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Verification of Pesticide Residue Detections Reported in Well Water by the U.S. Geological Survey Groundwater Ambient Monitoring and Assessment Program for Data Collected between May 2004 and June 2018

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February 2022

Summary

The Groundwater Protection Program (GWPP) of the Department of Pesticide Regulation (DPR) collects pesticide residue data from well sampling studies conducted within California. For residues of chemicals used in agricultural applications, the GWPP may conduct follow-up sampling to verify detections and to determine if the chemical residues are the result of agricultural use. Reported detections are subject to: (1) review of any submitted laboratory quality assurance and quality control data (QA/QC), and (2) verification of registered pesticide product applications in the landscape surrounding the wellhead. The United States Geological Survey (USGS), through the Groundwater Ambient Monitoring and Assessment (GAMA) Program, provides well water sampling data for the California State Water Resources Control Board. In a recent publication by the USGS, the data collected from 2004 through 2018 was subjected to a revised QA/QC methodology. This revision by the USGS resulted in some previously reported detections being updated to non-detection status. DPR's GWPP investigated the remaining detections from the USGS report to determine the recommended actions DPR should take in response to these reported detections. The factors in determining DPR's response to a detection are examination of the reported pesticide use around the wellhead, analysis of the landscape surrounding the wellhead, consistency in detections reported in a well over time, and comparison to detection frequency of known groundwater contaminants.

This assessment recommends the following actions in response to the reported detections:

Follow-up sampling is not recommended: detections were not verified from pesticide use and landscape analysis

- Acetochlor
- Alachlor
- 2,6-Diethylaniline
- Chlorpyrifos
- Fipronil
- Fipronil Sulfide
- Desulfinyl Fipronil
- Hydroxyatrazine
- Imazethapyr
- Pendimethalin
- Terbuthylazine
- Prometryn

Follow-up sampling was conducted by GWPP, but reported detections were not verified

- Diazinon
- Metribuzin
- Propanil
- Triclopyr

GWPP will evaluate the feasibility of a targeted groundwater study

- EPTC

Additional reported detections may trigger groundwater studies by GWPP

- Metalaxyl
- Metolachlor
- Myclobutanil

No action is necessary: pesticides are no longer registered for use

- Dieldrin
- Dinoseb
- Diphenamid

Introduction

The Groundwater Protection Program (GWPP) of the California Department of Pesticide Regulation (DPR) maintains a database of well sampling results from studies conducted in California to determine the presence of pesticide residues in groundwater. The Pesticide Contamination Prevention Act (PCPA) requires all state agencies to submit results of well sampling studies for pesticide residues to DPR. The data are compiled in the Well Inventory Database maintained by the GWPP. Data from these submissions supply two types of important information: (1) identification of new geographical locations with detections of pesticides known to have contaminated groundwater in other locations and, (2) detection of new pesticide residues that had not previously been detected in groundwater or determined to be groundwater contaminants. The GWPP evaluates this information and determines the need to conduct follow-up studies to verify the reported detections.

In the 1990s, the United States Geological Survey (USGS) initiated a nationwide water sampling and monitoring program, denoted the National Water Quality Assessment Program (NAWQA). Sampling of pesticide residues and other constituents in groundwater was one facet of the program. In California, the program was expanded to address a mandate by the legislature for the California State Water Resources Control Board to assess the condition of all groundwater basins in California. That mandate led to the creation of the Groundwater Ambient Monitoring and Assessment (GAMA) Program. The GAMA Program encompassed a large number of sampling locations. Owing to the large scope of the program, some aspects related to analytical methodology and quality assurance/quality control (QA/QC) procedures were limited compared to procedures employed by the GWPP. For example, large analytical screen analysis was standard procedure where results for many chemicals are derived from a single water sample — a procedure typically requiring higher levels of QA/QC for correct chemical residue identification. Other examples include wells with residue detections not routinely resampled for verification, and field QA/QC streamlined where field blank water samples were randomly portioned as only 10% of the total number of well water samples.

Fram and Stork (2019) provided an updated QA/QC analysis of the GAMA Program's data from 2004 through 2018. They subjected the initial well sampling dataset to an updated five-step QC procedure. The revised procedure included adjustments to results generated over time from laboratory blank samples. The addition of this procedure also affected the outcome of data generated by the NAWQA program (Medalie et al., 2019). Application of the revised QA/QC methodology to the GAMA Program's previously collected data resulted in changes to some sampling results from detected to non-detected status. One reason for the change in status was an increase in the method detection limit (MDL) for some chemicals.

Since detection of pesticide residues in well water, as reported by DPR's GWPP has potential regulatory consequences, rigorous QA/QC procedures are incorporated into the GWPP's sampling protocol to ensure verification of detections. For pesticide residues not previously detected in wells by the GWPP, a backup sample is analyzed to verify new detections. An integral step in the verification process is determining potential pesticide use around a

wellhead. In California, full reporting of agricultural pesticide use has been required since 1990. Pesticide use is reported within each section of land, where a "section" is defined by the Public Lands Survey Coordinate System as ideally a one-square-mile area and a "township" is a square area of land composed of 36 sections (Davis and Foote, 1966). The data for pesticide use in a section of land is available through DPR's Pesticide Use Reporting database (CDPR, 2020). A lack of reported pesticide use in a section or in surrounding sections of a chemical detection in well water indicates that agricultural use is an unlikely source for the detection of the residue. In an extreme example, acetochlor residues were reported in some well water samples. However, since acetochlor has never been a constituent in a registered pesticide product in California, agricultural use would not likely be the source of the detection. The nature of the landscape surrounding the wellhead is another factor used to verify or invalidate a detection. For example, a reported well water detection of a chemical used exclusively for production agriculture would be questionable if the wellhead was surrounded by a rural forested landscape. The cropping pattern surrounding the wellhead is another factor that provides a link between the application of a chemical and the detection of that chemical in well water. For example, a chemical registered exclusively for use on row crops is not likely to be used in a landscape near a well surrounded by orchards. The combination of no reported use and no appropriate landscape surrounding a wellhead indicates that agricultural use was highly unlikely to be the source of a reported detection. Other potential sources of the detection could be laboratory-derived errors or sample contamination during field sampling, transport, or storage. An additional verification method is to compare a reported detection of a previously undetected chemical to the detection patterns of chemicals known to move to groundwater from agricultural applications. The pathway for movement to groundwater within a specific landscape is similar for all chemicals. If a known groundwater contaminant is absent from a well despite equal or greater use near the well than that of a newly detected chemical residue, then the validity of the newly reported detection is questionable. Currently, pesticide active ingredients known to contaminate California's groundwater that could provide some level of validation of a new chemical detection are bromacil, diuron, hexazinone, norflurazon, and simazine. Breakdown products of these parent pesticides have also been detected in groundwater (CDPR, 2020a), and can similarly help validate detections of new chemicals. Although atrazine and its breakdown product are also known contaminants, detections of these chemicals were not used for comparison purposes in this analysis because the use of atrazine in California has been minimal since 1990. Although some additional uses of atrazine have returned, its lack of continuous historical applications and detections in groundwater minimizes its usefulness when verifying a detection of a new chemical.

Pesticide Use and Landscape Analysis for GAMA Program Detections

In accordance with the above discussion, verification of reported well water detections was conducted for the GAMA Program's revised dataset for wells sampled from May 2004 to June 2018. These revised detections were reported to DPR in May 2019 (Fram and Stork, 2019). The GWPP analysis of pesticide use and landscape surrounding each wellhead with a reported pesticide detection is described for agricultural chemical residues not previously verified in California's groundwater. Each reported chemical detection in the following sections includes:

- The reported numerical USGS parameter code for each chemical.
    - Chemicals could have multiple USGS parameter codes because these codes are associated with the specific chemical analytical methodology used for detection in the water sample (available at https://nwis.waterdata.usgs.gov/usa/nwis/pmcodes).
- Tables for each reported chemical specifying:
    - Well location as denoted by the Township/Range coordinates
    - Date sampled
    - Results of analysis for salient chemical residues
    - Revised Long-term Reporting Limit (LRL) for each chemical
    - Amount of pesticide use reported within the section of land containing the sampled well and in the eight sections of land surrounding the wellhead.
        - Reported pesticide use was summed from 1990 until one year prior to the reported detection.
- Graphics downloaded from Google Earth Pro™ (Google Earth, earth.google.com/web/) to show the landscape surrounding the sampled well.
    - The yellow pin in the graphic is the location of the well as reported by the latitude and longitude data supplied with the well sampling information.
    - The source for the image is located on the bottom left of the graphic.

The revised LRL is usually calculated as twice the concentration of the MDL determined for each chemical (Fram and Stork, 2019). Based on the detection verification methodology discussed above, if the detections are determined to not be a result of agricultural use, then DPR's GWPP recommends that follow-up sampling is unnecessary unless additional detections are reported and substantiated as a result of agricultural use.

Acetochlor: USGS Parameter Code 49260

Pesticide use and landscape analysis: Three detections were reported for acetochlor by the GAMA Program (Tables 1, 2, and 3). The concentrations for two detections were below the revised LRL. Acetochlor-containing pesticide products have never been registered for agricultural use in California, and no acetochlor use has been reported. Combined with analysis of the landscape around the wells, this indicated that agricultural use was not the source of the detections.

The landscape around the acetochlor detection in Santa Barbara County (Figure 1) indicated the presence of agriculture to the north and east with hilly, rural areas to the west and south. Metolachlor, another chemical in the same chloroacetanilide chemical family as acetochlor, was also detected in the water sample (Table 1). Although reported use of known groundwater contaminants (diuron, norflurazon, and simazine) around the wellhead was greater than the reported use of metolachlor, no detection of diuron or norflurazon was reported, and simazine's concentration was below metolachlor's reported concentration (Table 1).

The Tulare County acetochlor detection occurred in a section of land dominated by a lake (Figure 2). The surrounding sections were a combination of agricultural and suburban areas. A detection was also reported for metolachlor, but the concentration was less than that reported for acetochlor (Table 2). The reported use of diuron and simazine was much greater than the reported use of metolachlor. No detection was reported for 3,4-dichloroaniline, a breakdown product of diuron. Simazine was detected at 0.023 µg/L, a level that, while greater than the concentration for metolachlor, is low when compared to the total amount of reported used from 1990 until 2004 (27,216 pounds (lbs) for simazine compared to 541 lbs for metolachlor).

The landscape around the third detection of acetochlor in Yuba County was dominated by rice production, tree fruit, and nut crops (Figure 3). Residues of metolachlor again accompanied the detection of acetochlor (Table 3). Metolachlor is not registered for use on these crops and no use was reported in the area surrounding the well.

Recommendation: Agricultural use is an unlikely source for the reported detections of acetochlor as there is no connection between pesticide applications to soil and detection in these wells. A detection of metolachlor also occurred in each of these wells, and as discussed in the metolachlor-specific section below, detections of metolachlor also appear to be spurious suggesting problems with the methodology for analyzing chloroacetanilide chemicals.

No follow-up sampling is recommended.

Table 1. Detection of acetochlor in relation to other residues measured in a well sampled in Santa Barbara County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Santa Barbara: Well 4207N35W26F06SD: Depth 190 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 06/28/2008				
Acetochlor	0.008	0.01	NA	NA
Atrazine	0.01	0.008	0	0
Deethylatrazine	0.005	0.014	-	-
Diuron	0	0.04	192	318
3,4-Dichloroaniline	0	0.006	-	-
Metolachlor	0.011	0.02	0	377
Norflurazon	0	0.04	281	849
Simazine	0.008	0.01	449	876
Deethylsimazine	0	0.08	-	-

Figure 1. Landscape surrounding the wellhead with a reported detection of acetochlor in Santa Barbara County.

Table 2. Detection of acetochlor in relation to other residues measured in a well sampled in Tulare County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Tulare: Well 5417S27E31N101MZ: Depth 205 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 11/15/2005				
Acetochlor	0.0062	0.01	NA	NA
Atrazine	0.077	0.008	0	0
Deethylatrazine	0.003	0.014	-	-
Diazinon	0.003	0.006	0	984
Diuron	-	-	1,650	19,463
3,4-Dichloroaniline	0	0.006	-	-
Metolachlor	0.0033	0.02	0	541
Simazine	0.023	0.01	2,469	27,216

Figure 2. Landscape surrounding the wellhead with a reported detection of acetochlor in Tulare County.

