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Study GW18: Groundwater Protection List Monitoring for 2,4-Dichlorophenoxyacetic Acid Herbicide

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ABSTRACT

This study was conducted in 2018 to determine if 2,4-dichlorphenoxyacetic acid (2,4-D) had migrated into groundwater in areas of California with moderate to high reported agricultural use or in areas identified as vulnerable to groundwater contamination. The California Department of Pesticide Regulation's (DPR) Groundwater Protection Program (GWPP) sampled 60 wells located in eight California counties (Butte, Fresno, Kings, Merced, San Joaquin, Solano, Stanislaus, and Tulare). Of the 60 wells sampled, no wells had detectable concentrations of 2,4-D above the method detection limit (MDL).

Wells were also analyzed for other pesticides and degradates, resulting in 22 wells with detections of one or more known groundwater contaminants listed in Title 3 California Code of Regulations (3CCR section 6800[a]). Nineteen of these wells are located within Ground Water Protection Areas (GWPAs) and will not be investigated further since use of the detected pesticides is already regulated in these areas to protect groundwater. DPR will evaluate the three detections that are in areas where their use is not currently regulated to determine if further monitoring or regulatory action is required. All detections were below established drinking water quality standards.

BACKGROUND

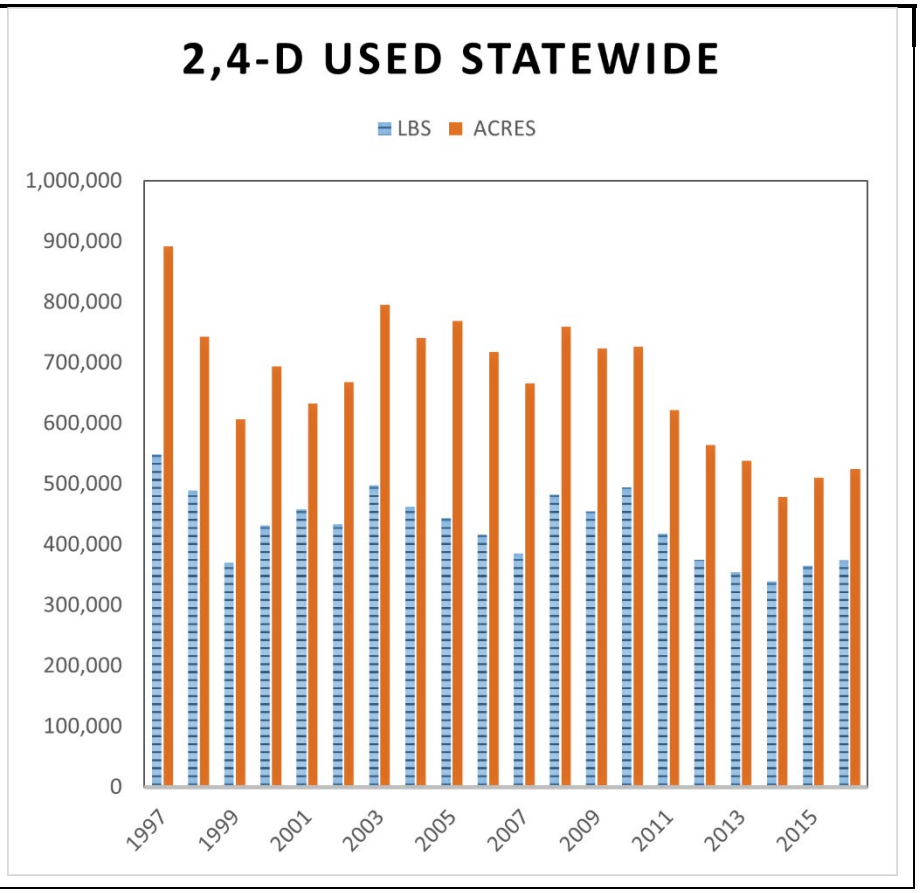
DPR is mandated by the Pesticide Contamination Prevention Act (PCPA) (Food and Agricultural Code [FAC] sections 13149–13152) to monitor for pesticides that have the potential to pollute groundwater based on their physical and chemical properties. These pesticides are placed on the Groundwater Protection List (GWPL) (3CCR section 6800[b]) and GWPP staff conduct monitoring to determine if these pesticides and/or their degradates have migrated to groundwater as a result

of agricultural use. The GWPP prioritized 2,4-D for monitoring because it is on the GWPL, is widely used throughout California, and was detected it in a single domestic well in Sutter County sampled by the GWPP as part of another study (Bergin, 2013; CDPR, 2021).

In the summer of 2018, staff from the GWPP conducted a groundwater monitoring study for the pesticide active ingredient (AI) 2,4-D to determine whether the herbicide had migrated to groundwater in areas with high reported agricultural use and shallow depth-to-groundwater. Due to its low affinity to bind to soil containing low organic matter, 2,4-D is expected to be moderately to highly mobile in sediment and mineral soils. Consequently, it is likely to leach through the soil profile if not degraded, and can potentially contaminate groundwater (Jervais et al., 2008). Additionally, 2,4-D is a widely used herbicide and has been marketed worldwide since the early 1940s. In the United States, 2,4-D is registered as a selective herbicide for control of broadleaf weeds and as a plant growth-regulator. The herbicide is a synthetic auxin, a plant growth hormone that causes uncontrolled cell growth and eventually leads to death in susceptible plants (Tu et al., 2001). Numerous commercial agricultural products contain 2,4-D as the AI. From 1997 to 2016, almost 8.6 million pounds of 2,4-D AI were used in California (CDPR, 2018) (Figure 1). In 2017, when the protocol for this study was finalized, approximately 1,500 actively registered 2,4-D products in California were labeled under various trade names (CDPR, 2018).

Figure 1. Reported use of 2,4-D in California in pounds of AI and acreage from 1997 to 2016 (CDPR, 2018).

Years	Pounds	Acres
1997	548,414	891,781
1998	489,413	742,892
1999	370,129	606,021
2000	431,755	693,800
2001	458,097	632,273
2002	433,381	667,375
2003	497,387	795,126
2004	462,428	740,364
2005	444,069	768,733
2006	415,912	718,025
2007	385,606	666,100
2008	482,094	759,047
2009	454,483	723,477
2010	494,054	726,176
2011	418,411	621,903
2012	374,999	563,552
2013	354,824	538,009
2014	338,987	478,460
2015	364,770	509,841
2016	373,997	524,764
Total	**8,593,210**	**13,367,719**



Well samples were also analyzed for other pesticides and degradates on the GWPL. The GWPP uses these data to prioritize focused monitoring of pesticides or degradates listed in 3CCR section 6800(b). These data are also used to assess the effectiveness of DPR's mitigation measures for the known groundwater contaminants listed in 3CCR section 6800(a) and to determine if regions regulated as GWPAs require expansion. The known groundwater contaminants include atrazine, bromacil, diuron, simazine, norflurazon, and some of their degradates.

METHODS

Sampling Methods

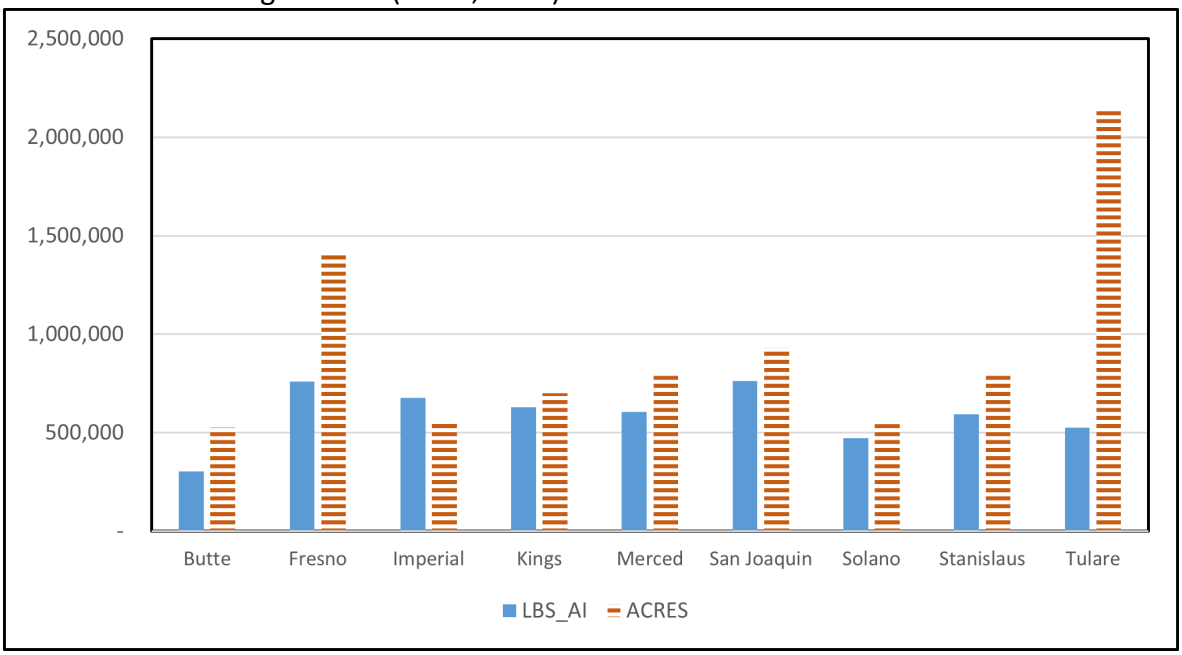
To determine areas of high use, GWPP staff examined the use of 2,4-D (AI) statewide (CDPR, 2018). Based on this examination, the eight counties with the highest use areas were initially selected for the study since they accounted for approximately 56% of the pounds applied statewide: Butte, Fresno, Kings, Merced, San Joaquin, Solano, Stanislaus, and Imperial (DaSilva, 2018) (Figure 2). Reported use in Imperial County was high; however, due to the lack of domestic drinking water wells in Imperial County, no samples were collected. Instead, five samples were collected in Tulare County, which was next on the list of target counties to be sampled based on the selection criteria. Appendix 1 (Figures 3-10) shows the use of 2,4-D per section in each county.

