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection and Worker Safety
Environmental Monitoring and Pest Management
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by

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EXECUTIVE SUMMARY

The Environmental Hazards Assessment Program of the California Department of Food and Agriculture conducted a well survey in Tulare County to determine the presence of the herbicides simazine, atrazine, prometon, bromacil and diuron in well water. These herbicides were chosen because of their use on crops grown in Tulare County and on rights-of-way throughout the state. Twelve sampling areas were distributed from the Fresno to Kern County borders of Tulare County. Each area, referred to as a cell, consisted of four one-square mile sections. Ten wells were sampled in each cell.

Simazine was detected in 54 of 122 samples, diuron in 36 of 122 samples, atrazine in 11 of 120 samples and bromacil in 11 of 120 samples. Prometon was not detected. Most concentration values were below 1 part per billion (ppb). The highest values were 1.7, 2.8, 8.5 and 6.7 ppb for simazine, diuron, atrazine and bromacil, respectively. Screens were conducted for organochlorine, organophosphate and chlorinated hydrocarbon pesticides in one well water sample from each cell. All screen results were negative.

The frequency of detection and the herbicide found differed in roughly the northern and southern areas sampled in the county. In the northern cells labeled A-G, the frequency of detection was high with 40-100% of wells sampled in a cell containing a residue for at least one herbicide. In contrast, the frequency of detection in the southern cells labeled H-L ranged from 10-50% of wells sampled in a cell. Another indication of the difference between the areas was the number of different herbicide residues detected in one well water sample. In the northern area, residues for 2 or more herbicides were found in 33 of the 72 wells sampled whereas in the southern area only 1 of the 50 wells contained residues for 2 or more herbicides. Lastly, residues for simazine, atrazine, bromacil and diuron were detected in the northern cells whereas simazine and atrazine were predominant in the southern area.

Data on the use of these herbicides for 1980-1984 were collected from the County Agricultural Commissioner. The data indicated that during this period atrazine was used only for rights-of-way, simazine and diuron were used on both crops and rights-of-way and bromacil was mainly used on crops. Thus, uses of herbicides on both crops and rights-of-way appeared to be sources for the presence of pesticide residues in well water. Some factors that may have accounted for the spatial separation of the occurrence of herbicides between the northern and southern areas were pesticide-soil interactions or cropping patterns. Further investigation is needed to identify the most likely sources of these herbicide residues in Tulare County well water.

ACKNOWLEDGMENTS

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We also wish to thank Cindy Garretson for organization of the well sampling program; the field personnel who collected samples; and the computer personnel who processed the data.

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I. INTRODUCTION

In October 1985, the Environmental Hazards Assessment Program (EHAP) of the California Department of Food and Agriculture (CDFA) conducted a study to assess the movement of the herbicides simazine and diuron through soil in citrus groves in Tulare County. As part of that study water samples were analyzed from twelve wells located near the study area. Nine of the wells were found to contain simazine and/or diuron. The wells were resampled and seven of the nine wells were confirmed to be positive.