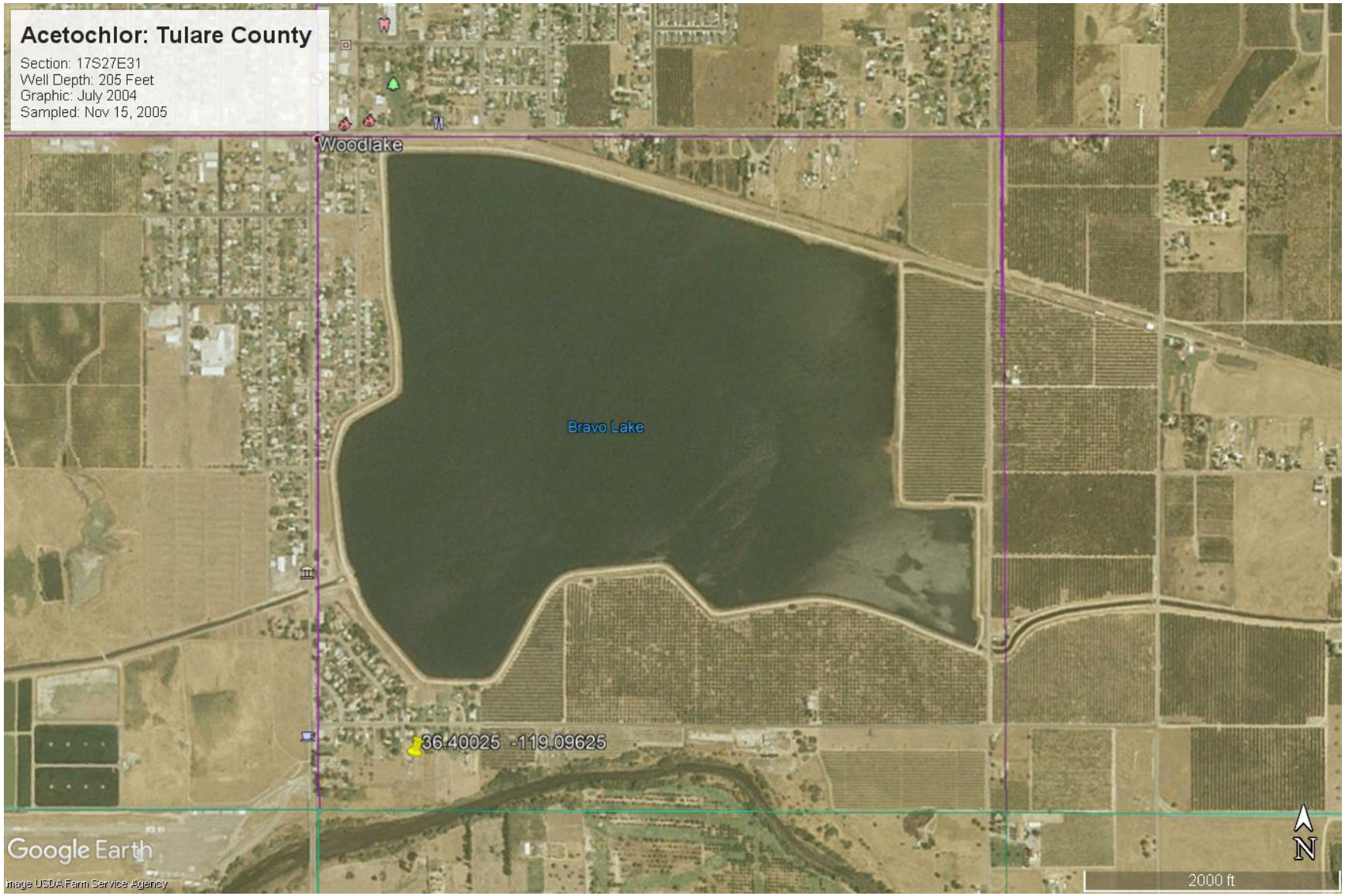
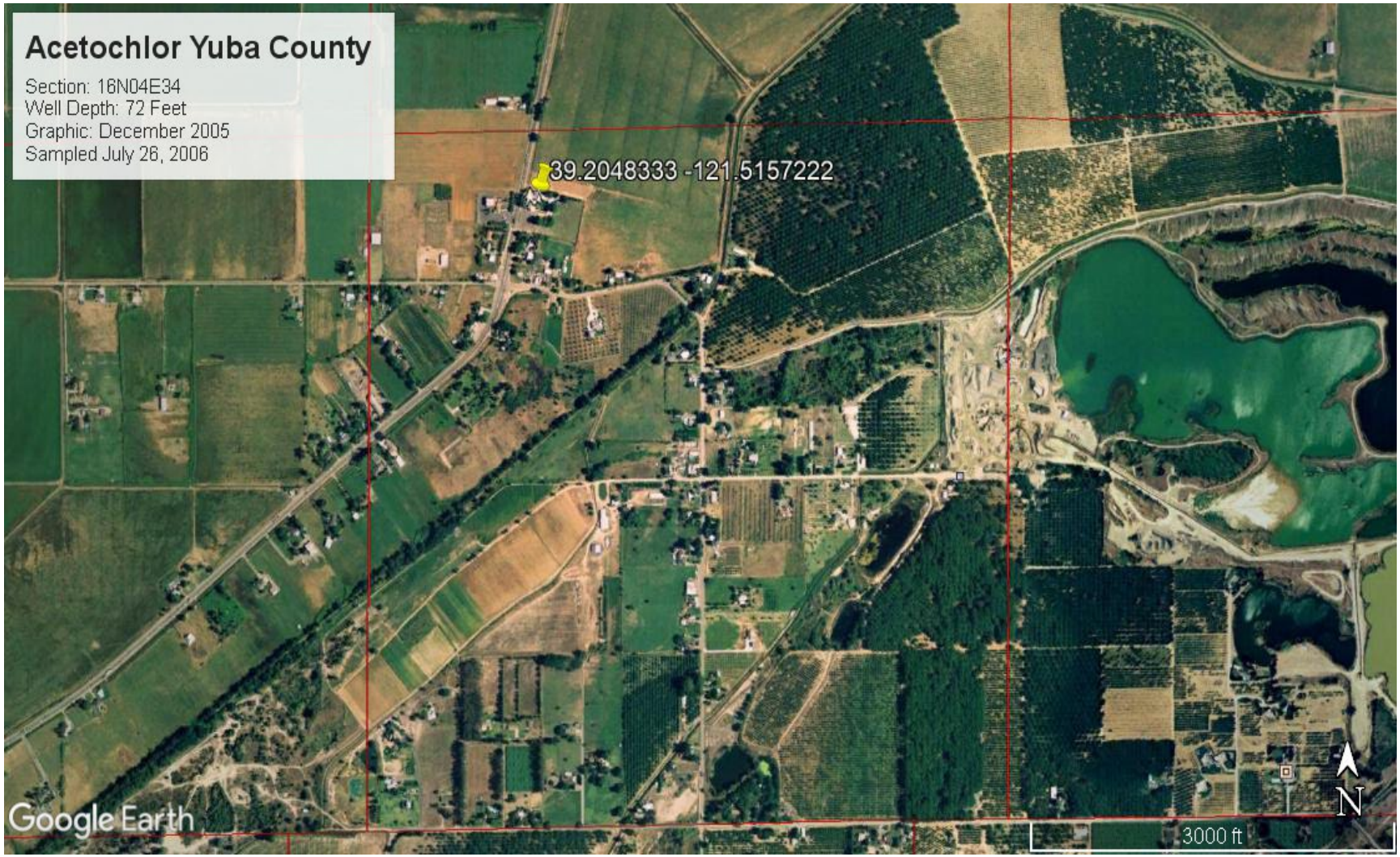


Table 3. Detection of acetochlor in relation to other residues measured in a well sampled in Yuba County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Yuba: Well 5816N04E34C01MD: Depth 72 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 07/26/2006				
Acetochlor	0.0558	0.01	NA	NA
Atrazine	0.0775	0.008	0	0
Deethylatrazine	0.0224	0.014	-	-
Chlorpyrifos	0.0078	0.01	867	3,961
Diuron	-	-	63	341
3,4-Dichloroaniline	0	0.006	-	-
Fipronil	0	0.04	Not Reported	Not Reported
Fipronil Sulfide	0	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0.0077	0.012	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Metolachlor	0.0281	0.02	0	0
Molinate	0	0.008	550	36,362
Prometon	0.019	0.012	0	0
Simazine	0	0.01	63	324
Deethylsimazine	0	0.08	-	-

Figure 3. Landscape surrounding the wellhead with a reported detection of acetochlor in Yuba County.



Alachlor: USGS Parameter Code 46342

Pesticide use and landscape analysis: One detection was reported for alachlor in a well sampled on three different occasions (Table 4). For the 2009 sample, detections were reported for alachlor, atrazine, and 3,4-dichloroaniline (a breakdown product of diuron), which is in contrast to the previous and later water samples taken in 2007 and 2017, respectively, where no pesticide residues were reported above their revised LRLs.

As of 2016, alachlor was no longer registered for use as a pesticide in California. Alachlor was previously registered for use on corn, beans, peas, sorghum, cotton, and sunflower. The landscape immediately surrounding the wellhead where the reported detection occurred includes an airport and correctional facility to the east and west, respectively, and agricultural land to the north and south (Figure 4). Crops present in the landscape surrounding the wellhead were alfalfa, oats, Sudan grass, wheat, barley, and corn. Although some corn was grown around the wellhead, no use of alachlor was reported within the section or in the surrounding eight sections of land. Some use was reported for the known groundwater contaminants diuron and hexazinone. Diuron use increased over time so detection of 3,4-dichloroaniline, a breakdown product of diuron, was possible. Based on diuron's continued use pattern, detections of 3,4-dichloroaniline in subsequent water samples would be expected; however, no residues were reported in the sample taken in 2017. Consequently, the detection and landscape pattern indicate that residues measured in the 2009 sample appear to be spurious and not related to agricultural use.

Recommendation: Agricultural use is a highly unlikely source for the reported detection of alachlor due to:

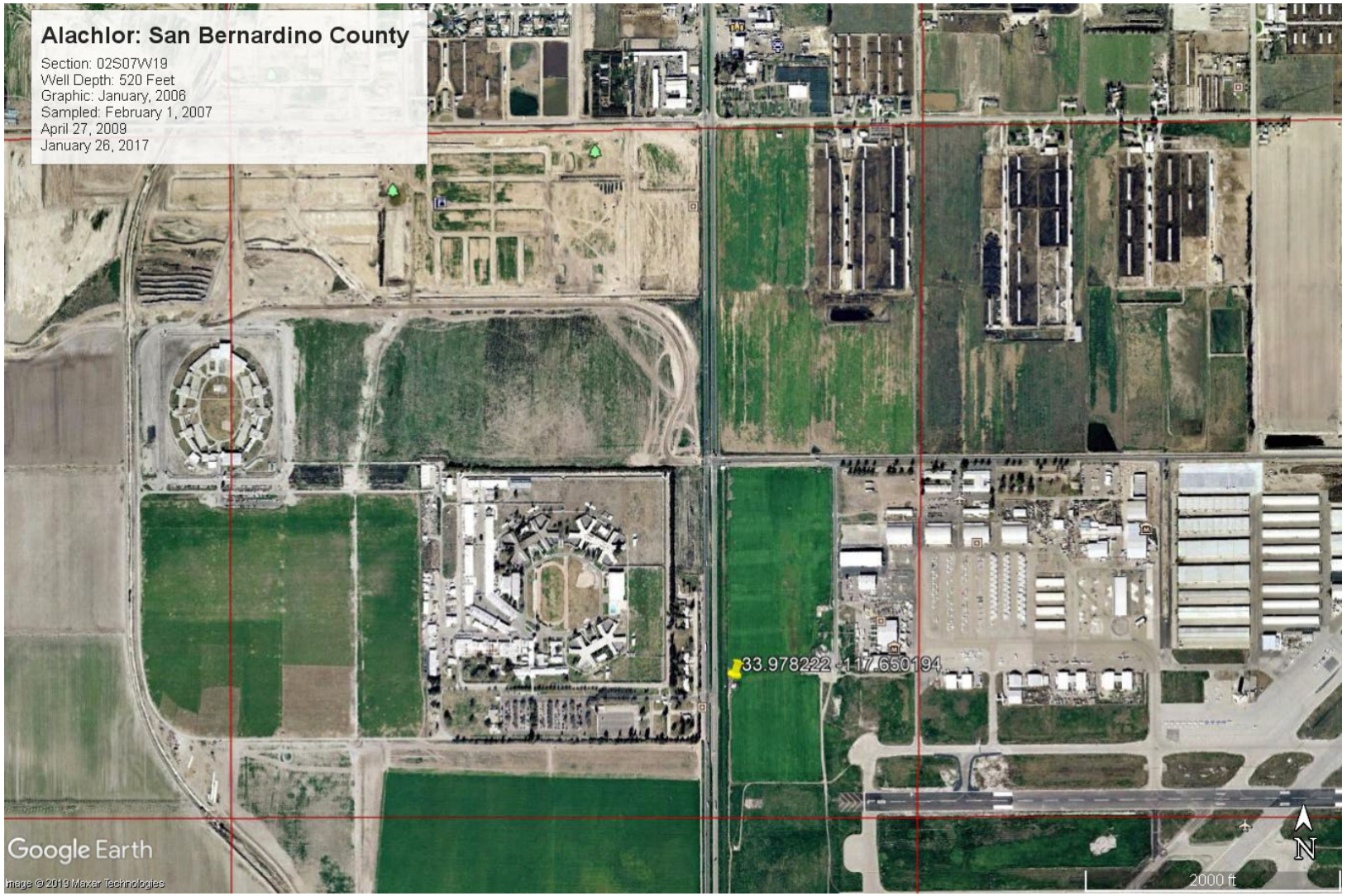
- No reported use of alachlor in the landscape surrounding the wellhead.
- No detections of alachlor or its breakdown product reported in water sampled from the same well before or after the 2009 sampling date when the detection was reported.
- A detection of diuron, a known groundwater contaminant, reported for the 2009 sampling was spurious as no residues were reported in the previous sample taken in 2007 or the later sample taken in 2017.
- GWPP has conducted targeted sampling for alachlor in areas of highest use in California without detection above 0.05 µg/L (Weaver and Nordmark, 2002; Bergin and Nordmark, 2012)
- These findings, taken together, indicate that agricultural use was not the source of the reported alachlor detection.

No follow-up sampling is recommended.