Within these eight counties, GWPP staff selected areas to sample by comparing and prioritizing sections based on the following factors:

1) Highest use of 2,4-D (pounds of AI) within a section
2) Pounds of 2,4-D used in the surrounding sections
3) Average depth-to-groundwater based on historical data
4) Previous reports of other pesticide detections in wells within or surrounding the section
5) Availability of wells to sample based on existing records in the Well Inventory Database

GWPP staff collected samples from 60 wells in the eight counties based on these factors. Identification of sampling locations was based on reported 2,4-D use with every effort made to ensure that sampling would occur within higher use sections (greater than 2,300 pounds). Due to variations in well location and well owner participation, acquiring samples within a given section was sometimes challenging; therefore, when necessary, wells were sampled in sections as close to the high use sections as possible. Samples were collected as described by Nordmark and Herrig (2011). At each well location, groundwater samples were collected from the wells for three analytical methods (2,4-D, Multi-Analyte Screen, and Triazine Screen; Table 1) and field blank samples containing deionized water were collected with the field samples (Richardson, 2011).

Figure 2. Pounds of 2,4-D applied and acres treated from 1997 through 2016 in the nine California counties with the highest use (CDPR, 2018).



Analytical Methods

The California Department of Food and Agriculture's (CDFA) Center for Analytical Chemistry (CAC) performed the chemical analyses. Table 1 lists each of the three analytical methods and the chemicals they detect. Some of the chemicals are analyzed for in both analytical methods. Samples were analyzed for a total of 49 pesticides and degradates. The reporting limit (RL) for all analytes was 0.05 parts per billion (ppb) and the method detection limits (MDL) are listed in the methods (CDFA, 2008, 2009, 2016). The RL is the lowest amount reported that is set at a level high enough to account for matrix effects (1 to 5 times the MDL) when following an analytical method. Trace detections are concentrations detected between the MDL (these vary) and the RL (0.05 ppb). Trace detections do not trigger any regulatory processes or response but serve as indicators of areas that may need follow-up or future groundwater monitoring.

2,4-D: The extracted groundwater was analyzed by a gas chromatograph equipped with a mass selective detector (MSD) (CDFA, 2008). The MDL for this analytical method was 0.015 ppb. Although this method was developed for surface water, using this method to analyze groundwater samples was determined to be acceptable because the surface water used to develop and validate the method was similar to clean groundwater.

Other GWPL Pesticides and Degradates (3CCR section 6800): Two analytical methods were utilized to analyze for these compounds: the Multi-Analyte Screen which includes 43 analytes (CDFA, 2016) and the Triazine Screen which includes 11 analytes (CDFA, 2009).

Table 1. Pesticides and degradates included in the CDFA laboratory analytical methods (CDFA 2008, 2009, 2016).

Multi-Analyte Screen			**Triazine Screen**	**2,4-D Analysis**
LCMS EMON-SM-05-032		**GCMS EMON-SM-05-032**	**EMON-62.9**	**EMON-SM-05-012**
Atrazine*	Linuron	Clomazone	ACET [2]	2,4-D
Azinphos-methyl	Mefenoxam/Metalaxyl[1]	Dichloran	Atrazine*	
Azoxystrobin	Methiocarb	Dichlobenil	Bromacil*	
Bensulide	Metolachlor	Disulfoton	DACT [3]	
Bromacil*	Metribuzin	Ethoprophos	DEA [4]	
Carbaryl	Napropamide	Ethyl parathion	Diuron*	
Carbofuran	Norflurazon*	Fonofos	DSMN [5]	
Diazinon	Oryzalin	Malathion	Hexazinone	
Dimethenamide	Prometon*	Methyl parathion	Norflurazon*	
Dimethoate	Simazine*	Phorate	Prometon*	
Diuron*	Tebuthiuron	Piperonyl butoxide	Simazine*	
Ethofumesate	Thiamethoxam	Prometryn		
Fenamiphos	Thiobencarb	Propanil		
Fludioxonil	Uniconazole	Triallate		
Imidacloprid				

[1] Mefenoxam and metalaxyl are stereoisomers. The laboratory cannot differentiate the two analytes.
[2] ACET: deisopropyl atrazine; degradate of atrazine and simazine
[3] DACT: diaminochlorotriazine; degradate of simazine
[4] DEA: deethyl atrazine; degradate of atrazine
[5] DSMN: desmethyl norflurazon; degradate of norflurazon
* Analytes are included in both screens

Quality Assurance and Quality Control

The CDFA's CAC analyzed quality control (QC) samples with every set of samples to assess laboratory precision. Peoples (2019) specifies the procedures followed for QC. During sample analysis for each extraction set (a group of samples extracted and processed as a batch), the laboratory simultaneously analyzed a laboratory matrix-blank and a QC matrix-spike. The laboratory matrix-blank was a sample of analyte-free groundwater collected from a well in the Sierra foothills. The QC consisted of the same source of analyte-free groundwater fortified (spiked) with all analytes in each screen. The QC matrix-spike results were evaluated by laboratory chemists, CDFA's CAC Quality Assurance Program, and the Environmental Monitoring Branch's (EM) Quality Assurance (QA) Officer to ensure analytical integrity. The evaluation included comparing the QC matrix-spike recoveries to control limits set at 3-times the standard deviation of the method validation data for each analyte fortified. Recoveries from the QC were used to assess and monitor ongoing sample analysis. The validation for the 2,4-D method varied more than that of the Multi-Analyte and Triazine Screen methods. Therefore, the control limits were set at 2-times the standard deviation of the method validation data (warning limits instead of control limits).

Additionally, EM's QA Officer submitted blind spikes to the laboratory disguised as field samples (Ganapathy, 2005); a blind spike consists of the analyte-free groundwater (matrix-blank sample) fortified with known concentrations of the chosen analytes. In addition to laboratory QC, samples containing deionized water (field blanks) were collected simultaneously with field samples and were analyzed to confirm the validity of detections when deemed necessary (Richardson, 2011).

RESULTS

Sample Analysis Results

2,4-D: None of the 60 wells sampled had detections of 2,4-D above the MDL of 0.015 ppb (Table 2).

Table 2. 2,4-D (EMON-SM-05-12) analytical results for all wells sampled.

Sample Number	County	Location Code	Township/Range-Section	Sample Date	Analysis Date	2,4-D
046	Fresno	10-01	15S/22E-05	6/26/2018	7/2/2018	ND
073	Fresno	10-02	15S/22E-16	6/26/2018	7/2/2018	ND
010	Fresno	10-03	15S/22E-05	6/26/2018	7/2/2018	ND
037	Fresno	10-04	15S/23E-31	6/26/2018	7/2/2018	ND
082	Fresno	10-05	16S/23E-06	6/26/2018	7/2/2018	ND
064	Fresno	10-06	16S/23E-07	6/27/2018	7/2/2018	ND
307	Fresno	10-07	16S/22E-13	6/27/2018	7/2/2018	ND
019	Fresno	10-08	16S/19E-16	6/27/2018	7/2/2018	ND
055	Fresno	10-09	16S/19E-26	6/27/2018	7/2/2018	ND
352	Fresno	10-10	16S/19E-36	6/28/2018	7/2/2018	ND
001	Kings	16-01	17S/22E-26	7/10/2018	7/17/2018	ND
298	Kings	16-02	17S/22E-27	7/10/2018	7/17/2018	ND
028	Kings	16-04	18S/22E-06	7/10/2018	7/17/2018	ND
316	Kings	16-05	18S/20E-10	7/10/2018	7/17/2018	ND
100	Tulare	54-01	16S/23E-34	7/11/2018	7/17/2018	ND
262	Tulare	54-02	16S/23E-22	7/11/2018	7/17/2018	ND
289	Tulare	54-03	16S/23E-32	7/11/2018	7/17/2018	ND
271	Tulare	54-04	16S/23E-32	7/11/2018	7/17/2018	ND
280	Tulare	54-05	16S/23E-36	7/12/2018	7/17/2018	ND
136	Butte	04-01	23N/01W-17	7/23/2018	7/30/2018	ND
091	Butte	04-02	23N/01W-20	7/23/2018	7/30/2018	ND
154	Butte	04-03	22N/01W-12	7/23/2018	7/30/2018	ND
163	Butte	04-04	22N/01E-19	7/23/2018	7/30/2018	ND
145	Butte	04-05	22N/01E-33	7/24/2018	7/30/2018	ND
109	Butte	04-06	21N/01E-21	7/24/2018	7/30/2018	ND
172	Butte	04-07	21N/01E-26	7/24/2018	7/30/2018	ND
181	Butte	04-08	21N/01E-12	7/25/2018	7/30/2018	ND
361	Merced	24-01	05S/11E-25	7/31/2018	8/6/2018	ND
217	Merced	24-02	05S/11E-26	7/31/2018	8/6/2018	ND