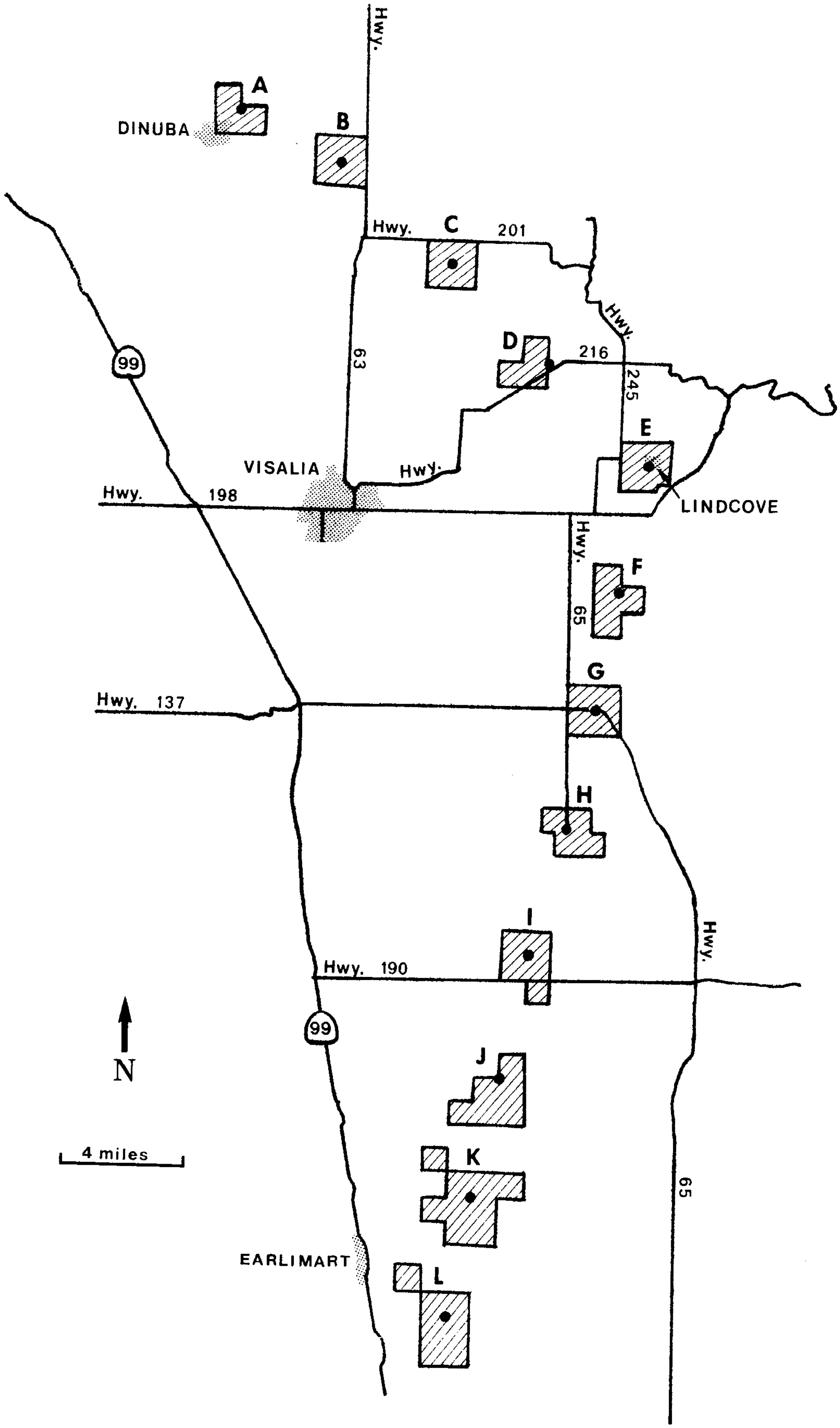
In order to determine the spatial extent of ground water pollution by herbicides in a portion of Tulare County, a comprehensive well sampling study was conducted in May, 1986. Well water samples were analyzed for the following herbicide residues: atrazine and prometon because they were structurally similar to simazine and they had previously been found at low levels in ground water in Glenn County in February 1986; and bromacil because it was widely used in citrus production.

II. MATERIALS AND METHODS

A. Study Design

Sampling occurred along two transects that emanated diagonally from the location of the original positive finds at Township-Range-Section 18S26E24, 18S27E17, and 18S27E19. One transect led northwest towards the border with Fresno County and the other transect led south-southwest nearly to the Kern County border (Figure 1). This design was used so that sampling areas covered a range of geographic and agricultural conditions. At approximately every four to five miles along each transect, a two by two mile area, referred to as a cell, was established. Each cell consisted of four-1 square mile sections as delineated by the USGS Public Survey Coordinate System. Cells were alphabetically labeled A-L from north to south. Ten randomly selected wells were sampled within each cell. Some of the cells in the southern part of the county had to be enlarged in order to produce a ten-well sample. A total of 122 wells were sampled - the original 12 wells

Figure 1. Sampling areas for the herbicide well study, Tulare County, 1986.



previously sampled in cell E, located at the junction of the two transects, and an additional 110 wells sampled in the 11 other cells.