Table 4. Detection of alachlor in relation to other residues measured in a well sampled in San Bernardino County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

San Bernardino: Well 3602S07W19Q101SZ: Depth 520 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 02/01/2007				
Alachlor	0	0.008	0	0
2,6-Diethylaniline	0	0.006	-	-
Atrazine	0	0.008	0	0
Diuron	0	0.04	136	340
3,4-Dichloroaniline	0	0.006	-	-
Hexazinone	0	0.026	34	239
Simazine	0	0.01	0	0
Deethylsimazine	0	0.08	-	-
Sampled 04/27/2009				
Alachlor	0.009	0.008	0	0
2,6-Diethylaniline	0	0.006	-	-
Atrazine	0.034	0.008	0	0
Diuron	0	0.04	136	530
3,4-Dichloroaniline	0.0092	0.006	-	-
Hexazinone	0	0.026	34	324
Simazine	-	-	0	0
Deethylsimazine	0	0.08	-	-
Sampled 01/26/2017				
Alachlor	0	0.008	0	4
2,6-Diethylaniline	0	0.006	-	-
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.01	-	-
Diuron	0	0.04	136	1,294
3,4-Dichloroaniline	0	0.006	-	-
Hexazinone	0	0.026	34	527
Simazine	0	0.01	0	0

Figure 4. Landscape surrounding the wellhead with a reported detection of alachlor in San Bernardino County.



2,6-Diethylaniline: USGS Parameter Code 82660

Pesticide use and landscape analysis: The GAMA Program reported four detections of 2,6-diethylaniline (Tables 5, 6, and 7). The concentrations of all four reported detections were below the revised LRL. 2,6-Diethylaniline is a breakdown product of alachlor. Table 5 contains results for the detection reported in Merced County; Table 6 includes results for detections in two separate wells reported in San Joaquin County; and Table 7 shows results for a detection in San Diego County.

For the reported detection in Merced County, no use of alachlor was reported within the section or in the surrounding eight sections where the well was located (Table 5). Lack of use is consistent with the cropping pattern in the landscape surrounding the well where alfalfa, wheat, tomato, melon, and barley crops were prevalent; alachlor was not registered for use on these crops. Although some cotton was grown, no applications of alachlor were reported prior to the detection in 2010 of its breakdown product 2,6-diethylaniline. Metolachlor is a pesticide in the same family as alachlor and has a similar potential to move to groundwater. Metolachlor is registered for use on a broader range of crops, including row and tree crops grown in the landscape surrounding the wellhead. Although metolachlor use was substantial within the section and in the surrounding eight sections, no detections were reported.

For the reported detections of 2,6-diethylaniline in two wells in San Joaquin County, no use of alachlor was reported within the section or in the eight sections of land surrounding the wellheads (Table 6). Substantial use of several known groundwater contaminants such as bromacil, diuron (or its breakdown product 3,4-dichloroaniline), norflurazon, and simazine occurred in these sections, but no detections were reported for these chemicals. Hexazinone was detected in one of the two wells in San Joaquin County and its use was indicated in the area. However, hexazinone detections are infrequent compared to the other known groundwater contaminants. The detection in this well was not consistent with the non-detections of other known groundwater contaminants with substantial reported use.

For the reported detection of 2,6-diethylaniline in San Diego County, the well was sampled in 2004, 2011, and 2014. 2,6-Diethylaniline was not detected in 2004 but was detected in 2011. The 2014 well water sample was not analyzed for 2,6-diethylaniline (Table 7). The reported detection in 2011 was accompanied by reported detections of seven other parent and breakdown products. There was no reported use of any of these parent chemicals within the section or in the surrounding eight sections of land. Also, no detections of any of the other seven residues were found at the two other sampling intervals (i.e., 2004 and 2014). The landscape is predominantly a rural, foothill area where agricultural production surrounding the wellhead was limited to small plantings of orange, avocado, lemon, and apple (Figure 5). The detection of residues in the well water sample taken in 2011 appears spurious, indicating that agricultural use was not the source for reported detections.

Recommendation: The potential for agricultural use to be the source of the reported 2,6-diethylaniline detection in the four wells is highly unlikely due to:

Merced County Detection

- No reported use of the parent alachlor in the landscape surrounding the wellhead.
- Cropping pattern inconsistent with alachlor use.
- No detection of metolachlor, a chemical related to alachlor with substantial use in the surrounding landscape and with a similar potential to move to groundwater.
- The concentration of 2,6-diethylaniline was below the revised LRL.

San Joaquin County Detections

- No reported use of the parent alachlor in the landscape surrounding the two wellheads.
- No detections of known groundwater contaminants even though substantial use was reported around the wellhead.
- No detection of metolachlor, a chemical related to alachlor, which had substantial use in the landscape surrounding one of the wells.
- The concentration of 2,6-diethylaniline in both wells was below the revised LRL.

San Diego County Detection

- No reported use of the parent alachlor or reported use of other detected residues in the landscape surrounding the wellhead.
- No detection of 2,6-diethylaniline in the same well prior to the reported detection.
- Minimal agriculture and minimal reported pesticide applications in the landscape surrounding the well.
- The concentration of 2,6-diethylaniline was below the revised LRL.
- No detections reported in well water samples obtained before (2004) and after (2014) the 2011 sampling date when six other chemical residues were detected. The detection of several chemicals in the single sample with no further detections in the same well sampled at other times indicates that the results from this analysis are suspicious.

These findings, taken together, indicate that agricultural use was not the source of the four reported 2,6-diethylaniline detections.

No follow-up sampling is recommended.

Table 5. Detection of 2,6-diethylaniline in relation to other residues measured in a well sampled in Merced County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Merced: Well 2409S11E10M101MZ: Depth Not Reported				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 06/30/2010				
Alachlor	0	0.008	0	0
2,6-Diethylaniline	0.005	0.006	-	-
1,2-Dichloropropane	0.039	0.026	Historical	-
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	-	-	1,570	7,028
3,4-Dichloroaniline	0.005	0.006	-	-
EPTC	0.074	0.0056	666	2,798
Hexazinone	0.045	0.026	316	2,117
Metolachlor	0	0.02	3,771	19,041
Prometon	0	0.012	0	0
Prometryn	0.006	0.01	2,011	12,271
Simazine	0	0.01	0	0

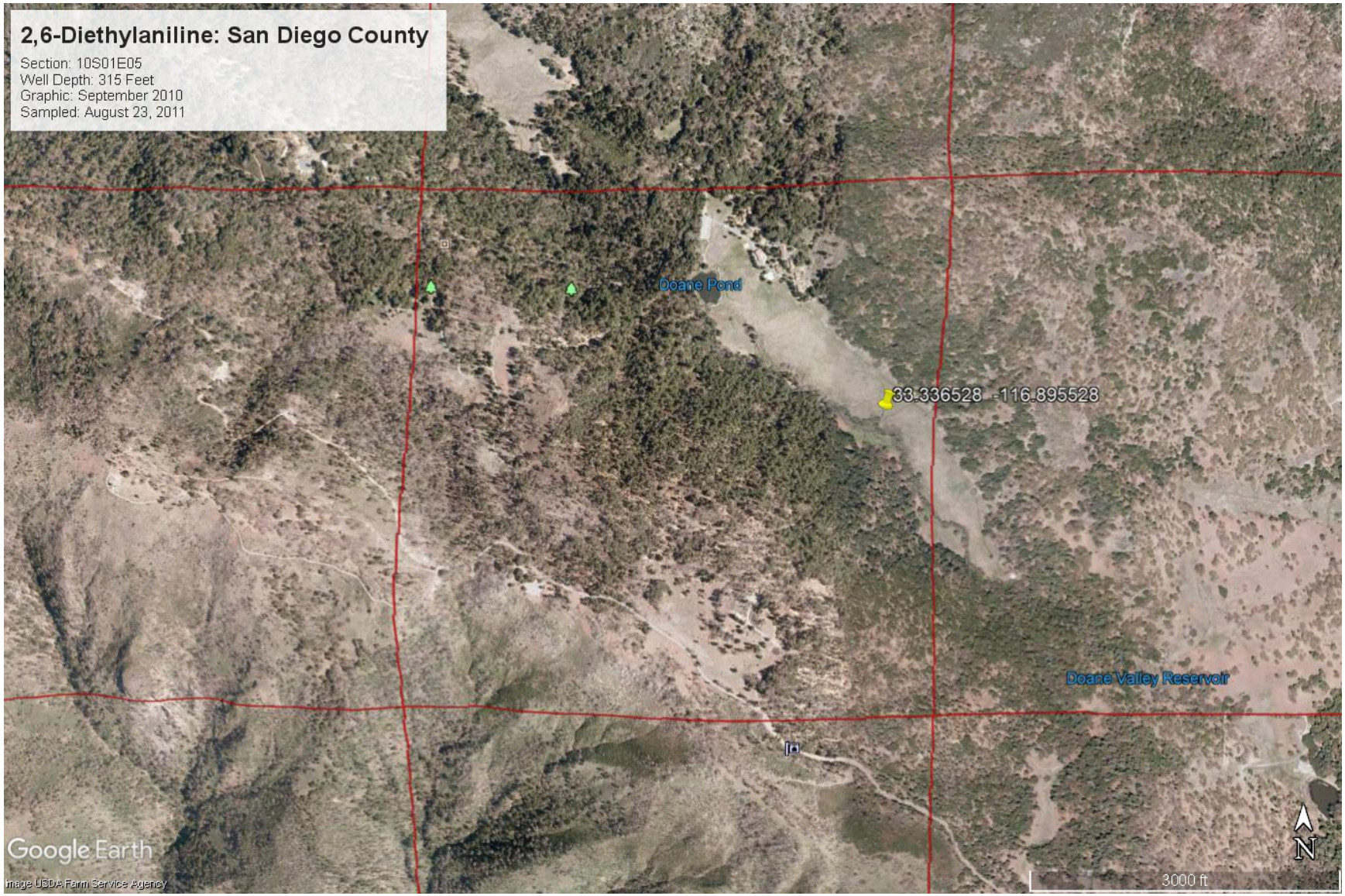
Table 6. Detections of 2,6-diethylaniline in relation to other residues measured in two wells sampled in San Joaquin County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

San Joaquin: Well 3901N05E16D101MZ: Depth Not Reported				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 02/09/2005				
Alachlor	0	0.008	0	0
2,6-Diethylaniline	0.004	0.006	-	-
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Bromacil	0	0.06	0	19
Diuron	0	0.04	1,274	25,515
3,4-Dichloroaniline	0	0.006	-	-
Hexazinone	0.066	0.026	541	4,138
Metolachlor	0	0.02	0	187
Simazine	0	0.01	15	2,528
San Joaquin: Well 3901S05E17C101MZ: Depth 83 Feet				
Sampled 02/08/2005				
Alachlor	0	0.008	0	0
2,6-Diethylaniline	0.004	0.006	-	-
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Bromacil	0	0.06	0	700
Diuron	0	0.04	763	21,126
3,4-Dichloroaniline	0	0.006	-	-
Hexazinone	0	0.026	0	6,382
Metolachlor	0	0.02	869	2,790
Norflurazon	0	0.02	1,155	514
Simazine	0	0.01	362	2,088

Table 7. Detection of 2,6-diethylaniline in relation to other residues measured in a well sampled in San Diego County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

San Diego: Well 3710S01E05H001SZ: Depth 315 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 07/19/2004				
Alachlor	0	0.008	0	0
2,6-Diethylaniline	0	0.006	-	-
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	0	0.04	0	0
3,4-Dichloroaniline	0	0.006	-	-
Fipronil	0	0.04	0	0
Fipronil Sulfide	0	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0	0.012	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Metolachlor	0	0.02	0	0
Prometon	0	0.012	0	0
Sampled 08/23/2011				
Alachlor	0	0.008	0	0
2,6-Diethylaniline	0.0031	0.006	-	-
Atrazine	0.0396	0.008	0	0
Deethylatrazine	0.0142	0.014	-	-
Diuron	-	-	0	0
3,4-Dichloroaniline	0.0290	0.006	-	-
Fipronil	0	0.04	0	0
Fipronil Sulfide	0	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0.006	0.012	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Metolachlor	0.0193	0.02	0	0
Prometon	0.0072	0.012	0	0
Sampled 05/15/2014				
Alachlor	0	0.008	0	0
Atrazine	0	0.008	0	0
Diuron	0	0.04	0	0
Fipronil	0	0.04	0	0
Fipronil Sulfide	0	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0	0.0120	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Metolachlor	0	0.02	0	0
Prometon	0	0.012	0	0

Figure 5. Landscape surrounding the wellhead with a reported detection of 2,6-diethylaniline in San Diego County.



Chlorpyrifos: USGS Parameter Code 38933

Pesticide use and landscape analysis: Two detections were reported for chlorpyrifos, one in a well in Yuba County (Table 3) and a second in a well in Kern County (Table 8). The concentrations of both reported detections were below the revised LRL. The cropping pattern and reported use of chlorpyrifos near the wellheads tends to support the detection of residues in the wells. However, acetochlor was also detected in the well in Yuba County at a concentration nearly ten times greater than the detection of chlorpyrifos. As discussed in the acetochlor-specific section above, the reported detection of acetochlor in this sample places doubt on the integrity of the analytical results, including the reported detections of other chemicals, because no pesticide product containing acetochlor has ever been registered for use in California. The reported detection pattern in that well water sample indicates that agricultural use was not the source of the reported detections.

The cropping pattern and reported use of chlorpyrifos near the wellhead in Kern County tends to support the chlorpyrifos detection. Reported detections and use patterns for diuron and simazine, which are known groundwater contaminants, support the analytical results for detection of simazine and 3,4-dichloroaniline (a breakdown product of diuron) (Table 8). However, concentrations of all three chemicals were in the low parts per trillion range and all were below their respective revised LRLs. Chlorpyrifos is primarily applied as a foliar spray, whereas diuron and simazine are applied directly to the soil. Based on these differences in application pattern, expected well water concentrations for diuron and simazine would be substantially higher because they have greater potential to move to groundwater due to direct application to soil.