Sample Number	County	Location Code	Township/Range-Section	Sample Date	Analysis Date	2,4-D
226	Merced	24-03	05S/11E-34	7/31/2018	8/6/2018	ND
370	Merced	24-04	06S/11E-01	7/31/2018	8/6/2018	ND
388	Merced	24-05	06S/12E-06	7/31/2018	8/6/2018	ND
397	Merced	24-06	07S/11E-14	8/1/2018	8/6/2018	ND
379	Merced	24-07	07S/12E-04	8/1/2018	8/6/2018	ND
415	Merced	24-08	06S/11E-19	8/1/2018	8/6/2018	ND
406	Merced	24-09	06S/13E-06	8/1/2018	8/6/2018	ND
424	Merced	24-10	06S/12E-27	8/2/2018	8/6/2018	ND
460	Solano	48-01	04N/02E-36	8/6/2018	8/16/2018	ND
514	Solano	48-02	06N/01E-24	8/7/2018	8/16/2018	ND
442	Solano	48-03	06N/01E-21	8/7/2018	8/16/2018	ND
469	Solano	48-04	06N/01W-13	8/7/2018	8/16/2018	ND
451	Solano	48-05	06N/01E-19	8/7/2018	8/16/2018	ND
433	Solano	48-06	07N/02E-01	8/7/2018	8/16/2018	ND
478	San Joaquin	39-01	02S/07E-17	8/13/2018	8/23/2018	ND
523	San Joaquin	39-02	02S/07E-21	8/13/2018	8/23/2018	ND
532	San Joaquin	39-03	02S/07E-22	8/13/2018	8/23/2018	ND
541	San Joaquin	39-04	02S/09E-23	8/13/2018	8/23/2018	ND
550	San Joaquin	39-05	02S/09E-09	8/14/2018	8/23/2018	ND
559	San Joaquin	39-06	02S/09E-05	8/14/2018	8/23/2018	ND
568	San Joaquin	39-07	02S/08E-12	8/14/2018	8/23/2018	ND
577	San Joaquin	39-08	02S/08E-11	8/14/2018	8/23/2018	ND
586	San Joaquin	39-09	01S/09E-27	8/14/2018	8/23/2018	ND
208	Stanislaus	50-01	05S/11E-01	8/13/2018	8/22/2018	ND
334	Stanislaus	50-02	04S/11E-26	8/13/2018	8/22/2018	ND
244	Stanislaus	50-03	04S/11E-31	8/13/2018	8/22/2018	ND
253	Stanislaus	50-04	04S/11E-30	8/13/2018	8/22/2018	ND
190	Stanislaus	50-05	04S/10E-07	8/14/2018	8/22/2018	ND
343	Stanislaus	50-06	04S/10E-18	8/14/2018	8/22/2018	ND
325	Stanislaus	50-07	05S/09E-02	8/14/2018	8/22/2018	ND
235	Stanislaus	50-08	04S/09E-18	8/14/2018	8/22/2018	ND

Location code = County number – chronological order of wells sampled in the county.
ND = no detections were above the method detection limit of 0.015 ppb.

Other GWPL Pesticides and Degradates: Of the 60 sampled wells, 22 had detections of one or more analytes above the RL (Table 3). Appendix 2 (Tables A-1 and A-2) shows individual sample results for the Triazine and Multi-Analyte Screens. The results of the detections are below currently established health-protective drinking water quality standards (Table 4).

The number of detections above the RL of 0.05 ppb are summarized by analyte as follows:

- DACT (diaminochlorotriazine, a simazine degradate) was detected in 19 wells
- ACET (deisopropyl atrazine, a simazine/atrazine degradate) was detected in 13 wells
- DSMN (a norflurazon degradate) was detected in seven wells
- Simazine was detected in four wells
- Norflurazon, atrazine, and DEA (an atrazine degradate) were detected in two wells each
- Bromacil was detected in one well

The number of wells with detections of at least one analyte above the RL of 0.05 ppb for each county are as follows:

- Seven wells in Fresno County
- Five wells in San Joaquin County
- Three wells each in Stanislaus and Solano counties
- Two wells in Merced County
- One well each in Butte and Tulare counties
- No wells in Kings County

In addition to the detections above the RL, there were also trace detections. For the Triazine Screen, trace concentrations or greater (above the RL) were detected in 36 wells. Except for prometon, every analyte in the screen was detected in at least one well. Hexazinone and diuron were the only two analytes that were not detected above the RL but were detected at trace concentrations (Appendix 2, Table A-1). For the Multi-Analyte Screen, metolachlor, ethoprophos, and phorate were detected at trace concentrations along with some triazine herbicides (Appendix 2, Table A-2).

The triazine herbicides that were analyzed as part of the Multi-Analyte Screen overlap with the herbicides analyzed as part of the Triazine Screen. These six overlapping analytes, listed in Table 5, were used to assess reproducibility when detections of these herbicides were reported. Table 5 compares detections of triazine herbicides from both screens. Reported detections in replicate samples submitted for both methods may yield trace detections matching non-detections since the detections are close to the MDL of both methods; the variation in recoveries was within acceptable limits.

Table 3. Concentrations (ppb) of Triazine Screen analytes detected in wells and the total number of wells sampled in a county.

Pesticide or Degradate	Butte	Fresno	Kings	Merced	San Joaquin	Solano	Stanislaus	Tulare	Total Wells with Detections of Each Pesticide
Atrazine	ND	*1 well (0.074, 0.081)	ND	ND	ND	*1 well (0.073, 0.081)	ND	ND	2 wells
DEA (degradate of atrazine)	ND	1 well (0.066)	ND	ND	ND	1 well (0.072)	ND	ND	2 wells
Bromacil	ND	*1 well (0.192, 0.231)	ND	ND	ND	ND	ND	ND	1 well
Norflurazon	ND	*1 well (0.123, 0.167)	ND	ND	ND	*1 well (0.061, 0.079)	ND	ND	2 wells
DSMN (degradate of norflurazon)	ND	2 wells (0.127, 0.187)	ND	2 wells (0.092, 0.260)	2 wells (0.185, 0.200)	ND	2 wells (0.068, 0.227)	ND	7 wells
Simazine	ND	4 wells (0.051 - 0.086)	ND	ND	ND	ND	ND	ND	4 wells
ACET (degradate of atrazine or simazine)	1 well (0.156)	4 wells (0.064 - 0.123)	ND	1 well (0.097)	4 wells (0.058 - 0.181)	ND	2 wells (0.058, 0.120)	1 well (0.068)	13 wells
DACT (degradate of simazine)	1 well (0.162)	6 wells (0.054 - 0.221)	ND	2 wells (0.102, 0.205)	5 wells (0.095 - 0.439)	1 well (0.215)	3 wells (0.331 - 0.504)	1 well (0.099)	19 wells
Total Wells with Detections for Each County/Wells Sampled**	**1/8**	**7/10**	**0/4**	**2/10**	**5/9**	**3/6**	**3/8**	**1/5**	**22/60**

ND = no detections were reported at or above the 0.05 ppb reporting limit. Trace results are not included on this table.

* Analyte was also detected with Multi-Analyte Screen.

** Wells with multiple detections were only counted once.

[1] ACET: deisopropyl atrazine; degradate of atrazine and simazine

[2] DACT: diaminochlorotriazine; degradate of simazine

[3] DEA: deethyl atrazine; degradate of atrazine

[4] DSMN: desmethyl norflurazon; degradate of norflurazon

Table 4. Drinking water quality standards for pesticides or degradates detected above the reporting limit of 0.05 ppb.

Pesticide or Degradate	Primary Agricultural Use	Drinking Water Quality Standard (ppb)			
		MCL[a]	Chronic HHBP[b]	PHG[c]	HHRL[d]
ACET	Degradate of Atrazine and Simazine	*	*	*	*
Atrazine	Herbicide	1	*	0.15	*
Bromacil	Herbicide	*	*	*	197
DACT	Degradate of Simazine	*	11	*	*
DEA	Degradate of Atrazine	*	*	*	*
DSMN	Degradate of Norflurazon	*	*	*	*
Norflurazon	Herbicide	*	8.9	*	*
Simazine	Herbicide	4	*	4	*

a. MCL: Maximum Contaminant Level: The highest level of a contaminant allowed in drinking water. This is an enforceable standard set by the California State Water Resources Control Board (SWRCB, 2021).

b. Chronic HHBP: Chronic Human Health Benchmarks for Pesticides: Levels of certain pesticides in water at or below which adverse health effects are not anticipated from lifetime exposure (non-cancer). These levels are set by the U.S. EPA (USEPA, 2021).

c. PHG: Public Health Goal: At this concentration, drinking water contaminants pose no significant health risk if consumed for a lifetime. These levels are set by the California Office of Environmental Health Hazard Assessment (OEHHA, 2022).

d. HHRL: Human Health Reference Level: This is a screening level identified by DPR's Human Health Assessment Branch. Concentrations below this level do not pose acute or chronic health risks to humans (Brown et al., 2021).

* No level currently established.

Table 5. Well sample results for analytes on both the Triazine and Multi-Analyte Screens. The table includes results for the six analytes that are duplicated in the two screens (Triazine Screen ppb/Multi-Analyte Screen ppb).

Location Code	Atrazine	Bromacil	Diuron	Norflurazon	Prometon	Simazine
10-01	ND/ND	ND/ND	T/T	0.123/0.167	ND/ND	T/0.051
10-02	ND/ND	ND/ND	ND/ND	T/T	ND/ND	T/T
10-03	0.074/0.081	0.192/0.231	T/T	ND/ND	ND/ND	T/0.060
10-05	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND	T/0.056
10-08	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND	0.069/0.086
10-09	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND	T/T
16-01	ND/ND	ND/ND	T/T	ND/ND	ND/ND	ND/ND
24-02	ND/ND	T/T	ND/ND	T/T	ND/ND	T/T
24-03	ND/ND	ND/T	ND/ND	T/T	ND/ND	T/T
39-06	ND/ND	ND/ND	T/T	ND/ND	ND/ND	ND/ND
39-07	ND/ND	ND/ND	ND/ND	T/T	ND/ND	T/ND
39-08	ND/ND	ND/ND	ND/ND	T/T	ND/ND	T/T
48-04	0.073/0.081	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND
48-05	ND/ND	ND/ND	ND/ND	0.061/0.079	ND/ND	ND/ND
50-03	ND/ND	ND/ND	ND/ND	T/T	ND/ND	T/ND
50-05	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND	T/T
54-04	T/ND	ND/ND	T/T	ND/ND	ND/ND	T/T
54-05	ND/ND	ND/ND	ND/ND	ND/ND	ND/ND	T/ND

ND = no detections were reported at or above the method detection limit.

T = Trace (positive result between the method detection limit and the reporting limit of 0.05 ppb).