B. Sampling Methods and Chemical Analyses

When possible, water samples were collected from a port located before the water storage tank and the wells were run for ten minutes before sampling to evacuate any standing water from the casing. Samples were collected in 1-liter amber glass bottles with aluminum foil-lined lids and held on wet ice during storage and transportation to the laboratory.

The primary laboratory that conducted the pesticide analyses was Agriculture and Priority Pollutants Laboratories (APPL) located in Fresno, California. Each well water sample was analyzed for the presence of simazine, atrazine, bromacil, diuron and prometon. One water sample from each cell was randomly chosen and prepared as an interlaboratory control sample. One-half of that sample was analyzed by APPL and the other half by California Analytical Laboratories (CAL) located in Sacramento, California. For one well in each cell an extra water sample was taken so that pesticide screening analyses could be conducted by APPL for organophosphates, carbamates and chlorinated hydrocarbons.

The extraction procedure used for all samples was the liquid-liquid extraction method in Environmental Protection Agency Manual SW 846 number 3510. The initial extraction solvent was methylene chloride. For gas chromatography (GC) analysis, the final solvent was hexane and for high pressure liquid chromatography (HPLC) analysis the final solvent was acetonitrile. Simazine and atrazine were analyzed by GC and HPLC. Bromacil and diuron were analyzed by HPLC.

The operating conditions for the GC were: the column was glass with 5% carbowax 20M-TPA on Supelcoport 80/100; the oven temperature was isothermal at 200°C; injection size was 4.4 ul; a nitrogen-phosphorus detector was used at 325°C; and the injector port temperature was 220°C.

The operating conditions for the HPLC confirmation of the triazines were: a carrying fluid of 10% acetonitrile and 90% water programmed to 100% acetonitrile over 30 minutes; injection size was 100 ul; detection wavelength was 254 nanometers and confirmation wavelength was 280 nanometers with comparison of the absorbance ratio of A_{254}/A_{280} to standards; and the column was a 10u C-18 column. Bromacil and diuron were confirmed by water gradient.

The following quality control measures were employed:

For methods development-5 replicates of blank water samples were spiked (blank matrix spike) and analyzed at 1.0 part per billion (ppb); and 5 replicate injections of standard solutions were made to a minimum level of 2 times the instrument detection limit.

For continuous quality control during analyses- a solvent spike, blank matrix, and blank matrix spike were analyzed with each extraction set; 5 replicate injections were made for 2 of the positive samples; confirmation analyses were made on all triazine positive samples using GC and HPLC; and confirmation analyses were conducted on 2 positive samples by mass spectrometry (MS).

III. RESULTS

A total of 122 wells were sampled throughout the study area. Twelve well water samples in cell E had been taken in a previous study. From those samples, 10 well samples were reanalyzed for all 5 herbicides. The results for simazine and diuron are included for the two additional wells. Some well samples had multiple observations per pesticide due to quality control replicate analyses. The mean of the replicate observations was used as the value of the residue in those wells.

A. Quality Control Analyses

Split-Sample - For simazine, the data for all quality control samples split between laboratories agreed with respect to the presence or absence of herbicide residues at the noted detection limits (Table 1). One positive sample detected by APPL was below the detection limit for CAL. The ratio of the positive split sample values (using results from CAL as the base measurement) ranged from 31-233% for individual comparisons with a mean and standard deviation of 99.5% and 48%, respectively. The overall mean agreed quite well but there was large individual variance. Much of the variance may be due to within laboratory precision because the replicate analyses within APPL differed by as much as 200%.

Table 1. Data for the interlaboratory split sample analyses conducted by APPL and Cal laboratories.