Recommendation: Although the amount of reported chlorpyrifos use tends to support the detections, several other factors indicate that agricultural use is not the source of the two reported detections due to:

- The reported chlorpyrifos concentrations in both wells were below the revised LRL.
- All reported detections from the well sampled in Yuba County are questionable because residues were reported for several chemicals with no reported agricultural use in the surrounding landscape. Acetochlor was detected but has never been registered for agricultural use in California. Furthermore, the reported acetochlor concentration was ten times greater than the concentration reported for the chlorpyrifos residue.
- For the Kern County well, residues of known groundwater contaminants were detected, but their concentrations were similar in magnitude to that reported for chlorpyrifos. Diuron and simazine are pre-emergent herbicides applied directly to soil and their concentrations are expected to be substantially higher than for chlorpyrifos.
- No other chlorpyrifos residue has been reported in wells sampled in similar agricultural landscapes in the San Joaquin Valley.

The weight of evidence indicates that agricultural use was not the source of the two reported chlorpyrifos detections.

No follow-up sampling is recommended.

Table 8. Detection of chlorpyrifos in relation to other residues measured in a well sampled in Kern County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Kern: Well 1528S26E11P101MZ: Depth 763 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 02/27/2006				
Chlorpyrifos	0.0061	0.01	5,098	26,443
Chlorpyrifos Oxon	0	0.056	-	-
Diuron	-	-	1,715	13,508
3,4-Dichloroaniline	0.0049	0.006	-	-
Simazine	0.008	0.01	1,942	20,121

Diazinon: USGS Parameter Code 39572

Pesticide use and landscape analysis: The GAMA Program reported two detections for diazinon, one in a well in Sonoma County (Table 9) and the second in a well in Tulare County (Table 2).

Significant use of diazinon was reported around the wellhead in Sonoma County. Of the 4,173 lbs reported used from 1990 until 2003, 4,104 lbs were applied to mushrooms. Since mushrooms require stable temperatures and high relative humidity for optimal growing conditions, they are grown indoors (http://sfp.ucdavis.edu/pubs/brochures/mushroom/). The exact location of the original well sampled could not be verified from the GAMA Program records. However, the GWPP conducted follow-up sampling of six domestic wells located near the original reported detection (Nordmark, 2014a). At a reporting limit of 0.05 µg/L, no residues were detected for diazinon, or for the 12 other chemicals included in the analytical screen that have been previously detected in other well water samples.

The detection of diazinon in the Tulare County well was accompanied by detections of acetochlor and four other chemicals (Table 2). As discussed in the acetochlor-specific section above, acetochlor has never been registered for use in California; therefore, a lack of physical connection between chemical use and the reported detection indicates that agricultural use was not the source of the detection. This casts doubt on the remaining chemical detections in the Tulare County well, particularly as the concentration reported for acetochlor was twice the concentration reported for diazinon. In addition, the diazinon concentration was below the revised LRL.

Recommendation: Agricultural use is a highly unlikely source for the reported detection of diazinon due to:

- Significant use of diazinon reported in the land section in Sonoma County was applied to mushrooms — a crop grown indoors.
- GWPP did not detect diazinon in wells sampled near the reported detection in follow-up sampling.
- The Tulare County detection is suspicious because of the co-detection of acetochlor, a chemical never registered for use in California.
- The Tulare County detection was half the revised LRL.

These findings, taken together, indicate that agricultural use was not the source of the two reported diazinon detections.

No follow-up well sampling is recommended.

Table 9. Detection of diazinon residue in relation to other residues measured in a well sampled in Sonoma County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Sonoma: Well 4905N07W30E101MZ: Depth 550 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 9/30/2004				
Diazinon	0.1080	0.006	4,173	345
1,2-Dichloropropane	0	0.029	Historical	-
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	-	-	0	0
2,6-Diethylaniline	0	0.006	-	-
Simazine	0	0.01	0	83

Dieldrin: USGS Parameter Code 3381

Pesticide use and landscape analysis: Three detections were reported for dieldrin from wells sampled in Monterey, Napa, and San Bernardino counties. Currently no products containing dieldrin are registered for use in California, and the last product registration became inactive in 1986. Major use was to control soil dwelling insects in row and tree fruit crops.

Recommendation: Unregistered pesticides are prohibited from use in California. Consequently, potential regulatory restrictions on their sales and use following detections in groundwater is not possible. **Therefore, no follow-up sampling is recommended.**

Dinoseb: USGS Parameter Code 49301

Pesticide use and landscape analysis: Two detections were reported for dinoseb from wells sampled in Kern and Madera counties. Currently no products containing dinoseb are registered for use in California, and the last product registration became inactive in 1988. Major use was to control weeds in row and tree fruit crops.

Recommendation: Unregistered pesticides are prohibited from use in California. Consequently, potential regulatory restrictions on their sales and use following detections in groundwater is not possible. **Therefore, no follow-up sampling is recommended.**

Diphenamid: USGS Parameter Code 4033

Pesticide use and landscape analysis: One detection was reported for diphenamid in a well sampled in Kern County. Currently no products containing diphenamid are registered for use in California. The last product registration became inactive in 1990. Most products were registered for use on dichondra ground cover, a popular lawn substitute.

Recommendation Unregistered pesticides are prohibited from use in California. Consequently, potential regulatory restrictions on their sales and use following detections in groundwater is not possible. **Therefore, no follow-up sampling is recommended.**

EPTC (EPTAM): USGS Parameter Code 82668

Pesticide use and landscape analysis: Twelve wells with EPTC detections were reported in six counties (Table 10). No applications of EPTC were reported in the landscape around five of the wells but substantial use was reported around the seven other wellheads. The highest concentration at 0.0737 µg/L in the well in Merced County triggers the GWPP response to conduct a well sampling survey around the reported detections.

Recommendation: GWPP will investigate the feasibility of a targeted EPTC groundwater study.

Table 10. Detections of EPTC in relation to pesticide use reported in the landscape surrounding each wellhead. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

EPTC Well Sampling and Use Information							
County	**Well**	**Well Depth (Feet)**	**Date Sampled**	**Detection (µg/L)**	**Revised LRL (µg/L)**	**Within Section (lbs)**	**Surrounding 8 Sections (lbs)**
Fresno	1013S15E19R05MD	78	04/06/2010	0.0142	0.0056	0	0
Fresno	1013S15E30B04MD	250	03/01/2010	0.0083	0.0056	0	0
Fresno	1014S16E03P101MZ	-	12/15/2005	0.0376	0.0056	660	0
Kern	1509N13W25N01SD	527	02/24/2012	0.0069	0.0056	0	0
			08/01/2013	0	0.0056	0	0
Kern	1525S25E10A101MZ	1,000	01/11/2006	0.0032	0.0056	0	0
Kern	1529S23E21H101MZ	460	02/06/2006	0.0324	0.0056	0	0
Kern	1532S26E10R01MD	1,007	01/23/2006	0.0093	0.0056	766	639
Madera	2012S14E28E101MZ	-	03/03/2010	0.0075	0.0056	303	598
Merced	2409S11E10M101MZ	-	06/30/2010	0.0737	0.0056	666	1,430
Sacramento	3405N04E35G01MD	244	12/14/2011	0.0069	0.0056	0	5,503
			04/22/2014	0	0.0056	0	5,503
Tulare	5422S26E33D101MZ	600	06/30/2010	0.0044	0.0056	757	2,590
Tulare	5422S27E07Q01MD	965	12/07/2005	0.0390	0.0056	84	2,252
			11/03/2008	0.0255	0.0056	84	2,324
			10/26/2015	0.0150	0.0056	84	2,554

Fipronil: USGS Parameter Code 62166

Pesticide use and landscape analysis: One detection of fipronil was reported in a well sampled in Fresno County (Table 11). For the water sample collected in 2008, residues were reported for this chemical and its sulfide degradation product with concentrations of both chemicals below the revised LRL. However, for the water samples collected from this same well in 2005 and 2015, no residues were reported for fipronil or any of its five breakdown products. Analytical results were reported for fipronil and its five breakdown products in the 2005 and 2015 samples, but only fipronil and two breakdown products were reported in the 2008 sample. Analysis of reported use of fipronil within a section is not possible because its products are registered primarily for home use, which do not have the same reporting requirements as those registered for agricultural use. Three other residues of known groundwater contaminants were consistently detected at all three sampling dates — atrazine, DBCP, and simazine. As indicated by the landscape surrounding the well, this area was historically agricultural with suburban development increasing over time (Figure 6). The detections of the known groundwater contaminant, simazine, are consistent with agricultural use and indicate continuity with detections in the well water samples over time. Although the detection of fipronil might be due to the onset of suburban development, its detection and that of its sulfide degradation product in the sample taken in 2008 is contrary to the expectation of their presence in this same well in 2005 and 2015.

Recommendation: Agricultural use does not appear to be the source of the fipronil detection in this sample due to:

- The reported fipronil concentration was below the revised LRL.
- Detection of simazine residues were due to reported agricultural use around the wellhead. Historically, fipronil was not registered for agricultural use.
- Consistent detections of atrazine, DBCP, and simazine in all three samples from the same well indicate continuity between presence in groundwater and detection in well water samples over time. Detection of fipronil residues in only the 2008 sample and not in the previous or subsequent samples is contrary to this consistency.
- Increase in suburban development with potential increase in home use in fipronil over time could be a source for residues. Although residues were reported in the sample in 2008, no residues were reported in the later sample taken in 2015, again contrary to consistency in results relative to the other chemicals detect in the well.

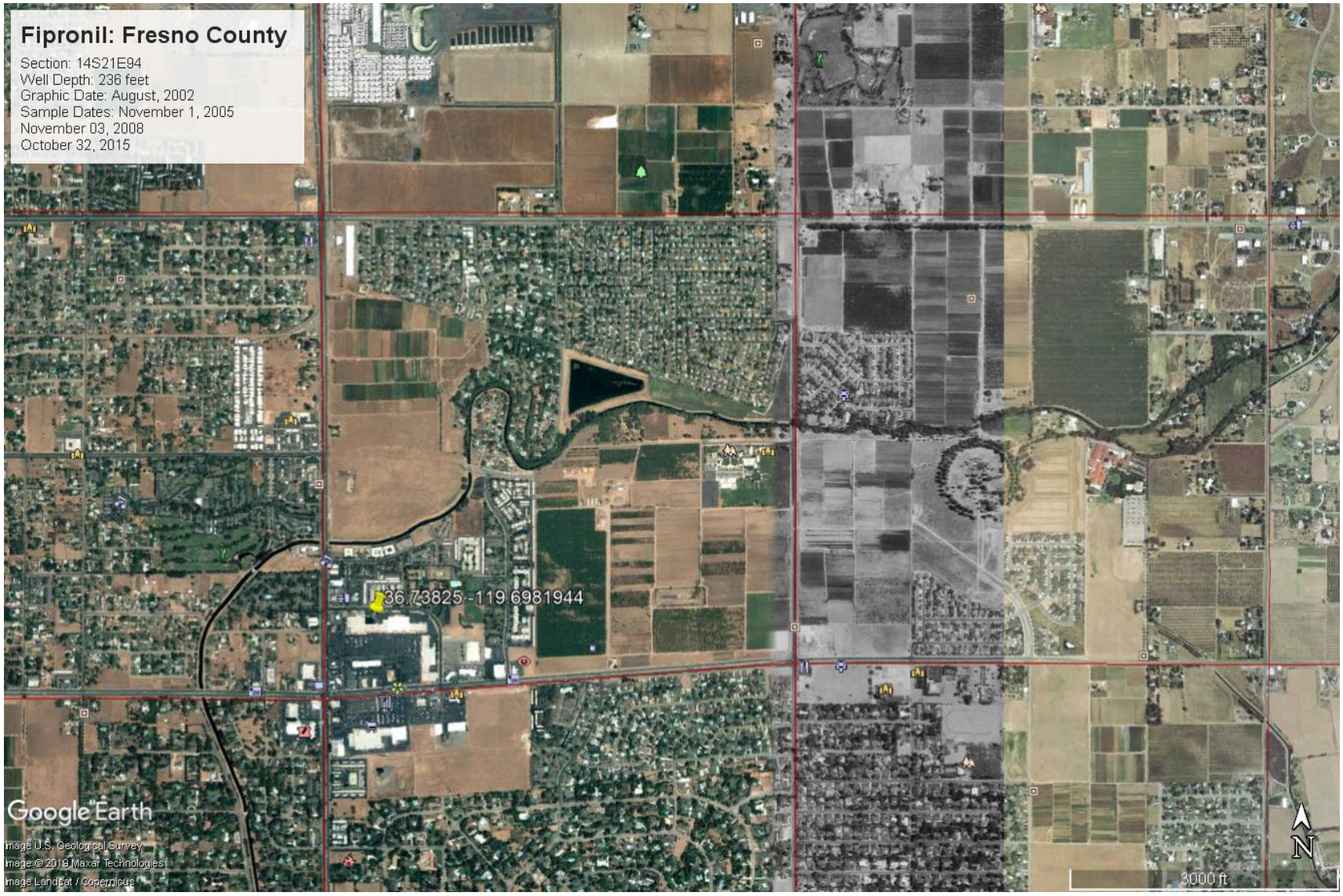
These findings, taken together, indicate that agricultural use was not the source of the reported fipronil detection.

No follow-up sampling is recommended.