Results of the Quality Assurance and Quality Control

Results from laboratory matrix-blanks had no detectable analytes, and the QC matrix spikes and blind spikes were all within control limits except a few triazine analytes that were below the lower control limits. Table 6 contains all the QC results for 2,4-D; the QC results were within warning limits. Tables 7-9 summarize the QC conducted for 2,4-D, the Triazine Screen, and the Multi-Analyte Screen. Table 10 shows all blind spike results. Additionally, for the Triazine Screen analysis, propazine surrogate was added by the laboratory to every sample to show recovery of an analyte similar to those in the screen. The surrogate recoveries are reported along with the well sample results in Appendix 2, Table A-1.

Table 6. Quality Control (QC) results for 2,4-D from CDFA laboratory. One QC matrix-spike was analyzed with each extraction set.

Extraction Date	Extraction Set [Blind Spikes in Brackets]	Spiked Level (ppb)	Results (ppb)	% Recovery
7/2/2018	10, 19, 37, 46, 55, 64, 73, 82, 307, 352	0.15	0.102	68.0
7/17/2018	01, 28, 100, [127], 262, 271, 280, 289, 298, 316	0.15	0.114	76.0
7/30/2018	91, 109, 136, 145, 154, 163, 172, 181	0.15	0.140	93.3
8/6/2018	217, 226, 361, 370, 379, 388, 397, 406, 415, 424	0.15	0.182	121
8/16/2018	433, 442, 451, 460, 469, 514	0.15	0.112	74.7
8/22/2018	190, [199], 208, 235, 244, 253, 325, 334, 343	0.15	0.131	87.3
8/23/2018	478, 523, 532, 541, 550, 559, 568, 577, 586	0.15	0.101	67.3
Average recovery				83.9
Deviation				17.5
Upper Warning Limit				140
Lower Warning Limit				54.9

Table 7. Quality Control (QC) summary for seven 2,4-D analysis extraction sets.

QC Type	Total Number	Results
Lab matrix-blanks	7	ND (All)
QC matrix-spikes	7	All within warning limits
Blind spikes	2	All within warning limits

ND = no detections were reported at or above the method detection limit.

Table 8. Quality Control (QC) summary for Triazine Screen extraction sets.

QC Type	Total Number	Results
Lab matrix-blanks	11	ND (All)
QC matrix-spikes	11	ACET had 3 recoveries (ranging from 69.0 to 73.0%) below the LCL of 74.5%. DEA had one recovery at 71.0% that was below the LCL of 74.7%. All other analytes were within Control Limits for all 11 spikes.
Blind spikes	1	All within control limits

ND = no detections were reported at or above the method detection limit.
LCL = lower control limit

Table 9. Quality Control (QC) summary for Multi-Analyte Screen extraction sets.

QC Type	Total Number	Results
Lab matrix-blanks	6	ND (All)
QC matrix-spikes	6	All within control limits
Blind spikes	1	All within control limits

ND = no detections were reported at or above the method detection limit.

Table 10. Blind spike levels and recoveries.

Sample Number	Extraction Date	Analysis Screen	Analyte	Spike Level (ppb)	Result (ppb)	% Recovery	Control Limits %	Control Limit Exceeded
127	7/17/2018	2,4-D	2,4-D	0.30	0.25	83.3	50-170	No
129	7/16/2018	Multi-Analyte	Carbaryl	0.25	0.238	95.5	64.6-144	No
			Dimethoate	0.15	0.153	102	72.5-116	No
			Fenamiphos	0.20	0.163	81.5	73.5-118	No
			Fonofos	0.15	0.172	115	48.4-147	No
			Prometryn	0.10	0.089	89.0	46.3-156	No
199	8/22/2018	2,4-D	2,4-D	0.15	0.128	85.3	50-170	No
200	8/17/2018	Triazine	ACET	0.15	0.147	98.0	74.5-109	No
			Bromacil	0.15	0.133	88.7	68.6-117	No
			Hexazinone	0.20	0.147	73.5	68.5-110	No
			Norflurazon	0.25	0.208	83.2	52.6-151	No

DISCUSSION AND CONCLUSIONS

2,4-D: Samples collected and analyzed from 60 wells located in areas of high 2,4-D use resulted in no detectable concentrations of 2,4-D. Data from DPR's Well Inventory Database (WIDB) show that 10,127 wells were analyzed for 2,4-D over the last 35 years by DPR and other public agencies in California. Of those samples, 19 wells (0.19%) sampled by other public agencies had reported detections of 2,4-D (CDPR, 2021). The detections reported by these agencies were not confirmed in subsequent testing of the same well by DPR. Since 1987, DPR has conducted 10 groundwater monitoring studies for 2,4-D in response to reported detections; the herbicide was not detected in these studies (CDPR, 2021). In 2014, DPR detected 2,4-D in a domestic well in Sutter County. Subsequently, DPR was unable to resample the original well after several attempts to contact the owner; however, 2,4-D was not detected when sampling multiple wells surrounding the original well (Bergin, 2013; CDPR, 2021).

Other GWPL Pesticides and Degradates: Of the 22 wells in this study with detections of 3CCR section 6800(a)-listed pesticides/degradates, 19 are located in GWPAs. No further investigations of these detections were determined to be necessary since the levels of detection were below the established drinking water quality standards and these pesticides are already regulated to protect groundwater in these areas under 3CCR section 6487.

Three of the wells with detections of 3CCR section 6800(a)-listed pesticides/degradates are located outside GWPAs in the following counties and locations by County Township/Range-Section (COMTRS):

- Butte County 22N/01E-19 (Location Code 04-04)
- Fresno County 16S/19E-26 (Location Code 10-09)
- Solano County 06N/01E-24 (Location Code 48-02)

DPR will evaluate these three detections to determine if further monitoring or regulatory action is required. The trace detections found in this study do not trigger any regulatory processes or response but can serve as indicators of areas that may need follow-up or future groundwater monitoring.

No 3CCR section 6800(b)-listed pesticides were detected in any of the 60 wells above the RL.

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APPENDIX 1: FIGURES

Figure 3. 2,4-D use per section and location of wells sampled in Butte County (CDPR, 2018).

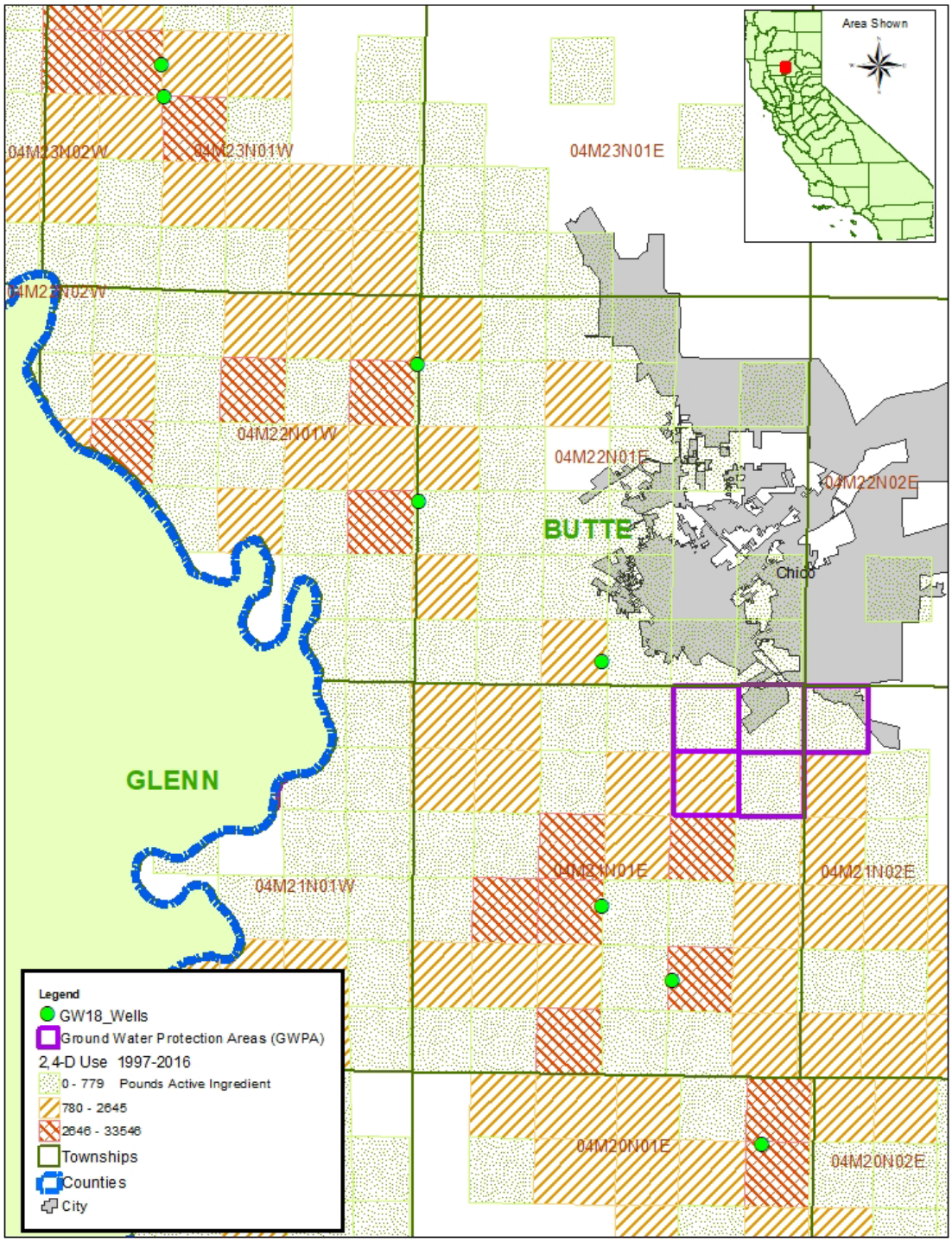


Figure 4. 2,4-D use per section and location of wells sampled in Fresno County (CDPR, 2018).