	Herbicide (ppb) and Analyzing Laboratory									
	Simazine [a]		Diuron [a]		Bromacil [a]		Atrazine [a]		Prometon [a]	
Sample	APPL	CAL	APPL	CAL	APPL	CAL	APPL	CAL	APPL	CAL
A2	1.16, .61 [b]	1.0	ND	ND	ND	ND	ND	ND	ND	ND
B1	ND [c]	ND	ND	ND	ND	ND	ND	ND	ND	ND
C1	.49,.45	.5	.65,.4	.61	ND	ND	ND	ND	ND	ND
D1	.87,1.07,.48	.8	.17,.38,.65	.3	ND	ND	ND	ND	ND	ND
E6	.8	.6	.3	.33	.15 [d]	ND	ND	ND	ND	ND
E9	.5	.7	.54	.52	ND	ND	ND	ND	ND	ND
E10	1.4	.6	.54	1.7	ND	ND	ND	ND	ND	ND
F1	.77,.66,.62	.8	.4,.55	.29	ND	ND	ND	ND	ND	ND
G1	1.04	3.4	ND	ND	.1 [d]	ND	ND	ND	ND	ND
H1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
I1	.04 [d]	ND	ND	ND	ND	ND	ND	ND	ND	ND
J1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
K1	ND	ND	ND	ND	ND	4.2 [e]	ND	ND	ND	ND
L1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a] Minimum detection limits for simazine, diuron, bromacil, atrazine and prometon for APPL of 0.02, 0.05, 0.1, 0.02, and 0.02 ppb, respectively and for CAL of 0.2, 0.1, 2.0, 0.2 and 0.2 ppb, respectively.

[b] Replicate analyses listed separately.

[c] None Detected.

[d] The value for APPL was lower than the CAL Detection limit.

[e] Value determined as a false positive result.

For diuron, the data for all quality control samples split between laboratories agreed with respect to the presence or absence of herbicide residues at the noted detection limits (Table 1). The ratio between laboratories of the positive split sample values (using CAL as the base measurement) ranged from 32-217% for individual comparisons with a mean and standard deviation of 113% and 58%, respectively. The overall mean for APPL was biased slightly higher than CAL.

For bromacil, most of the split samples were negative and the laboratories generally agreed with respect to the presence or absence of herbicide residues at the noted detection limits (Table 1). Two positive samples detected by APPL were below the limit of detection for CAL. CAL reported a positive result for one of the negative samples but upon further investigation this result was determined to be a false positive.

Neither laboratory found detectable residues of atrazine or prometon (Table 1).

Mass Spectrometry Confirmation - Two samples with the highest detectable residues, 8.5 ppb for atrazine and 6.7 ppb for bromacil were chosen from the whole study for confirmation by mass spectrometry. The mass spectrometry results confirmed the presence of atrazine and bromacil in their respective samples. The concentrations of simazine and diuron were below levels of detection by this technique.

B. Detection of Herbicide Residues

Sixty of the 122 well samples (49%) contained one or more herbicide residues. Simazine, diuron, atrazine and bromacil were detected in 54, 36, 11 and 11 of the samples, respectively (Table 2). The highest detected level for each herbicide was 8.5, 6.7, 2.8 and 1.7 ppb for atrazine, bromacil, diuron and simazine, respectively. Prometon was not detected in any of the samples.

The data for each herbicide reflected a positively skewed distribution as indicated by the consistently lower value of the median compared to the mean value (Table 2). This was most evident in the data for atrazine and bromacil which also had a much lower incidence of positive detections. This information may be useful in the design of further studies to quantify the risk of exposure to pesticides in well water.

Table 2. Statistical summary of the occurrence of herbicide residues in well water samples taken in Tulare County.