Table 11. Detection of fipronil in relation to other residues measured in a well sampled in Fresno County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Fresno: Well 1014S21E04N01MD: Depth 236 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 11/01/2005				
Fipronil	0	0.04	Not Reported	Not Reported
Fipronil Sulfide	0	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0	0.012	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Atrazine	0.015	0.008	0	0
Deethylatrazine	0	0.014	-	-
DBCP	0.35	0.03	Historical	-
Diuron	-	-	0	653
3,4-Dichloroaniline	0	0.006	-	-
Hexazinone	0	0.026	0	171
Simazine	0.012	0.01	41	708
Sampled 11/03/2008				
Fipronil	0.0215	0.04	Not Reported	Not Reported
Fipronil Sulfide	0.0086	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Atrazine	0.0186	0.008	0	0
Deethylatrazine	0.014	0.014	-	-
DBCP	0.22	0.03	Historical	-
Diuron	-	-	0	653
3,4-Dichloroaniline	0.0059	0.006	-	-
Hexazinone	0	0.026	0	231
Simazine	0.0876	0.01	41	708
Sampled 10/21/2015				
Fipronil	0	0.04	Not Reported	Not Reported
Fipronil Sulfide	0	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0	0.012	-	-
Desulfinyl Fipronil Amide	0	0.0290	-	-
Atrazine	0.0068	0.008	0	0
Deethylatrazine	0	0.014	-	-
DBCP	0.073	0.03	Historical	-
Diuron	-	-	0	653
3,4-Dichloroaniline	0	0.006	-	-
Hexazinone	0	0.026	0	285
Simazine	0.0063	0.01	41	821

Figure 6. Landscape surrounding the wellhead with a reported detection of fipronil in Fresno County.



Fipronil Sulfide: USGS Parameter Code 62167

Pesticide use and landscape analysis: Three detections of fipronil sulfide were reported. The concentrations of these detections were approximately 50% lower than the revised LRL. One detection in a well sampled in Fresno County was previously reviewed in the fipronil-specific section above (Table 11). For the same reasons noted in that discussion of its parent, the detection of fipronil sulfide appears spurious because it was measured only once out of three separate sampling intervals of the same well. In contrast, residues for several other chemicals were measured at all three sampling intervals.

The landscape surrounding the well water detection of fipronil sulfide in section 02S11W05 in Los Angeles County is dominated by natural landscape with minimal suburban development (Figure 7). Applications of other pesticides in the area include those made to outdoor, container-grown plants, indicating the presence of nurseries, and to strawberries. Despite fipronil being registered for use on outdoor, container-grown plants, its use was not reported within the section containing the wellhead or in the eight surrounding sections of land. Accompanying detections of atrazine, diuron, prometon, and simazine indicate applications of these pesticides were likely made to control weeds in non-cropped areas such as roadsides (Table 12).

Similarly, for the well located in section 05N17W25 in Los Angeles County, the landscape indicated mostly natural terrain with an industrial presence and limited suburban development (Figure 8). Since there was no indication of agricultural applications for pesticides within the section, the detection of simazine most likely originated from non-crop weed control use (Table 13).

Recommendation: Agricultural use does not appear to be the source of fipronil sulfide detections in these samples due to:

- All three reported concentrations are approximately 50% less than the revised LRL.
- The main use of the parent fipronil is to control insects with applications targeted within and around housing or industrial structures. Few structures were present in the two sections of land containing the wellheads in Los Angeles County.
- A third detection was reported in Fresno County, but it too appeared to be spurious because:
    - Detection of atrazine, DBCP, and simazine residues were due to historical agricultural use around the wellhead. Historically, the parent fipronil was not registered for agricultural use.
    - Consistent detections of atrazine, DBCP, and simazine in the same well on three different occasions indicate confidence in their presence in groundwater. Detection of fipronil sulfide residues in only the 2008 sample and not in the subsequent sample taken in 2015 is contrary to this expectation.
    - Increase in suburban development with potential increase in fipronil use over time could be a source for residues. Although residues were reported in the

sample in 2008, no residues were reported in the later sample taken in 2015, again contrary to expectations of a subsequent detection of fipronil sulfide.

These findings, taken together, indicate that agricultural use was not the source of the three reported fipronil sulfide detections.

No follow-up sampling is recommended.

Table 12. Detection of fipronil sulfide in relation to other residues measured in a well sampled in section 02S11W05 in Los Angeles County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Los Angeles: Well 1902S11W05N04SD: Depth 414 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 11/01/2005				
Fipronil	0	0.04	Not Reported	Not Reported
Fipronil Sulfide	0.009	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0	0.012	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Atrazine	0.02	0.008	0	0
Deethylatrazine	0.018	0.014	-	-
Diuron	0.16	0.04	0	0
3,4-Dichloroaniline	0.012	0.006	-	-
Prometon	0.011	0.012	0	0
Simazine	0.06	0.01	0	9
Deethylsimazine	0	0.08	-	-

Figure 7. Landscape surrounding the wellhead with a reported detection of fipronil sulfide in section 02S11W05 in Los Angeles County.

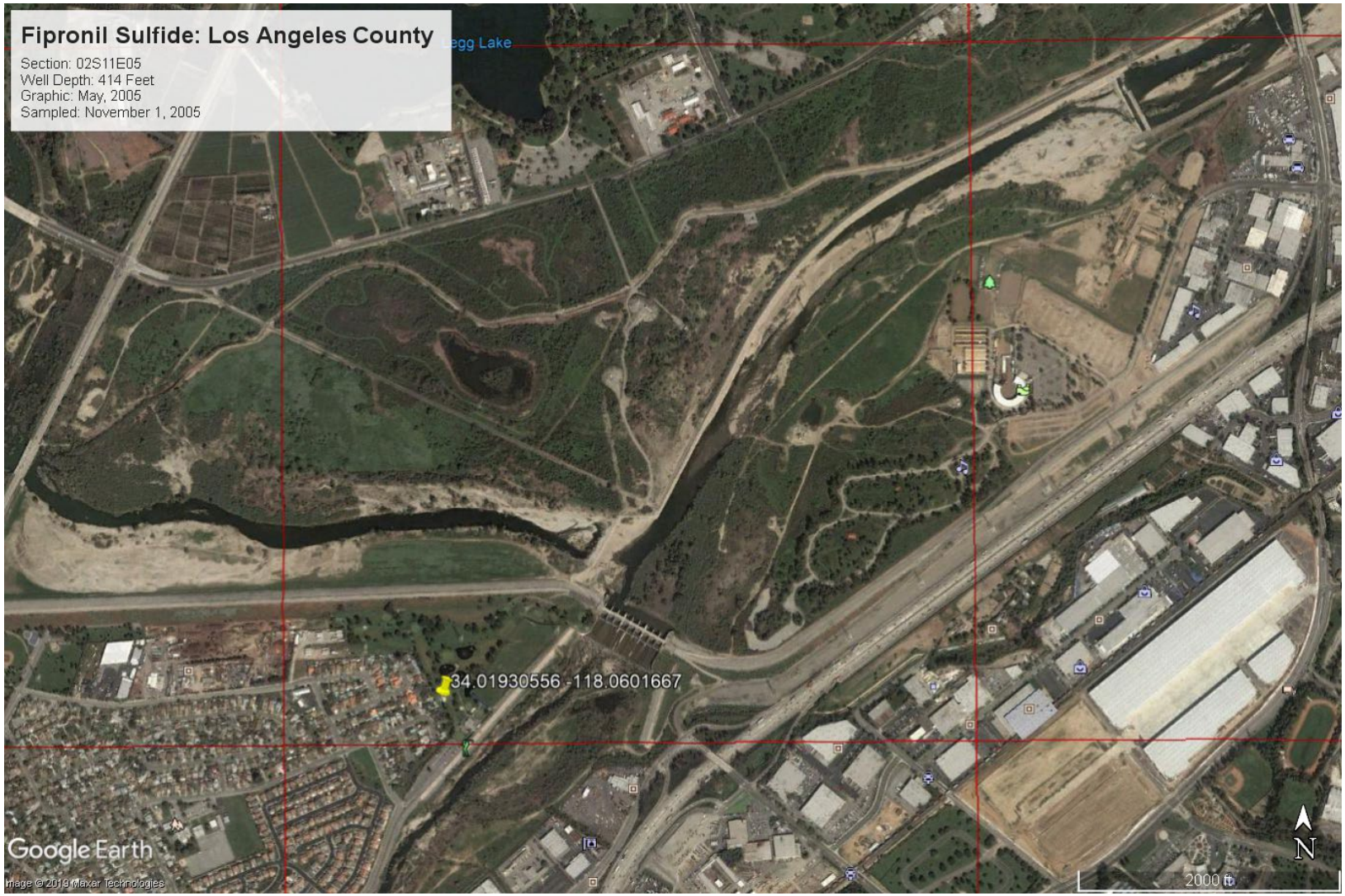


Table 13. Detection of fipronil sulfide in relation to other residues measured in a well sampled in section 05N17W25 in Los Angeles County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Los Angeles: Well 1905N17W25G102SZ: Depth 203 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 11/03/2008				
Fipronil	0	0.04	Not Reported	Not Reported
Fipronil Sulfide	0.008	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0	0.012	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	-	-	0	0
3,4-Dichloroaniline	0.0059	0.006	-	-
Simazine	0.01	0.01	0	0
Deethylsimazine	0	0.08	-	-

Figure 8. Landscape surrounding the wellhead with a reported detection of fipronil sulfide in section 05N17W25 in Los Angeles County.

Desulfinyl Fipronil: USGS Parameter Code 62170

Pesticide use and landscape analysis: Three detections of desulfinyl fipronil were reported. The concentrations for these detections were approximately 50% lower than the revised LRL. One detection was reported in a Yuba County well where detections of acetochlor, chlorpyrifos, and three other residues were also reported in the single sample (Table 3). As discussed in the acetochlor-specific section above for this well, no acetochlor products have been registered for use in California. Therefore, the reported detection of acetochlor indicated the residues in this sample did not originate from agricultural use. Additionally, the reported acetochlor detection was almost ten times the concentration of the reported detection of either chlorpyrifos or desulfinyl fipronil, providing further evidence that the residues in this well did not originate from agricultural use.

A second detection was reported in a well in San Diego County in 2011 where multiple detections of other residues were also observed (Table 7). The landscape was rural with minimal housing or agriculture (Figure 5). As discussed for 2,6-diethylaniline-specific section above, no residues of any chemicals were reported previously in 2004 or later in 2014 in samples taken from the same well. The combination of landscape and a single detection in only one of three sampling periods indicates that the results from 2011 were spurious and that agricultural use was not the likely source of detections in this sample.

For the third detection which occurred in Riverside County, the landscape in 1996 was a mix of rural estates and suburban development (Figure 9). Aerial photography over time indicates that the area has been infilled with suburban housing. Other residues detected in the well, specifically atrazine, prometon, and simazine, suggest the use of pre-emergent herbicides for non-crop weed control (Table 14). Residues for the parent fipronil or its breakdown products other than desulfinyl fipronil were not detected in the sample.

Recommendation: Agricultural use is not likely the source of desulfinyl fipronil detections in these samples due to:

- All three reported concentrations are approximately 50% less than the revised LRL.
- The detection in the Yuba County well is highly suspicious because of a reported detection of acetochlor, a chemical with no registered products in California. The reported concentration of desulfinyl fipronil was considerably lower than the acetochlor concentration (Table 3).
- Unfavorable landscape analyses: The area around the wellhead in San Diego County was rural, indicating no potential for use of the parent fipronil. The area around the wellhead in Yuba County was dominated by rice production, also indicating low potential for use of the parent fipronil.

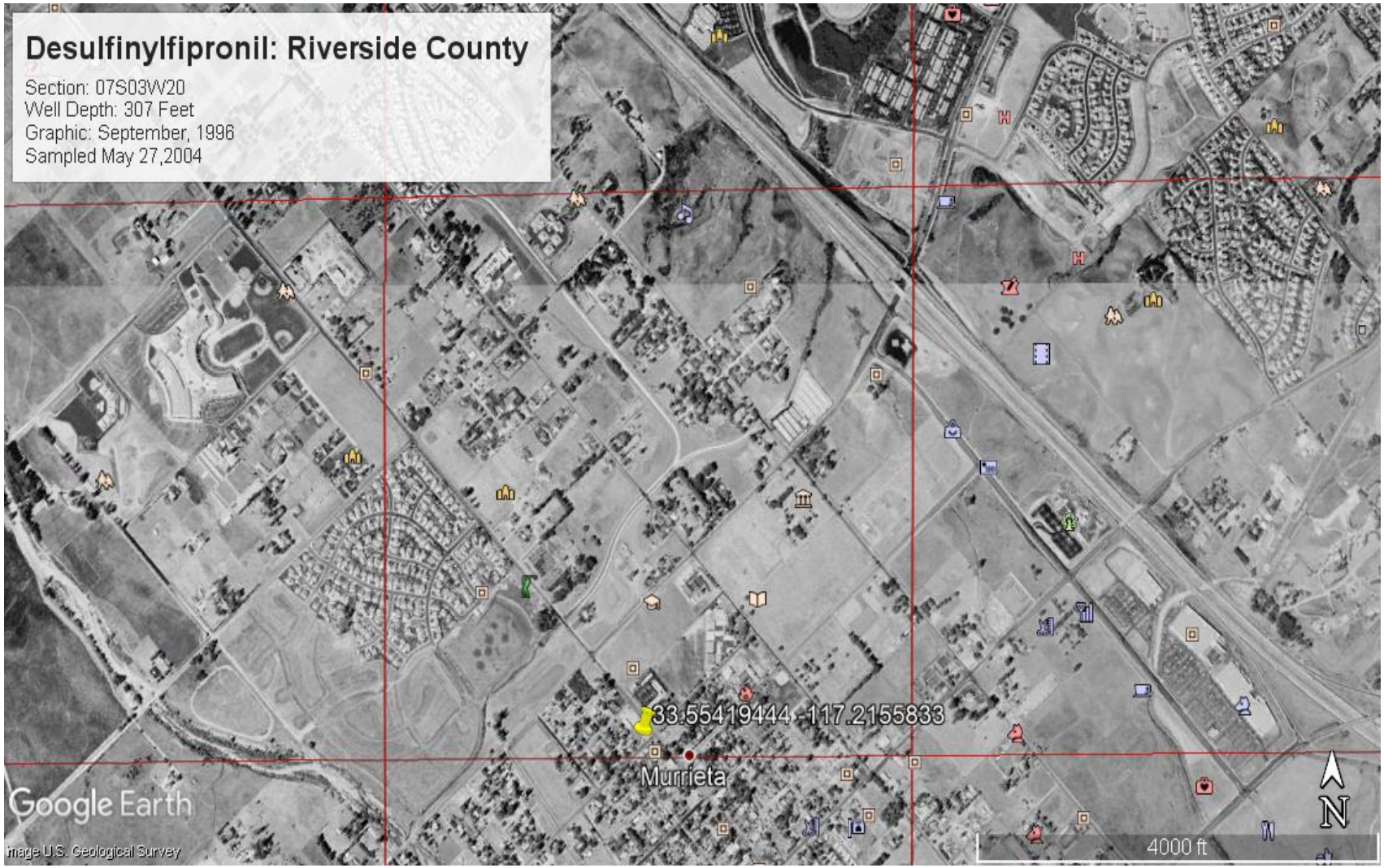
These findings, taken together, indicate that agricultural use was not the source of the three reported desulfinyl fipronil detections.