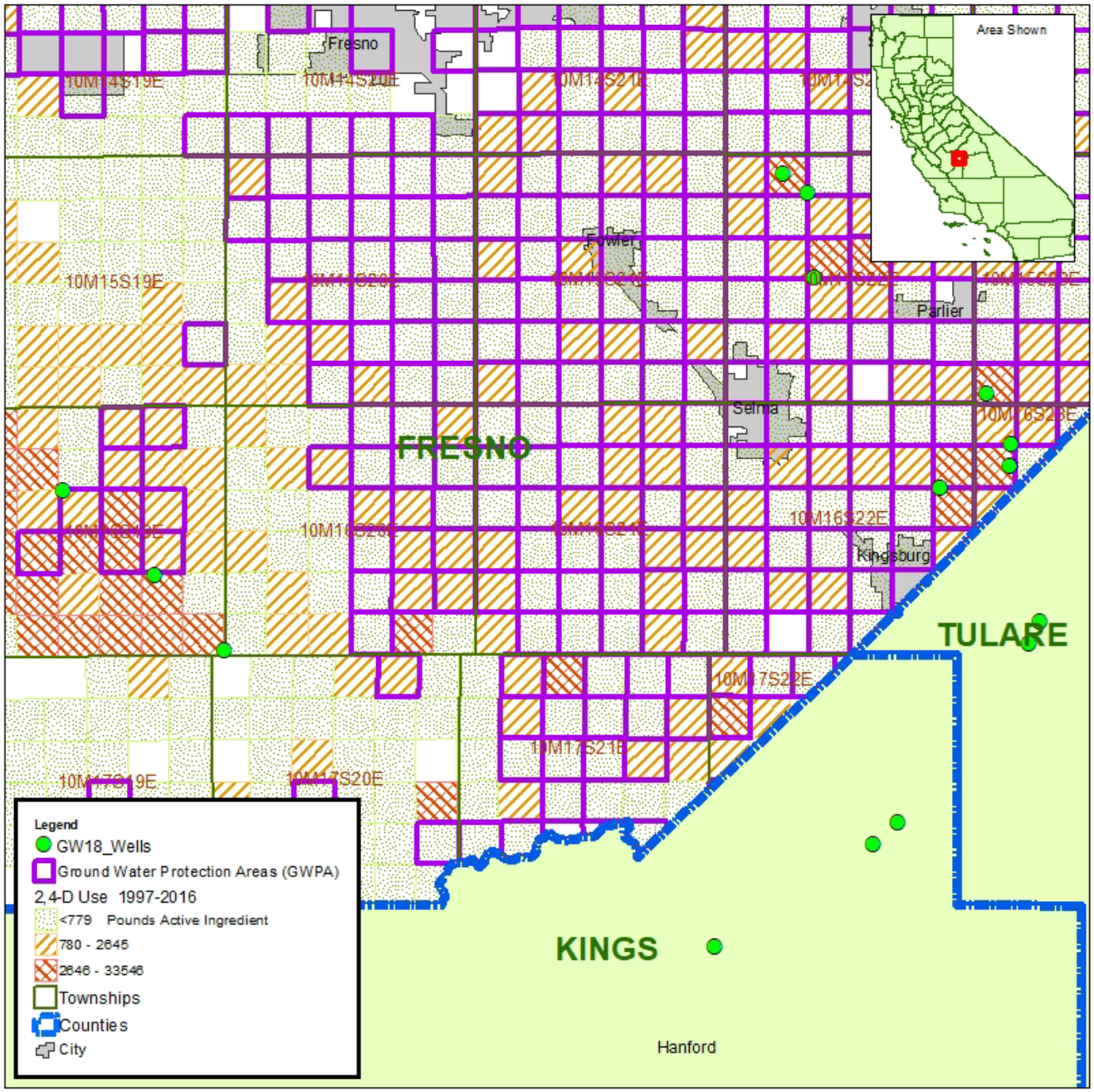


Figure 5. 2,4-D use per section and location of wells sampled in Kings County (CDPR, 2018).

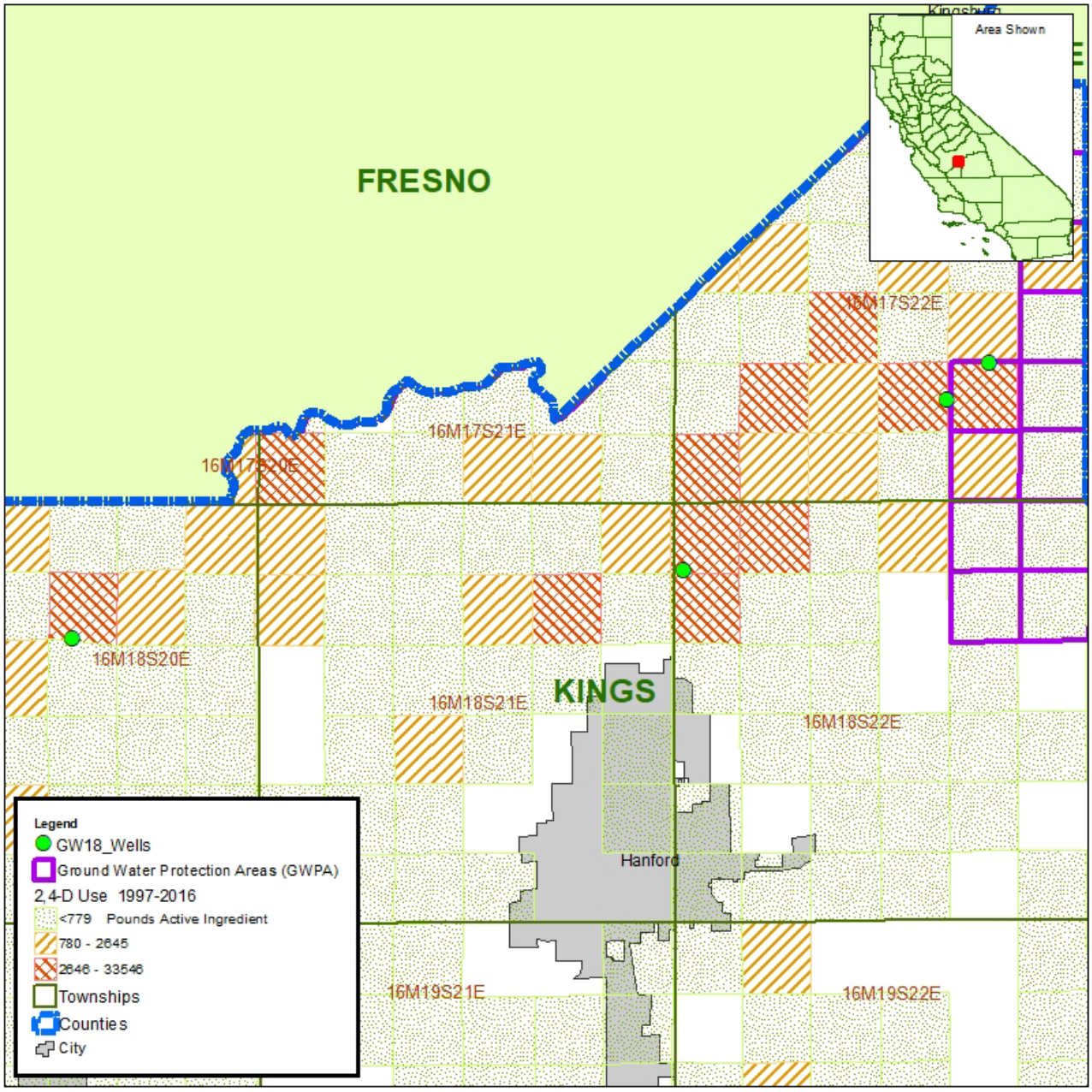


Figure 6. 2,4-D use per section and location of wells sampled in Merced County (CDPR, 2018).