Herbicide	Number of Wells sampled	Number of Positive wells	Mean of Positive values (ppb)	Median of Positive values (ppb)	Range of Positive values (ppb)
Simazine	122	54	0.36	0.31	0.01–1.7
Diuron	122	36	0.49	0.36	0.03–2.8
Atrazine	120	11	0.91	0.09	0.02–8.5
Bromacil	120	11	1.62	0.56	0.09–6.7

C. Spatial Distribution of Herbicide Residues

Both the frequency of positive detections of residues in well water samples and the type of pesticide detected were dependent on the geographical location of the cells. Two distinct regions were apparent. One region encompassed cells A-G where a high frequency of occurrence of residues in well water was noted (Table 3). Residues were detected for atrazine, simazine, bromacil and diuron with many of the wells in this region containing residues for 2 or 3 herbicides (Table 4). The other region encompassed cells I-L where the frequency of detection was lower and the number of compounds detected dropped to only 2, atrazine and simazine. No multiple residues were detected in wells in this region. Cell H, located between these two regions, had a low frequency of occurrence of positive detections but it contained one well with two herbicide residues and a detection for diuron.

D. Pesticide Screens

All analyses of pesticide screens for organophosphates, carbamates and chlorinated hydrocarbons were negative at detection limits of 0.05-1.0 ppb for organophosphates, 1.0 ppb for carbamates and 0.05 ppb for chlorinated hydrocarbons (Table 5). In contrast, herbicide residues were detected in six of the wells used in the screening process with two of the wells containing residues of 3 herbicides-simazine, bromacil and diuron. Cell E, the area originally sampled, was not included in the pesticide screens.

IV. DISCUSSION

The results indicated widespread presence of certain herbicides in well water in Tulare County. Most concentrations were low, generally below 1 ppb. The California Department of Health Services has established action levels for atrazine and simazine of 15 and 150 ppb, respectively. The highest concentrations found were 8.5 and 1.7 ppb for atrazine and simazine, respectively, which are both below the action levels. Action levels have not yet been established for bromacil or diuron, for which the highest levels of detection were 6.7 and 2.8 ppb, respectively.

Table 3. Number of wells containing herbicide residues compared to the number of wells sampled in each cell compiled for pooled residues and for each component herbicide.

Cell	Number of Wells with Residues/Total Wells Sampled for:				
	All Residues	Atrazine	Simazine	Bromacil	Diuron
A	7/10	3/10	7/10	1/10	3/10
B	7/10	2/10	6/10	1/10	6/10
C	4/10	1/10	4/10	1/10	2/10
D	10/10	2/10	9/10	3/10	9/10
E	9/12	0/10	8/12	2/10	9/12
F	4/10	0/10	4/10	1/10	3/10
G	7/10	0/10	7/10	2/10	3/10
H	2/10	1/10	1/10	0/10	1/10
I	5/10	0/10	5/10	0/10	0/10
J	1/10	1/10	0/10	0/10	0/10
K	1/10	1/10	0/10	0/10	0/10
L	3/10	0/10	3/10	0/10	0/10
Total	60/122	11/120	54/122	11/120	36/122

Table 4. Number of wells in each cell containing 1, 2 or 3 herbicide residues.

	Number of Wells Containing:		
Cell	1 residue	2 residues	3 residues
A	3	1	3
B	2	2	3
C	1	2	1
D	2	3	5
E	1	7	1
F	1	2	1
G	3	3	1
H	1	1	0
I	5	0	0
J	1	0	0
K	1	0	0
L	3	0	0

Table 5. Results of pesticide screens and herbicide analyses conducted on 1 well water sample obtained from each cell.

Cell	Pesticide Screens			Herbicides (ppb)			
	Organophosphates[a]	Carbamates[a]	Chlorinated Hydrocarbons[a]	Atrazine[b]	Simazine[b]	Bromacil[b]	Diuron[b]
A	ND[c]	ND	ND	ND	0.89	ND	ND
B	ND	ND	ND	ND	ND	ND	ND
C	ND	ND	ND	ND	0.54	0.32	0.53
D	ND	ND	ND	ND	0.81	ND	0.40
F	ND	ND	ND	ND	0.62	0.26	0.10
G	ND	ND	ND	ND	0.55	0.24	ND
H	ND	ND	ND	ND	ND	ND	ND
I	ND	ND	ND	ND	0.04	ND	ND
J	ND	ND	ND	ND	ND	ND	ND
K	ND	ND	ND	ND	ND	ND	ND
L	ND	ND	ND	ND	ND	ND	ND

[a] Minimum detection limits of 0.05—1.0, 1.0 and 0.05 ppb for organophosphates, carbamates and chlorinated hydrocarbon screens, respectively.