No follow-up sampling is recommended.

Table 14. Detection of desulfinyl fipronil in relation to other residues measured in a well sampled in Riverside County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Riverside: Well 3307S03W20C09SD: Depth 307 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 05/27/2004				
Fipronil	0	0.04	Not Reported	Not Reported
Fipronil Sulfide	0	0.016	-	-
Fipronil Sulfone	0	0.024	-	-
Desulfinyl Fipronil	0.0069	0.012	-	-
Desulfinyl Fipronil Amide	0	0.029	-	-
Atrazine	0.0075	0.008	0	0
Deethylatrazine	0	0.014	0	0
Diuron	-	-	0	1,262
3,4-Dichloroaniline	0.0034	0.006	-	-
Metalaxyl	0.0112	0.014	0	0
Myclobutanil	0.0050	0.034	0	20
Prometon	0.0096	0.012	0	0
Simazine	0.0109	0.01	0	1,421

Figure 9. Landscape surrounding the wellhead with a reported detection of desulfinyl fipronil in Riverside County.



Hydroxyatrazine: USGS Parameter Code 50355

Pesticide use and landscape analysis: One detection of hydroxyatrazine was reported in a well sampled in Sacramento County (Table 15). The concentration was approximately 50% lower than the revised LRL. This well was part of a monitoring well cluster where samples were taken at 220-, 500-, and 995-foot depths. The reported detection was measured in water sampled at 500 feet with no detections at the other two depths. As indicated in Figure 10, rice was the dominant agricultural crop in the landscape surrounding the well. The sample at the 500-foot depth also contained detections of molinate, diuron, and 3,4-dichloroaniline (a breakdown product of diuron). Molinate and diuron were not detected at the other two depths whereas 3,4-dichloroaniline was. Diuron use was not reported in the surrounding area from 1990 to 2004. However, detections could be from non-crop roadside use as these applications are not reported on a section basis. Normally, simazine is used in conjunction with diuron for non-crop use because this combination prevents growth of both grassy and broadleaf weeds. No residue of simazine or its degradation product was detected at the three depths and diuron was not detected in either the shallower or deeper well. Propanil and thiobencarb, like molinate, are rice pesticides that were also subject to analysis in the water samples of the well cluster. Despite relatively heavy use of propanil and thiobencarb within the section, residues of these chemicals were not reported at any of the sampled depths. Excluding the residues reported for 3,4-dichloroaniline, the detections for hydroxyatrazine, molinate, and diuron in the single, medium depth sample appear spurious.

Recommendation: Agricultural use is not likely the source of the detection of hydroxyatrazine in this sample due to:

- No consistency in detection of hydroxyatrazine among the three sampled depths.
- No detection of other atrazine breakdown products that are detected in groundwater more frequently than hydroxyatrazine.
- No verified detections in similar intensive agricultural areas.
- No detection of other rice herbicides used at comparable amounts and with similar potential to move to groundwater.
- No detection in other wells where atrazine or its breakdown product had been measured.
- The reported concentration was nearly one-half the concentration of the revised LRL.

These findings, taken together, indicate that agricultural use was not the source of the reported hydroxyatrazine detection.

No follow-up sampling is recommended.

Table 15. Detection of hydroxyatrazine in relation to other residues measured in well samples in Sacramento County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Sacramento: Sampled 04/13/2005				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Well 3410N04E27R02MD: Depth 995 Feet				
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Hydroxyatrazine	0	0.08	-	-
Diuron	0	0.04	0	0
3,4-Dichloroaniline	0.012	0.006	-	-
Molinate	0	0.008	9,597	57,291
Propanil	0	0.014	10,246	54,440
Simazine	0	0.01	0	0
Deethylsimazine	0	0.08	-	-
Thiobencarb	0	0.01	16,130	53,892
Triclopyr	0	0.08	541	2,574
Well 3410N04E27R03MD: Depth 500 Feet				
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Hydroxyatrazine	0.042	0.08	-	-
Diuron	0.03	0.04	0	0
3,4-Dichloroaniline	0.062	0.006	-	-
Molinate	0.016	0.008	9,597	57,291
Propanil	0	0.014	10,246	54,440
Simazine	0	0.01	0	0
Deethylsimazine	0	0.08	-	-
Thiobencarb	0	0.01	16,130	53,892
Triclopyr	0	0.08	541	2,574
Well 3410N04E27R04MD: Depth 220 Feet				
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Hydroxyatrazine	0	0.08	-	-
Diuron	0	0.04	0	0
3,4-Dichloroaniline	0.003	0.006	-	-
Molinate	0	0.008	9,597	57,291
Propanil	0	0.014	10,246	54,440
Simazine	0	0.01	0	0
Deethylsimazine	0	0.08	-	-
Thiobencarb	0	0.01	16,130	53,892
Triclopyr	0	0.08	541	2,574

Figure 10. Landscape surrounding the wellhead with a reported detection of hydroxyatrazine in Sacramento County.

Imazethapyr: USGS Parameter Code 50407

Pesticide use and landscape analysis: Two detections of imazethapyr were reported, one in Fresno County and the other in San Diego County (Tables 16 and 17). For the reported detection in Fresno County, two wells were sampled in the same location where the deeper well contained the imazethapyr residue. No imazethapyr was detected in the shallower well. The revised LRL was the same for both samples. The landscape surrounding the well was predominately agricultural with tree crops and vines grown within the entire section (Figure 11). No use of imazethapyr was reported within the section although 207 lbs of use occurred in the surrounding eight sections from 1990 to 2004 (Table 16). Much greater amounts of diuron and simazine were reported used within the section. Residues of diuron were reported in both wells, and simazine was reported in the deeper well but not in the shallower well. The reported imazethapyr concentration was equal to that measured for diuron, even though the amount reported used was considerably lower. Diuron is a known groundwater contaminant with other detections reported in Fresno County wells. As no other detections of imazethapyr were reported in wells sampled in Fresno County, or in any other county throughout the intensely farmed San Joaquin Valley, this reported detection of imazethapyr appears spurious and most likely did not originate from agricultural use.

The second reported detection of imazethapyr was in a well in San Diego County that was sampled twice. A detection was reported in 2004 but not in 2014 (Table 17). The concentration reported was below the revised LRL. No use of imazethapyr was reported in the section or in the eight sections surrounding the well. Furthermore, there was no reported use of diuron or simazine, and no detection of either of these pesticides or their breakdown products in that well (Table 17). Although there was some agriculture in the area surrounding the wellhead, suburban infill and industrial sites dominated the landscape (Figure 12). Imazethapyr is registered for use on alfalfa, beans, wheat, rye, oats, peas, and corn. Historically, melons, tomato, strawberry, peppers, outdoor-grown greenhouse crops, and corn were the major crops grown in the area surrounding the wellhead. In suburban areas diuron and simazine were historically used for non-crop weed control along roadsides, but this type of use is not recorded on a section basis. Due to the lack of imazethapyr residue detection in the subsequent sample, the lack of detection of known groundwater contaminants, and the landscape surrounding the well, agricultural use was not the likely source for the detection of imazethapyr.

Recommendation: Agricultural use is not likely to be the source of detection due to:

- No consistency in detection between closely adjacent wells sampled at the same time (Fresno County) and a well sampled over time (San Diego County).
- No verified detections in similar intensely farmed San Joaquin Valley.
- No substantial use to verify the detection.
- Landscape analysis in San Diego County does not support a lone detection of imazethapyr.

These findings, taken together, indicate that agricultural use was not the source of the two reported imazethapyr detections.

No follow-up sampling is recommended.

Table 16. Detection of imazethapyr in relation to other residues measured in one of two wells sampled in Fresno County. The wells are located at the same site where the depth of the well with the detection was 208 feet and the other well depth was shallower at 140 feet. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

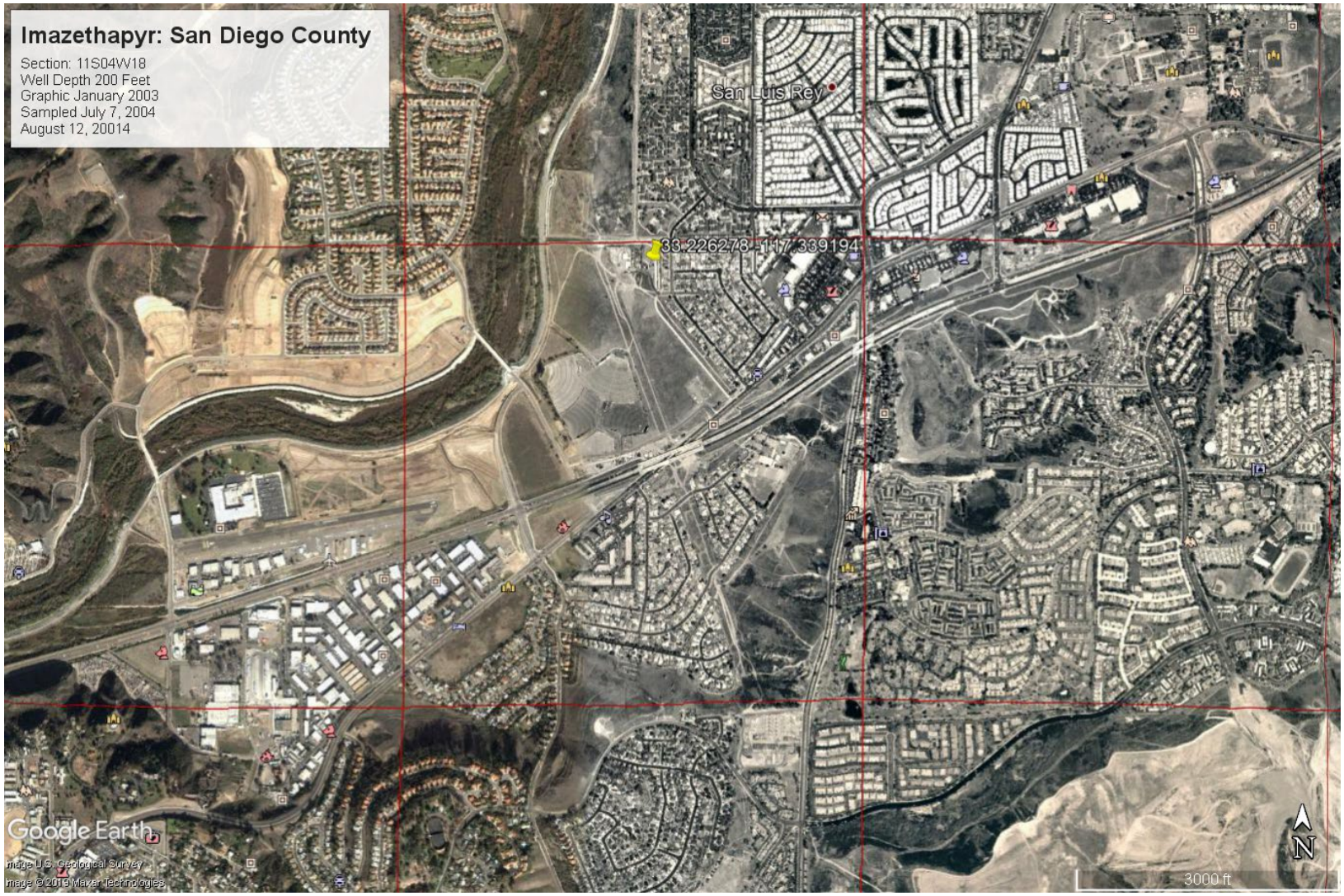
Fresno: Sampled 11/26/2005				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Well 1014S19E29A102MZ: Depth 208 Feet				
Imazethapyr	0.4253	0.08	0	207
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	0.4391	0.04	322	1,483
3,4-Dichloroaniline	0.082	0.006	-	-
Hexazinone	0	0.026	0	1,307
Myclobutanil	0	0.034	1,653	3,243
Prometryn	0.0056	0.01	0	76
Simazine	0.027	0.01	1,952	12,028
Deethylsimazine	0	0.08	-	-
Well 1014S19E29A101MZ: Depth 140 Feet				
Imazethapyr	0	0.08	0	207
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	0.5423	0.04	322	1,483
3,4-Dichloroaniline	0.288	0.006	-	-
Hexazinone	0	0.026	0	1,307
Myclobutanil	0.0336	0.034	1,653	3,243
Prometryn	0	0.01	0	76
Simazine	0	0.01	1,952	12,028
Deethylsimazine	0	0.08	-	-

Figure 11. Landscape surrounding the wellhead with a reported detection of imazethapyr in Fresno County.