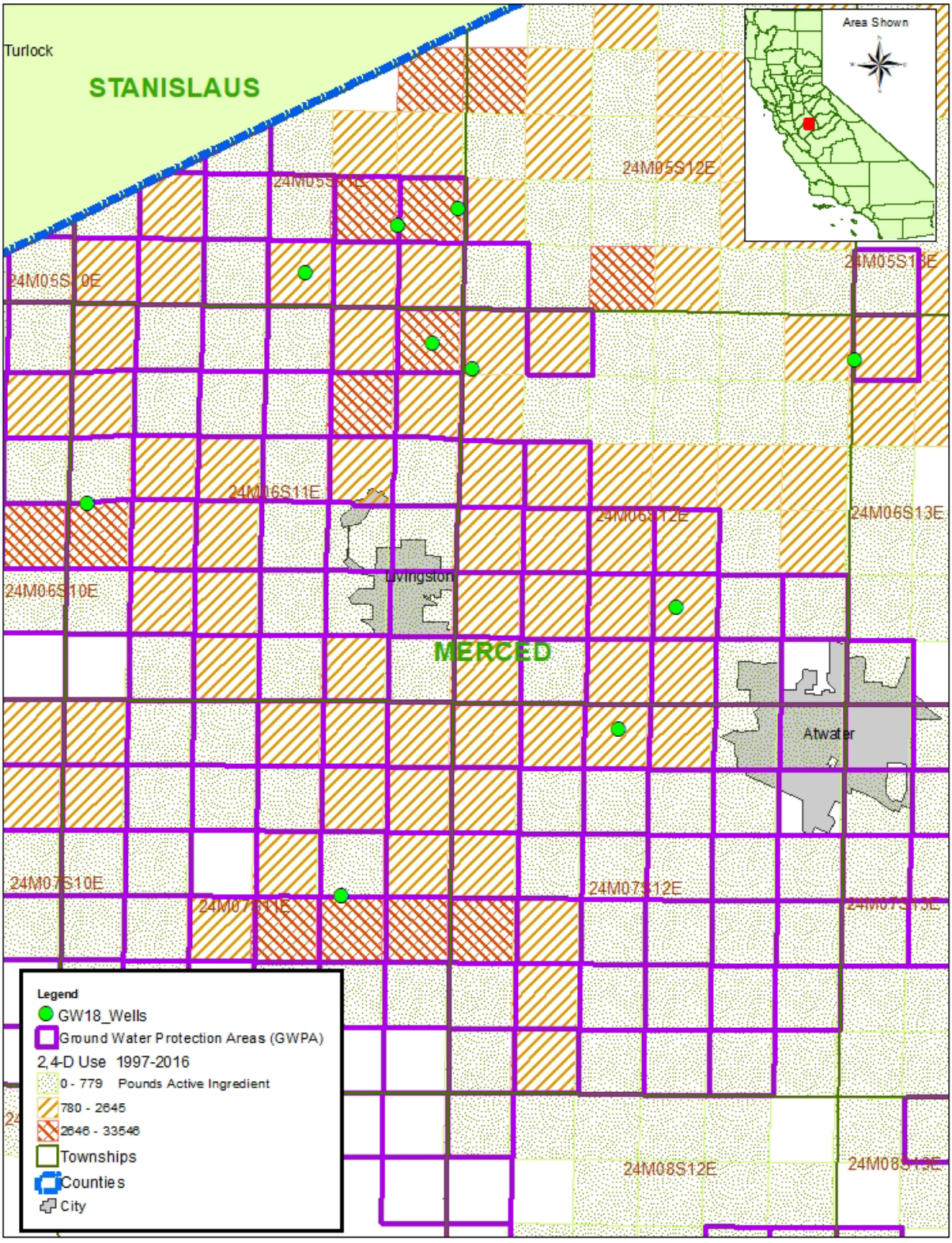


Figure 7. 2,4-D use per section and location of wells sampled in San Joaquin County (CDPR, 2018).

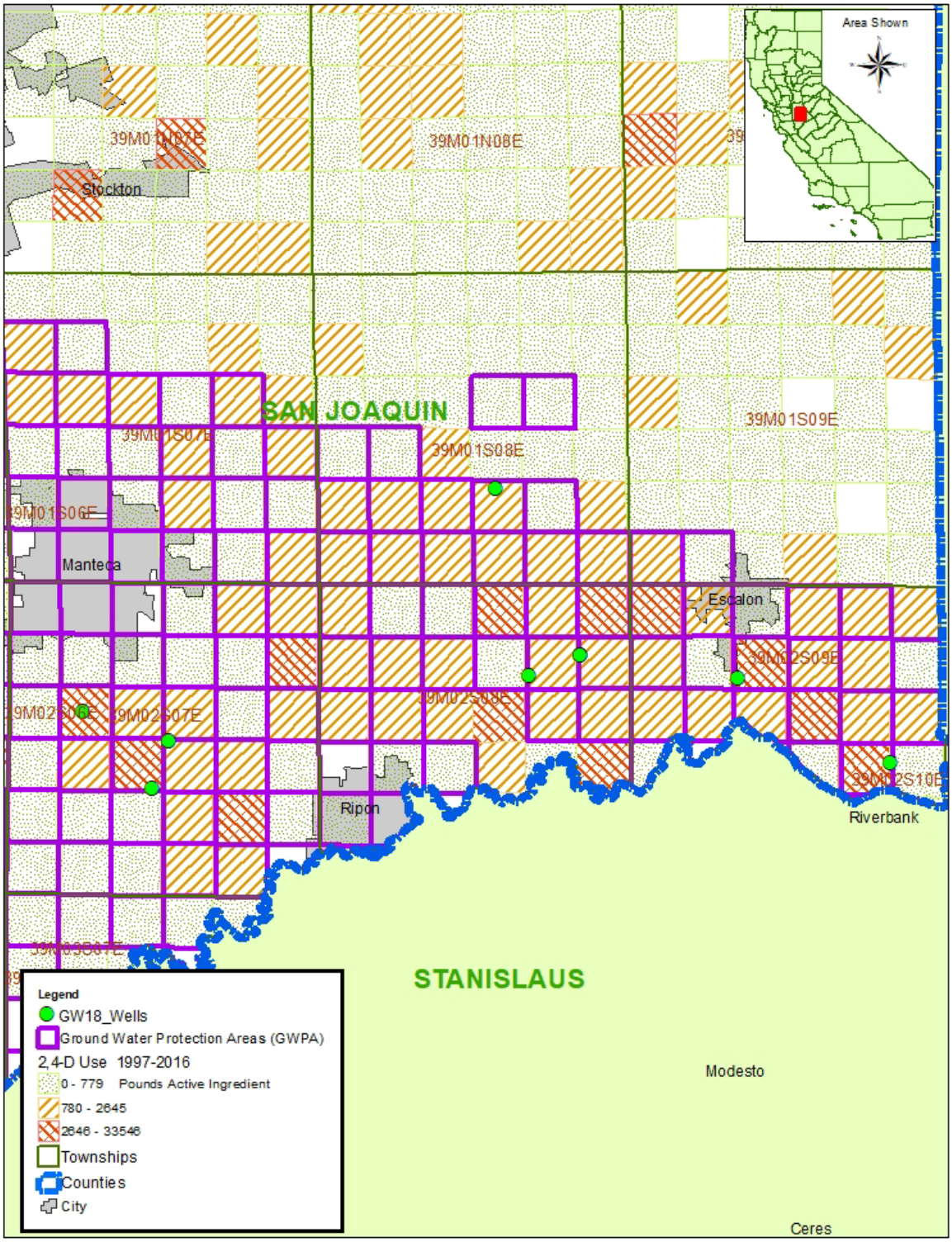


Figure 8. 2,4-D use per section and location of wells sampled in Solano County (CDPR, 2018).

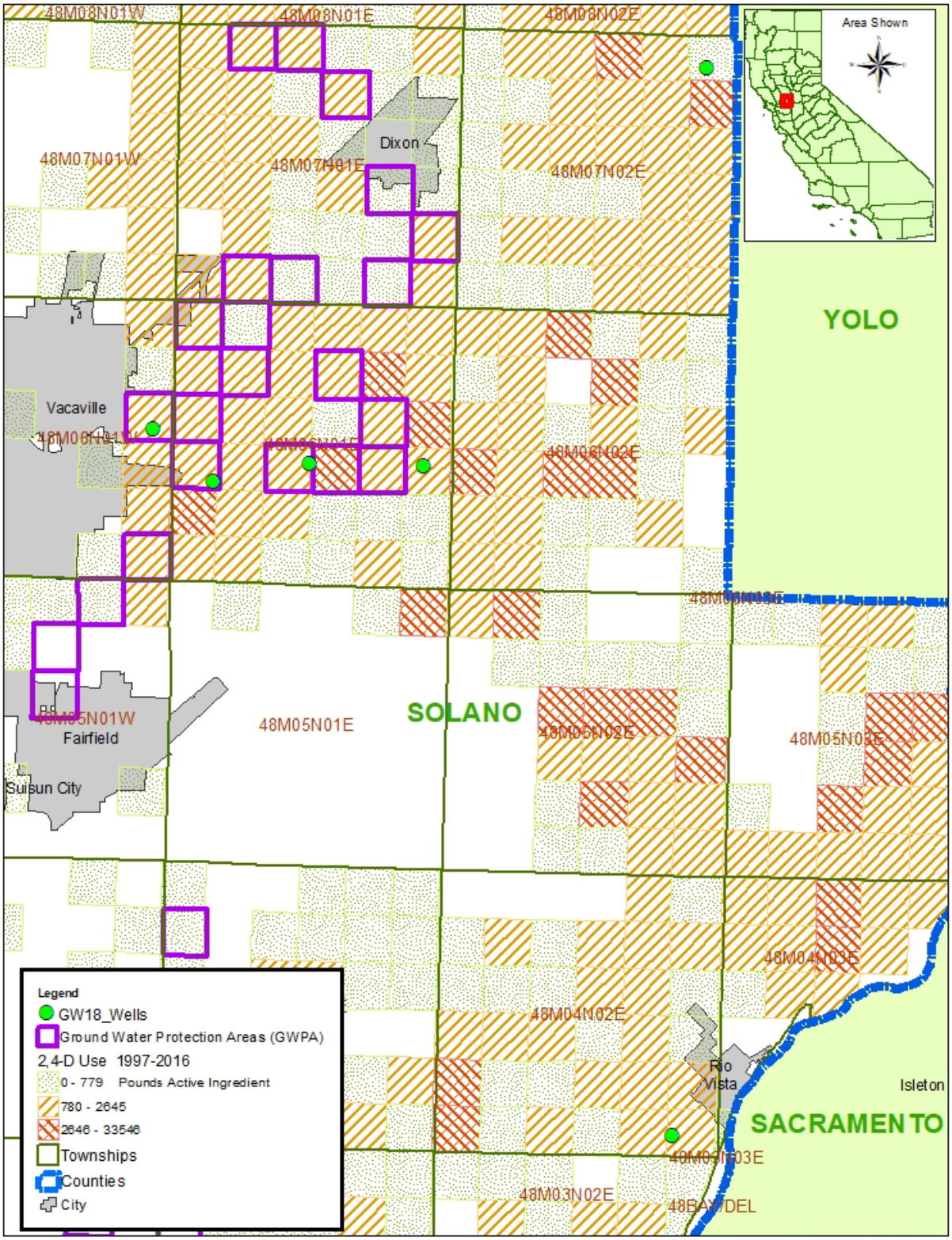


Figure 9. 2,4-D use per section and location of wells sampled in Stanislaus County (CDPR, 2018).