[b] Minimum detection limits of 0.02,0.02,0.1 and 0.05 for atrazine, simazine, bromacil and diuron, respectively.

[c] None detected.

Data on estimated patterns of herbicide use in Tulare County for 1980-1984 were obtained from the County Agricultural Commissioner (Table 6). Although these data may be incomplete, the patterns of use aid in explaining the spatial occurrence of the residues. First, prometon was not registered for crop use and it was not used for rights-of-way in Tulare County. This correlates with no detection of prometon in any of the well samples. Second, the major use for atrazine was on rights-of-way. Atrazine was detected in wells both in the northern and southern portions of the study area indicating that rights-of-way use could be a widespread source of residues in ground water. Third, simazine, diuron and bromacil were used on rights-of-way and on cropped areas. Residues in well water could have resulted from either of these practices but the combination of uses would increase the potential for ground water contamination. The greater frequency of detection for simazine compared to atrazine could be attributed to the wider use of simazine (total from Table 6 of 8,837 and 84,680 lbs for atrazine and simazine, respectively). Also, the greater frequency of diuron detections compared to bromacil could also be related to greater use (total from Table 6 of 155,109 and 40,271 lbs for diuron and bromacil, respectively).

It is interesting to note that detection of bromacil and diuron residues was mainly limited to the northern cells A-G whereas simazine was detected throughout the study area. Two factors may have caused this effect: 1) differences in pesticide loading between the cells owing to specific cell cropping patterns or 2) spatial differences in surface and/or subsurface soil properties that resulted in differential retardation of pesticides. Further data are needed to correlate geologic and agricultural factors to the spatial occurrence of specific pesticide residues in well water.

Residues were not detected in the organophosphate, carbamate and chlorinated hydrocarbon screens conducted at the noted detection limits. Six of the well water samples used in the screens contained herbicide residues with 2 of the wells containing three residues. Since the use patterns for pesticides in the screen analyses are unknown, the exact meaning of these negative results is unclear.

Table 6. Estimated annual use of atrazine, bromacil, diuron and simazine in Tulare County for 1980–1984 obtained from the Agricultural Commissioner, reported in pounds.

Herbicide	Use	1980	1981	1982	1983	1984
Atrazine	Rights-of-Way	337	529	4,149	822	3,000
Bromacil	Citrus	2,118	13,084	5,362	9,849	5,210
	Non-Agricultural	–	25	22	–	–
	Public Health	–	316	130	71	130
	Rights-of-Way	1,323	840	121	1,573	97
Diuron	Alfalfa	9,782	9,000	9,857	13,306	4,757
	Citrus	6,880	14,457	9,786	15,666	10,694
	Cotton	1,344	1,013	128	19	–
	Pasture	–	136	176	208	74
	Grape	468	228	814	431	273
	Fallow	640	1,734	152	1,076	810
	Olive	307	800	344	40	793
	Rights-of-Way	7,197	3,580	17,260	3,466	3,789
	Walnut	1,086	1,300	605	232	401
Simazine	Almond	–	4	56	46	224
	Avocado	–	182	52	345	515
	Citrus	7,105	7,102	5,839	6,055	6,821
	Grape	8,730	8,638	5,079	4,904	3,175
	Non-Agricultural	32	88	184	420	568
	Olive	214	371	419	489	857
	Pasture	–	–	–	66	92
	Peach/Plum	348	131	48	48	171
	Rights-of-Way	1,289	2,358	1,797	2,315	1,151
	Turf	2,474	265	–	–	–
	Walnut	719	1,006	705	690	493