Table 17. Detection of imazethapyr in relation to other residues measured in a well sampled in San Diego County. The well was sampled twice in 2004 and then again in 2014. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

San Diego: Well 3711S04W18C11SD: Depth 200 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 07/13/2004				
Imazethapyr	0.07	0.08	0	0
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	0	0.04	0	0
3,4-Dichloroaniline	0	0.006	-	-
Simazine	0	0.01	0	0
Deethylsimazine	0	0.08	-	-
Sampled 08/12/2014				
Imazethapyr	0	0.08	0	0
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	0	0.04	0	0
Simazine	0	0.01	0	0
Deethylsimazine	0	0.08	-	-

Figure 12. Landscape surrounding the wellhead with a reported detection of imazethapyr in San Diego County.



Metalaxyl: USGS Parameter Code 61596

Pesticide use and landscape analysis: Eleven detections of metalaxyl were reported in six counties (Table 18). The concentrations of seven detections were below the revised LRL. The GWPP conducted sampling in Los Angeles and Stanislaus counties around the wells with reported concentrations above GWPP's reporting limit of 0.05 µg/L (Nordmark, 2015a and 2015b).

The original well in Los Angeles County was resampled along with another well located nearby. Both wells were municipal drinking water wells. The GWPP conducted sampling in May 2015, ten years after the original detection of metalaxyl due to a delay in the receipt of the GAMA Program's data. Simazine residues were subsequently detected in both wells, but metalaxyl residues were not (Nordmark, 2015a). The sample from the GAMA Program also had reported detections of atrazine and simazine. Although no use of these pesticides was reported around the wellhead, atrazine and simazine may have been applied for weed control in groundwater recharge basins located near the municipal wells before these practices were restricted. This non-crop use would explain the lack of atrazine and simazine use reported near the wellheads.

For the reported detection in Stanislaus County, six wells were sampled by the GWPP around the original well; the original well was not resampled because it was a monitoring well. The samples were analyzed for numerous pesticides and degradates at the reporting limit of 0.05 µg/L. Only the metolachlor breakdown products, metolachlor ethanesulfonic acid (ESA) and metolachlor oxanilic acid (OXA), were detected in four of the six wells. Residues of other known groundwater contaminants were not detected (Nordmark, 2015b). The GAMA Program reported the presence of the parent metolachlor in the sample at a concentration of 0.045 µg/L, but subsequent resampling only detected the breakdown products.

Recommendation: Although the reported metalaxyl detections were not verified by GWPP resampling in the area of the detections, the number of detections in areas with reported use indicate potential of metalaxyl residues to move to groundwater. **GWPP will continue to evaluate reported metalaxyl detections and conduct follow-up groundwater studies as needed.**

Table 18. Detections of metalaxyl in relation to pesticide use reported in the landscape surrounding each wellhead. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Metalaxyl Well Sampling and Use Information							
County	**Well**	**Well Depth (Feet)**	**Date Sampled**	**Detection (µg/L)**	**Revised LRL (µg/L)**	**Within Section (lbs)**	**Surrounding 8 Sections (lbs)**
Los Angeles	1901S10W17A03SD	500	07/12/2005	0.144	0.014	0	0
Los Angeles	1902S11W05G07SD	712	06/14/2005	0.0148	0.014	0	10
Los Angeles	1902S12W25G01SD	520	08/16/2006	0.0097	0.014	0	0
Los Angeles	1903S12W16H01SD	572	08/14/2006	0.0083	0.014	<1	5
Riverside	3307S03W20C09SD	307	05/27/2004	0.0112	0.014	0	0
Riverside	3308S02W19J03SD	490	05/26/2004	0.0112	0.014	0	128
San Diego	3711S04W04K05SD	135	07/14/2004	0.0094	0.014	0	160
San Luis Obispo	4011N25W25P01SD	203	07/31/2008	0.0082	0.014	137	1,122
Stanislaus	5006S08E09E01MD	430	05/19/2010	0.0148	0.014	92	209
Stanislaus	5006S08E09E03MD	115	05/19/2010	0.0543	0.014	92	209
Ventura	5602N20W19F04SD	759	04/10/2007	0.01	0.014	32	1,079

Metolachlor: USGS Parameter Code 39415

Pesticide use and landscape analysis: The GAMA Program reported 12 wells with detections of metolachlor (Table 19). The concentrations for nine of the 14 reported detections were below the revised LRL. No use of metolachlor was reported in the section or in the surrounding eight sections of land for five of the wellheads. The highest reported concentration (0.16 µg/L) was from a well located in a remote area of San Bernardino County near a vehicle refueling stop (Figure 13). The surrounding landscape is undeveloped desert. No use of any agricultural pesticide product has been reported in the landscape surrounding that wellhead. Metolachlor is in the acetonitrile class of chemicals and, as indicated in the acetochlor- and alachlor-specific sections above, might represent a problem with residue analysis — the highest reported metolachlor concentration was in a well (San Bernardino County) with no connection between agricultural use and the reported well water detection. The GWPP has conducted targeted sampling in high-use areas for alachlor, metolachlor, and their breakdown products (Bergin and Nordmark, 2012). Only the ESA and OXA breakdown products of the parent chemicals have been detected above the reporting limit of 0.05 µg/L. Recent USGS well monitoring data included analysis of the ESA and OXA breakdown products. Preliminary review of those data indicates that the breakdown products were detected in well water samples, but the parent was not.

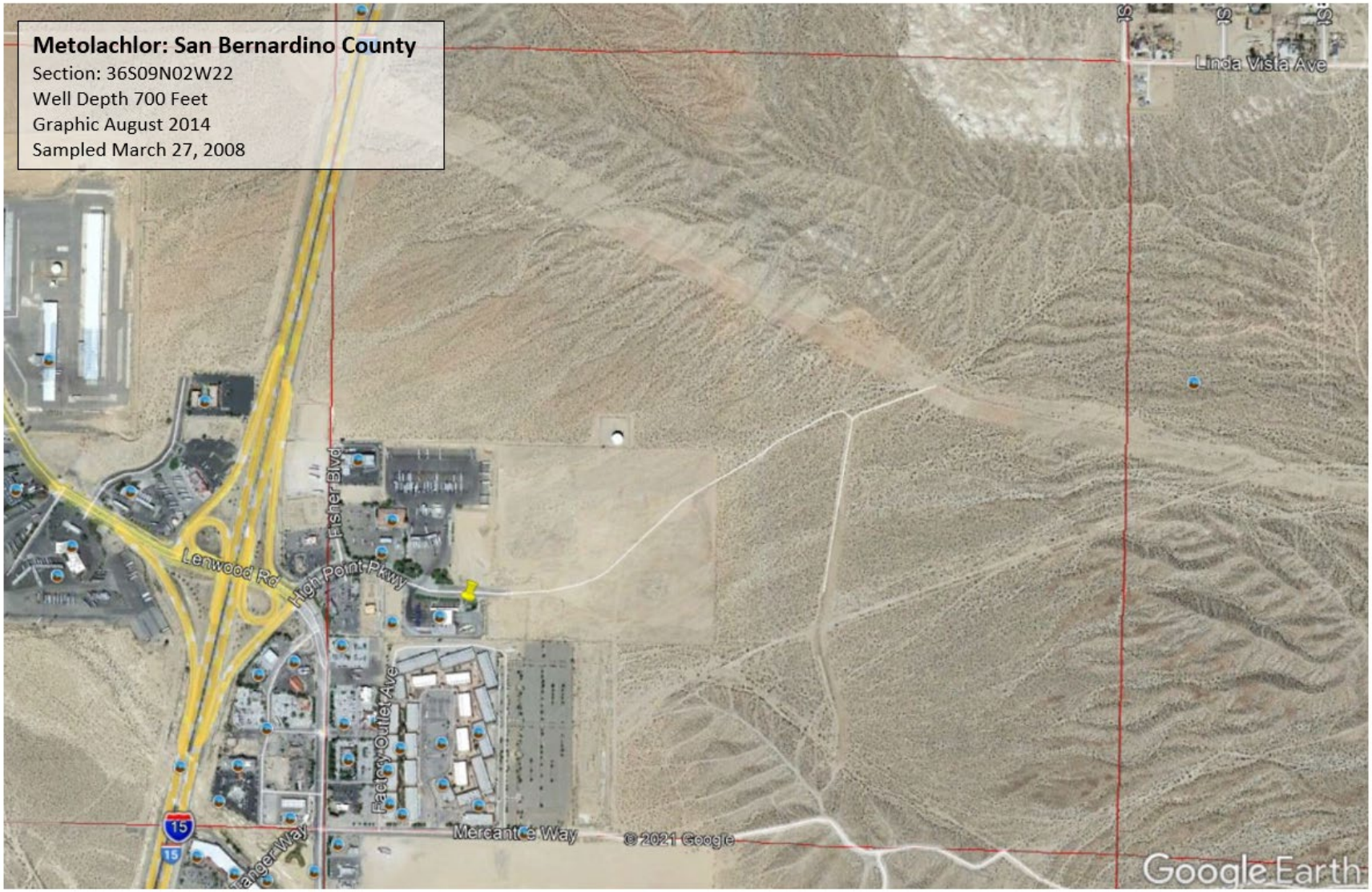
Recommendation: Metolachlor products are registered for use on a wide variety of crops. Although metolachlor breakdown products have been detected in groundwater, the presence of metolachlor has yet to be verified by GWPP in any well water sample at a concentration above 0.05 µg/L.

Although previous retrospective studies have not resulted in detection above 0.05 µg/L, further sampling should be considered for both the parent and breakdown products as use of metolachlor has increased over time. GWPP will continue to evaluate reported metolachlor detections and conduct follow-up groundwater studies as needed.

Table 19. Detections of metolachlor in relation to pesticide use reported in the landscape surrounding each wellhead. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Metolachlor Well Sampling and Use Information							
County	**Well**	**Well Depth (Feet)**	**Date Sampled**	**Detection (µg/L)**	**Revised LRL (µg/L)**	**Within Section (lbs)**	**Surrounding 8 Sections (lbs)**
Kern	1527S25E33J01MD	694	01/12/2006	0.013	0.02	496	3,396
Kern	1530S28E05M101MZ	637	01/10/2006	0.014	0.02	0	0
Kings	1622S19E18P101MZ	-	06/09/2010	0.015	0.02	45	703
San Bernardino	3609N02W22N101SZ	700	03/27/2008	0.16	0.02	0	0
San Diego	3710S01E05H001SZ	315	07/15/2004	0	0.02	0	0
			08/23/2011	0.019	0.02		
			05/15/2014	0	0.02		
San Diego	3710S01W05L001SZ	200	06/30/2004	0.011	0.02	0	0
			05/01/2014	0	0.02		
San Joaquin	3901N07E27P101MZ	365	01/12/2005	0.012	0.02	176	4,157
Santa Barbara	4207N35W26F06SD	190	06/25/2008	0.011	0.02	0	953
Stanislaus	5005S09E20A01MD	104	04/03/2006	0.035	0.02	723	8,732
Stanislaus	5006S08E09E01MD	430	05/19/2010	0.0234	0.02	1,823	14,996
	5006S08E09E02MD	255	05/20/2010	0.0129	0.02		
	5006S08E09E03MD	115	05/19/2010	0.0455	0.02		
Stanislaus	5007S09E04J07MD	113	03/29/2010	0.014	0.02	0	2,865
Yuba	5816N04E34C01MD	72	07/26/2006	0.028	0.02	0	0

Figure 13. Landscape surrounding the wellhead with a reported the highest concentration reported for metolachlor in San Bernardino County.



Metribuzin: USGS Parameter Code 82630

Pesticide use and landscape analysis: One detection of metribuzin was reported in a well in Yolo County (Table 20). Some use was reported within the landscape surrounding the well. However, reported use for the known groundwater contaminants, diuron and hexazinone, was much higher, and no detections were reported for these chemicals. The GWPP conducted follow-up sampling approximately eight years later when the metribuzin detection was reported to DPR. Although the exact location of the original well could not be verified from the reporting agency's data, water samples were obtained from five domestic wells located in the area of the reported metribuzin detection (Nordmark, 2014b). No metribuzin residues were detected above the reporting limit of 0.05 µg/L. In addition, residues were not detected for twelve other known groundwater contaminant chemicals included in the analytical screen used for these well water samples.

Recommendation: Although some metribuzin use was reported in the landscape around the well, use of diuron and hexazinone, which are known groundwater contaminants, was greater and no residues of these chemicals were detected. The GWPP conducted follow-up sampling in wells located near the original detection but did not detect any additional metribuzin residues, nor were there any detections of residues for 12 other chemicals frequently detected in well water.

Follow-up sampling has been conducted for the detection in Yolo County with no indication that the reported residue was due to nonpoint source agricultural applications.