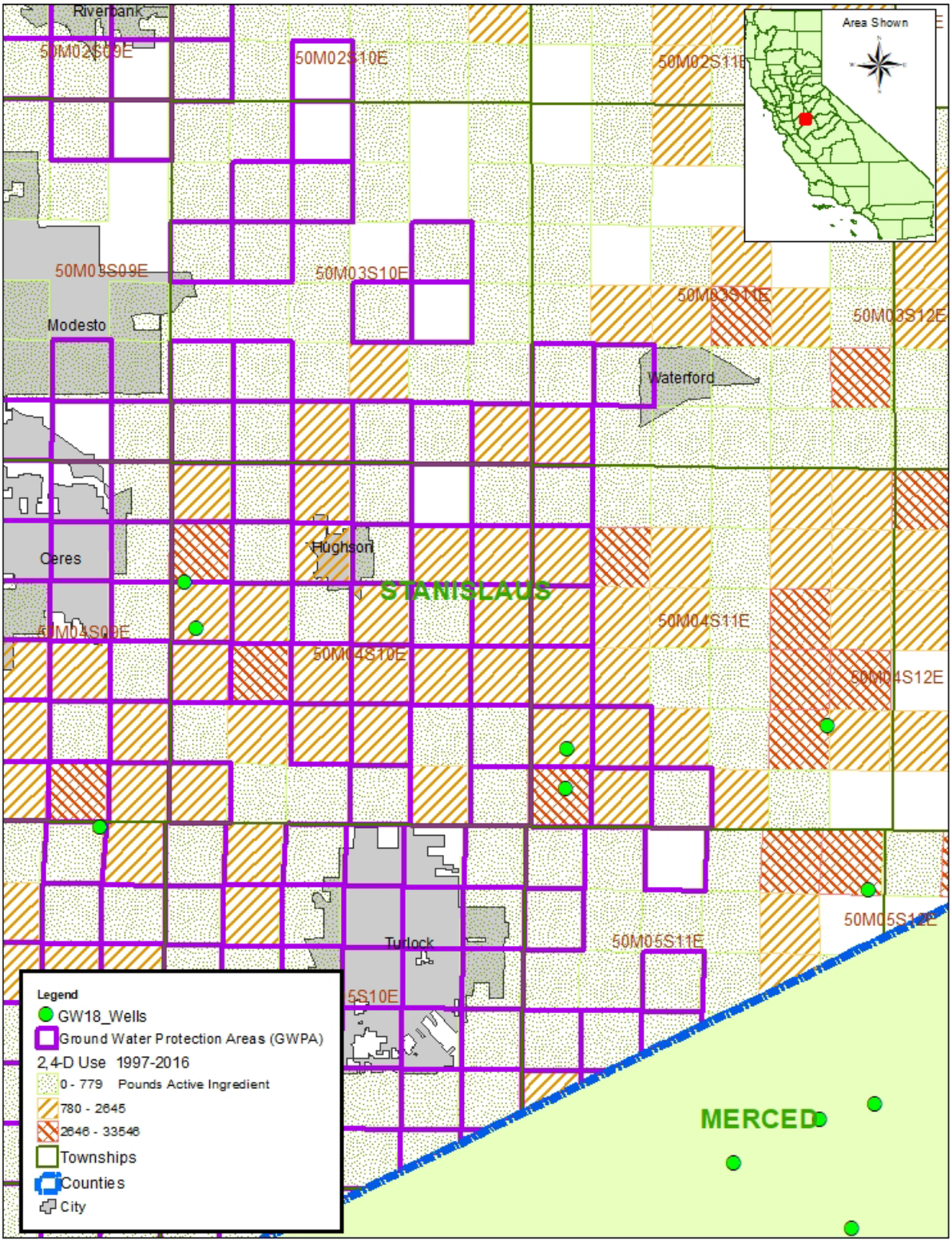
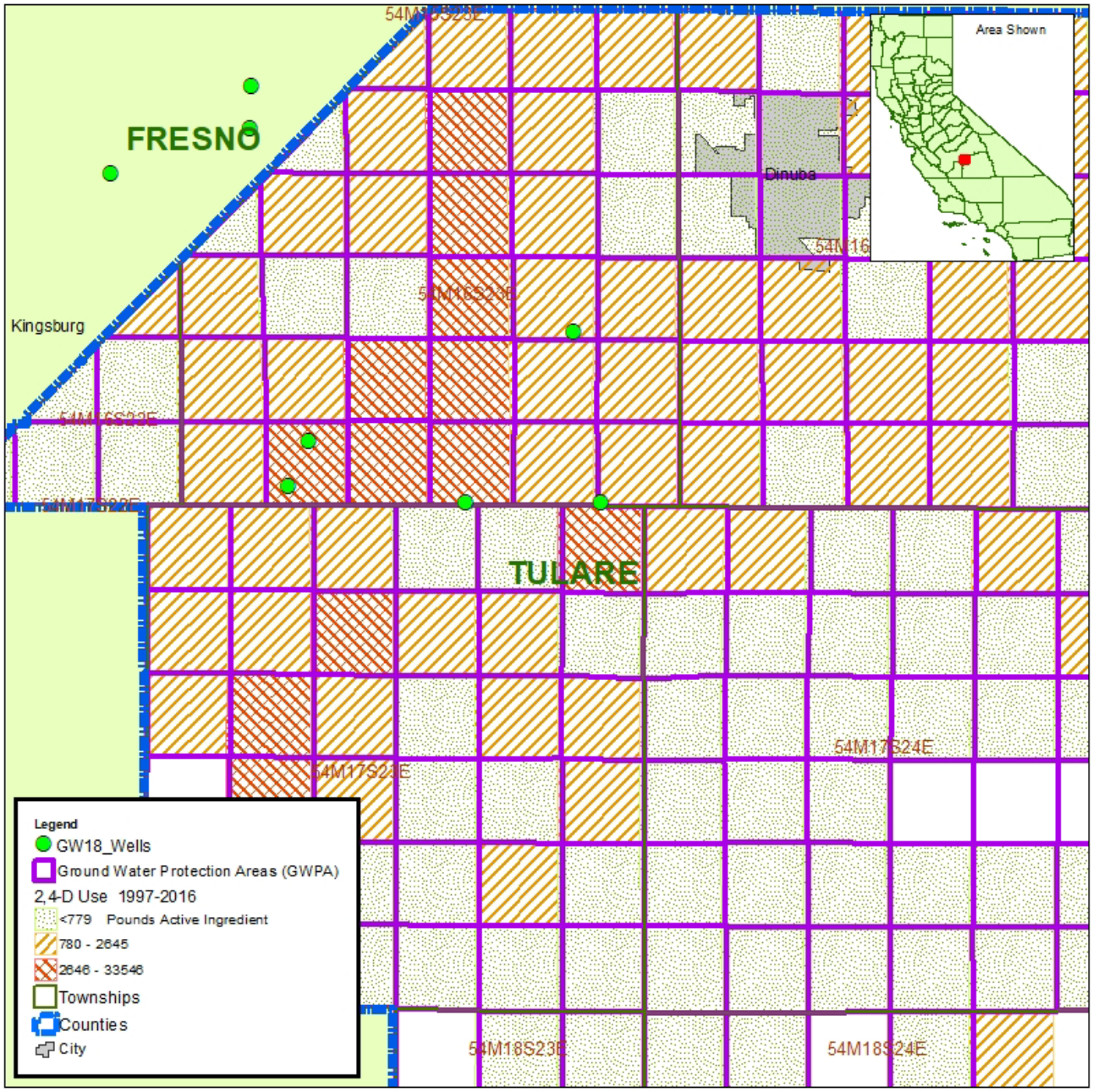


Figure 10. 2,4-D use per section and location of wells sampled in Tulare County (CDPR, 2018).



APPENDIX 2: TABLES

Table A-1. Triazine Screen (EMON-SM-62.9) results* (ppb) and propazine surrogate recoveries for all wells sampled.

County	Location Code	Analysis Date	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN	Hexazinone	Norflurazon	Simazine	Propazine %
Butte	04-01	7/30/2018	ND[1]	ND	ND	ND	ND	ND	ND	ND	ND	ND	76.0%
Butte	04-02	7/30/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	86.0%
Butte	04-03	7/30/2018	trace[2]	ND	ND	trace	trace	ND	ND	ND	ND	ND	83.5%
Butte	04-04	7/30/2018	0.156	ND	ND	0.162	ND	ND	ND	ND	ND	ND	82.5%
Butte	04-05	7/30/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	81.5%
Butte	04-06	7/30/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	87.0%
Butte	04-07	7/30/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	80.5%
Butte	04-08	7/30/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	82.0%
Fresno	10-01	7/2/2018	0.105	ND	ND	0.166	ND	trace	0.187	ND	0.123	trace	80.0%
Fresno	10-02	7/2/2018	trace	ND	ND	0.087	ND	ND	0.127	ND	trace	trace	71.0%
Fresno	10-03	7/2/2018	0.123	0.074	0.192	0.221	0.066	trace	trace	trace	ND	trace	81.5%
Fresno	10-04	7/2/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	74.0%
Fresno	10-05	7/2/2018	0.064	ND	ND	trace	ND	ND	ND	ND	ND	trace	83.5%
Fresno	10-06	7/2/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	84.0%
Fresno	10-07	7/2/2018	trace	ND	ND	0.172	ND	ND	ND	ND	ND	ND	73.5%
Fresno	10-08	7/2/2018	0.117	ND	ND	0.154	ND	ND	ND	ND	ND	0.069	76.5%
Fresno	10-09	7/2/2018	trace	ND	ND	0.054	ND	ND	ND	ND	ND	trace	80.5%
Fresno	10-10	7/2/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	80.5%
Kings	16-01	7/17/2018	trace	ND	ND	Trace	ND	trace	ND	ND	ND	ND	77.5%
Kings	16-02	7/17/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	73.5%
Kings	16-04	7/17/2018	trace	ND	ND	ND	ND	ND	ND	ND	ND	ND	74.0%
Kings	16-05	7/17/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	73.0%
Merced	24-01	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	72.0%
Merced	24-02	8/6/2018	trace	ND	trace	0.102	ND	ND	0.092	ND	trace	trace	87.0%

County	Location Code	Analysis Date	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN	Hexazinone	Norflurazon	Simazine	Propazine %
Merced	24-03	8/6/2018	0.097	ND	ND	0.205	ND	ND	0.260	ND	trace	trace	68.5%
Merced	24-04	8/6/2018	ND	ND	ND	Trace	ND	ND	trace	ND	ND	ND	79.5%
Merced	24-05	8/6/2018	ND	ND	ND	Trace	ND	ND	ND	ND	ND	ND	81.0%
Merced	24-06	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	75.5%
Merced	24-07	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	76.0%
Merced	24-08	8/6/2018	ND	ND	ND	ND	ND	ND	ND	trace	ND	ND	72.5%
Merced	24-09	8/6/2018	trace	ND	ND	Trace	ND	ND	ND	ND	ND	ND	69.0%
Merced	24-10	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	77.0%
San Joaquin	39-01	8/23/2018	0.058	ND	ND	0.231	ND	ND	ND	ND	ND	ND	72.5%
San Joaquin	39-02	8/23/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	68.0%
San Joaquin	39-03	8/23/2018	trace	ND	ND	0.439	ND	ND	ND	ND	ND	ND	73.5%
San Joaquin	39-04	8/23/2018	ND	ND	ND	Trace	ND	ND	ND	ND	ND	ND	74.5%
San Joaquin	39-05	8/23/2018	ND	ND	ND	ND	trace	ND	ND	ND	ND	ND	84.0%
San Joaquin	39-06	8/23/2018	0.059	ND	ND	0.158	ND	trace	trace	ND	ND	ND	83.0%
San Joaquin	39-07	8/23/2018	0.181	ND	ND	0.371	ND	ND	0.185	ND	trace	trace	85.5%
San Joaquin	39-08	8/23/2018	0.095	ND	ND	0.095	ND	ND	0.200	ND	trace	trace	84.5%
San Joaquin	39-09	8/23/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	78.0%
Solano	48-01	8/16/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	79.5%
Solano	48-02	8/16/2018	trace	ND	ND	0.215	ND	ND	ND	ND	ND	ND	79.0%
Solano	48-03	8/16/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	86.5%
Solano	48-04	8/16/2018	ND	0.073	ND	ND	0.072	ND	ND	ND	ND	ND	85.5%
Solano	48-05	8/16/2018	ND	ND	ND	ND	ND	ND	trace	ND	0.061	ND	77.5%
Solano	48-06	8/16/2018	ND	ND	ND	Trace	ND	ND	ND	ND	ND	ND	89.0%
Stanislaus	50-01	8/22/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	70.5%
Stanislaus	50-02	8/22/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	63.0%
Stanislaus	50-03	8/22/2018	0.058	ND	ND	0.331	ND	ND	0.227	trace	trace	trace	77.0%
Stanislaus	50-04	8/22/2018	trace	ND	ND	0.332	ND	ND	0.068	ND	ND	ND	78.0%

County	Location Code	Analysis Date	ACET	Atrazine	Bromacil	DACT	DEA	Diuron	DSMN	Hexazinone	Norflurazon	Simazine	Propazine %
Stanislaus	50-05	8/22/2018	0.120	ND	ND	0.504	ND	ND	trace	ND	ND	trace	76.0%
Stanislaus	50-06	8/22/2018	ND	ND	ND	trace	ND	ND	ND	ND	ND	ND	75.0%
Stanislaus	50-07	8/22/2018	ND	ND	ND	trace	ND	ND	ND	ND	ND	ND	76.0%
Stanislaus	50-08	8/22/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	69.5%
Tulare	54-01	7/17/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	86.0%
Tulare	54-02	7/17/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	79.5%
Tulare	54-03	7/17/2018	trace	ND	ND	trace	ND	ND	ND	ND	ND	ND	73.5%
Tulare	54-04	7/17/2018	0.068	trace	ND	0.099	ND	trace	ND	ND	ND	trace	83.0%
Tulare	54-05	7/17/2018	ND	ND	ND	ND	ND	ND	ND	ND	ND	trace	77.0%

*Prometon is not included in this table because it was not detected in any samples.

Field blanks submitted for positive samples were all non-detects.

[1] ND = No detections were reported at or above the method detection limit.

[2] Trace = Positive result between the method detection limit and the reporting limit of 0.05 ppb.

Table A-2. Multi-Analyte Screen (EMON-SM-05-032) results* (ppb) for all wells sampled.

County	Location Code	Sample Number	Sample Code	Analysis Date	Atrazine	Bromacil	Diuron	Metolachlor	Norflurazon	Simazine	Etho-prophos	Phorate
Butte	04-01	138	P3	8/1/2018	ND[1]	ND	ND	ND	ND	ND	ND	ND
Butte	04-02	093	P3	8/1/2018	ND	ND	ND	ND	ND	ND	ND	ND
Butte	04-03	156	P3	8/1/2018	ND	ND	ND	ND	ND	ND	ND	ND
Butte	04-04	165	P3	8/1/2018	ND	ND	ND	ND	ND	ND	ND	ND
Butte	04-05	147	P3	8/1/2018	ND	ND	ND	ND	ND	ND	ND	ND
Butte	04-06	111	P3	8/1/2018	ND	ND	ND	ND	ND	ND	ND	ND
Butte	04-07	174	P3	8/1/2018	ND	ND	ND	ND	ND	ND	ND	ND
Butte	04-08	183	P3	8/1/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-01	048	P3	7/2/2018	ND	ND	trace[2]	ND	0.167	0.051	ND	ND
Fresno	10-01	054	FB3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-02	075	P3	7/2/2018	ND	ND	ND	ND	trace	trace	ND	ND
Fresno	10-02	081	FB3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-03	012	P3	7/2/2018	0.081	0.231	trace	ND	ND	0.060	ND	ND
Fresno	10-03	018	FB3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-04	039	P3	7/2/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-05	084	P3	7/2/2018	ND	ND	ND	ND	ND	0.056	ND	ND
Fresno	10-05	090	FB3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-06	066	P3	7/2/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-07	309	P3	7/2/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-08	021	P3	7/2/2018	ND	ND	ND	ND	ND	0.086	ND	ND
Fresno	10-08	027	FB3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-09	057	P3	7/2/2018	ND	ND	ND	ND	ND	trace	ND	ND
Fresno	10-09	063	FB3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Fresno	10-10	354	P3	7/2/2018	ND	ND	ND	ND	ND	ND	ND	ND
Kings	16-01	003	P3	7/16/2018	ND	ND	trace	ND	ND	ND	ND	ND
Kings	16-02	300	P3	7/16/2018	ND	ND	ND	ND	ND	ND	ND	ND

County	Location Code	Sample Number	Sample Code	Analysis Date	Atrazine	Bromacil	Diuron	Metolachlor	Norflurazon	Simazine	Etho-prophos	Phorate
Kings	16-04	030	P3	7/16/2018	ND	ND	ND	ND	ND	ND	ND	ND
Kings	16-05	318	P3	7/16/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-01	363	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-02	219	P3	8/6/2018	ND	trace	ND	ND	trace	trace	ND	ND
Merced	24-03	228	P3	8/6/2018	ND	trace	ND	ND	trace	trace	ND	ND
Merced	24-04	372	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-05	390	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-06	399	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-07	381	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-08	417	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-09	408	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
Merced	24-10	426	P3	8/6/2018	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	39-01	480	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	39-02	525	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	39-03	534	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	39-04	543	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	39-05	552	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
San Joaquin	39-06	561	P3	8/20/2018	ND	ND	trace	ND	ND	ND	ND	trace
San Joaquin	39-07	570	P3	8/20/2018	ND	ND	ND	ND	trace	ND	ND	ND
San Joaquin	39-08	579	P3	8/20/2018	ND	ND	ND	trace	trace	trace	ND	ND
San Joaquin	39-09	588	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
Solano	48-01	462	P3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Solano	48-02	516	P3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Solano	48-03	444	P3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND
Solano	48-04	471	P3	8/14/2018	0.081	ND	ND	ND	ND	ND	ND	ND
Solano	48-05	453	P3	8/14/2018	ND	ND	ND	ND	0.079	ND	ND	ND
Solano	48-06	435	P3	8/14/2018	ND	ND	ND	ND	ND	ND	ND	ND

County	Location Code	Sample Number	Sample Code	Analysis Date	Atrazine	Bromacil	Diuron	Metolachlor	Norflurazon	Simazine	Etho-prophos	Phorate
Stanislaus	50-01	210	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	50-02	336	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	50-03	246	P3	8/20/2018	ND	ND	ND	ND	trace	ND	ND	ND
Stanislaus	50-04	255	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	50-05	192	P3	8/20/2018	ND	ND	ND	ND	ND	trace	ND	ND
Stanislaus	50-06	345	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	50-07	327	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	50-08	237	P3	8/20/2018	ND	ND	ND	ND	ND	ND	ND	ND
Tulare	54-01	102	P3	7/16/2018	ND	ND	ND	ND	ND	ND	ND	ND
Tulare	54-02	264	P3	7/16/2018	ND	ND	ND	ND	ND	ND	trace	ND
Tulare	54-03	291	P3	7/16/2018	ND	ND	ND	ND	ND	ND	ND	ND
Tulare	54-04	273	P3	7/16/2018	ND	ND	trace	ND	ND	trace	ND	ND
Tulare	54-05	282	P3	7/16/2018	ND	ND	ND	ND	ND	ND	ND	ND

*The chemicals analyzed with EMON-SM-05-032 that were not detected are not included in this table: azoxystrobin, bensulide, carbaryl, diazinon, dimethenamide, dimethoate, ethofumesate, fludioxonil, imidacloprid, linuron, mefenoxam/metalaxyl, methiocarb, metribuzin, napropamide, oryzalin, prometon, tebuthiuron, thiamethoxam, thiobencarb, and uniconazole.

FB3 = Field blank sample analyzed for a positive well.

[1] ND = No detections were reported at or above the method detection limit.

[2] Trace = Positive result between the method detection limit and the reporting limit of 0.05 ppb.