Table 20. Detection of metribuzin in relation to other residues measured in a well sampled in Yolo County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Yolo: Well 5710N01E10J101MZ: Depth 340 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 08/02/2006				
Metribuzin	0.113	0.028	28	702
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	0	0.04	312	2,596
3,4-Dichloroaniline	0	0.006	-	-
Hexazinone	0	0.026	0	1,415
Simazine	0.01	0.01	432	304
Deethylsimazine	0	0.08	-	-

Myclobutanil: USGS Parameter Code 61599

Pesticide use and landscape analysis: The single reported detection of myclobutanil occurred in the same set of wells in Fresno County where a residue of imazethapyr was reported (Table 16). In contrast to the detection noted for imazethapyr, the myclobutanil residue was reported in the shallower well. Considerable use of myclobutanil was reported within the section and the surrounding eight sections of land where the detection occurred. Furthermore, myclobutanil has use directions indicating applications to the soil. Both the reported use and use directions support the myclobutanil well water detection. The total amount of reported use for myclobutanil was higher than for diuron, but the reported concentration was over an order of magnitude lower than the concentrations measured for diuron.

Recommendation: Pesticide use around the wellhead and the method of application support the potential for myclobutanil residues to move to groundwater. However, the detection was found in only one of two adjacent wells sampled. Also, no other residues of myclobutanil have been reported in areas with similar use patterns to that of the section where the reported detection occurred in the intensely farmed San Joaquin Valley.

The potential need for follow-up sampling exists. The reported detection should be a factor in the prioritization of analytical method development and future monitoring for pesticides on the Groundwater Protection List.

Pendimethalin: USGS Parameter Code 82683

Pesticide use and landscape analysis: The GAMA Program reported two detections of pendimethalin. The concentration of one detection was below the revised LRL. One well located in Monterey County was sampled twice, in 2005 and 2013 (Table 21). The other well located in San Bernardino County was also sampled twice, in 2007 and 2009 (Table 22).

The landscape around the reported detection in Monterey County was mountainous, indicating very little potential for agricultural use of pesticide products (Figure 14). Between 1990 and 2012, no use of pendimethalin was reported within the section of land where the well was sampled or within the surrounding mountainous eight sections (Table 21). The concentration of pendimethalin was below the revised LRL. No use of other known groundwater contaminants was reported around the well, nor were there any reported detections of residues in the well water sample.

The second reported pendimethalin detection was from a well located in the city of Redlands in San Bernardino County (Figure 15). Pendimethalin was reported in the 2007 sample but not in the follow-up sample taken in 2009 (Table 22). Prior to the reported detection, no pendimethalin use was reported within the section or surrounding sections of land. The landscape surrounding the well was predominantly suburban with some larger estates, indicating the unlikelihood of significant agricultural applications. Detections were reported for atrazine, diuron, simazine, and their breakdown products. No use was reported for these chemicals; therefore, these detections were most likely from non-crop roadside applications.

Recommendation: Agricultural use does not appear to be the source of pendimethalin detections due to:

- The detection in the well located in Monterey County was below the revised LRL.
- The landscape around both wellheads indicated very little agriculture and no reported use of pendimethalin in the area.
- No residues of pendimethalin have been reported in wells sampled in known vulnerable areas in California where pendimethalin has been used in the landscape surrounding wellheads.
- In both wells, pendimethalin residue was reported in only one of the two samples taken.

These findings, taken together, indicate that agricultural use was not the source of the two reported pendimethalin detections.

No follow-up sampling is recommended.

Table 21. Detection of pendimethalin in relation to other residues measured in a well sampled in Monterey County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Monterey: Well 2713S03E15F101MZ: Depth 472 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 9/13/2005				
Pendimethalin	0	0.022	0	0
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	0	0.04	0	0
3,4-Dichloroaniline	0	0.006	-	-
Simazine	0	0.01	0	0
Deethylsimazine	0	0.08	-	-
Sampled 3/07/2013				
Pendimethalin	0.0110	0.022	0	0
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Diuron	-	-	0	0
3,4-Dichloroaniline	0	0.006	-	-
Simazine	0	0.01	0	0

Figure 14. Landscape surrounding the wellhead with a reported detection of pendimethalin in Monterey County.

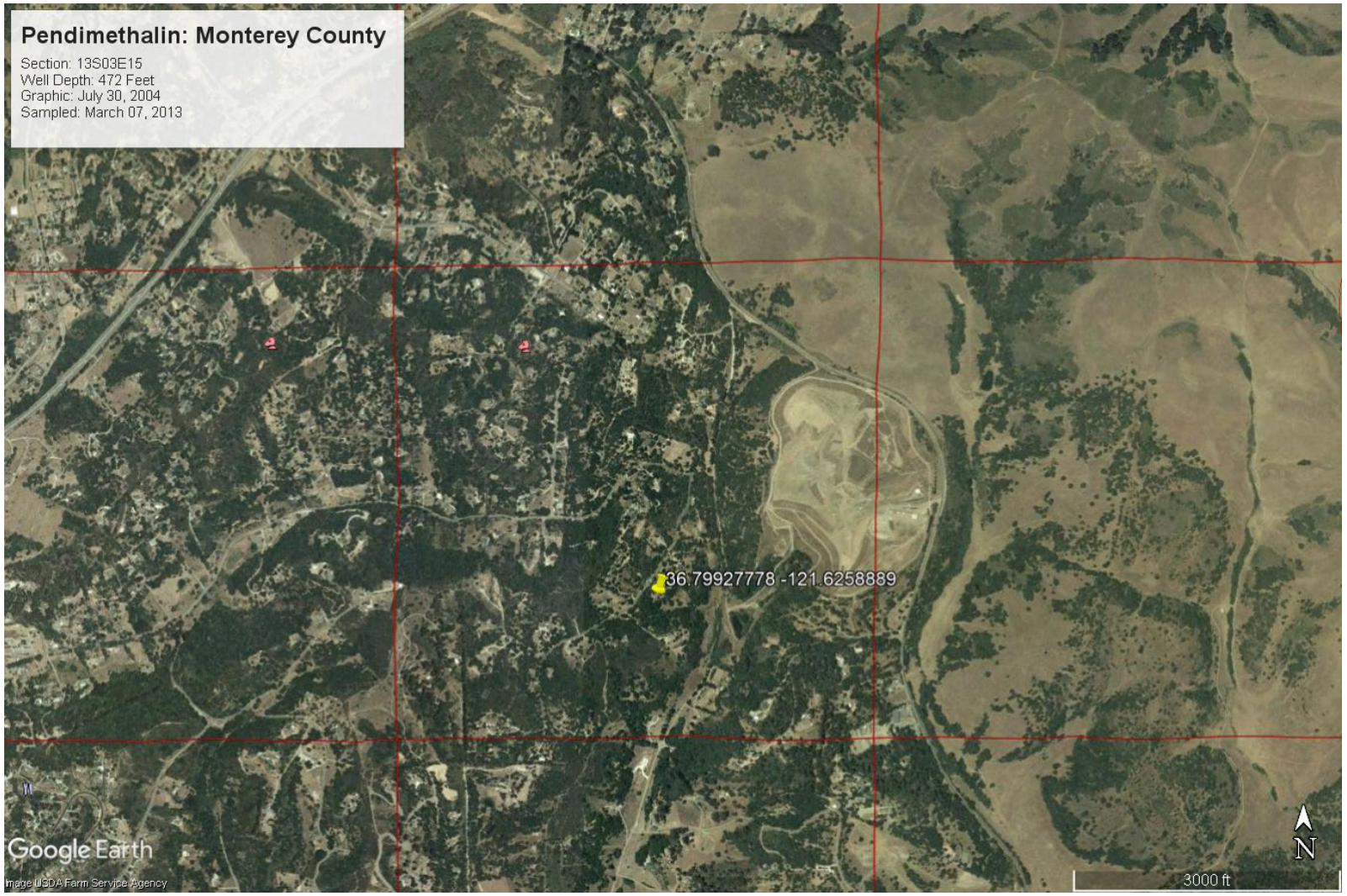
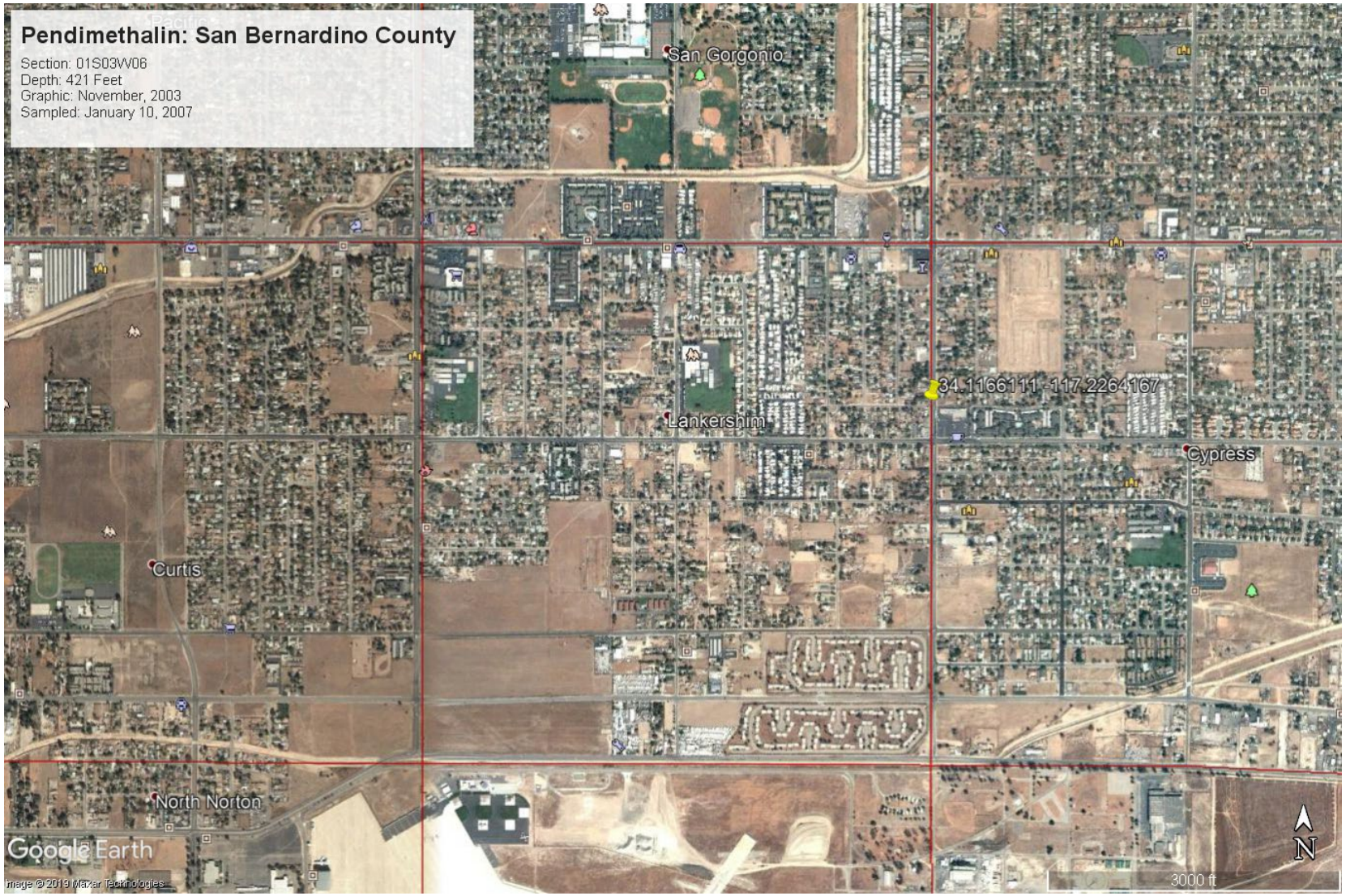


Table 22. Detection of pendimethalin in relation to other residues measured in a well sampled in San Bernardino County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

San Bernardino: Well 3601S03W06H04SD: Depth 421 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 1/10/2007				
Pendimethalin	0.039	0.022	0	0
Atrazine	0.015	0.008	0	0
Deethylatrazine	0.011	0.014	-	-
Diuron	0.01	0.04	0	0
3,4-Dichloroaniline	0	0.006	-	-
Simazine	0.124	0.01	0	0
Deethylsimazine	0.06	0.08	-	-
Sampled 4/23/2009				
Pendimethalin	0	0.022	0	0
Atrazine	0.0092	0.008	0	0
Deethylatrazine	0.0104	0.014	-	-
Diuron	-	-	0	0
3,4-Dichloroaniline	0	0.006	-	-
Simazine	0.102	0.01	0	0
Deethylsimazine	0.0462	0.08	-	-

Figure 15. Landscape surrounding the wellhead with a reported detection of pendimethalin in San Bernardino County.



Prometryn: USGS Parameter Code 04036

Pesticide use and landscape analysis: The GAMA Program reported eight detections of prometryn with all values below the revised LRL of 0.01 µg/L (Table 23). Prometryn had been registered for use as an herbicide on a wide variety of crops, but currently has only one product registered for use on cotton and specialty crops such as parsley, fennel, rhubarb, and cilantro. Prometryn was used substantially in the landscape surrounding the wellheads in Kern and Merced counties. However, use was very low around the wellheads in Fresno, Riverside, and Ventura counties. The second highest concentration at 0.0081 µg/L was reported in a well sampled in Riverside County where there was no indication of use in the landscape surrounding the wellhead (Table 24). Prometryn was not detected in the well when it was resampled ten years later in 2014.

Detections of several known groundwater contaminants and other pesticides in the original sample in 2004 may have been spurious because no residues of any chemicals were measured in the sample taken in 2014. The landscape in the area around the wellhead in Riverside County was a naturally vegetated catchment for runoff water from foothills located to the north, east, and south (Figure 16).

Recommendation: Use in the landscape surrounding the wellheads appears to substantiate some of the detections, whereas lack of use around others does not. All the detections were below the revised LRL at 0.01 µg/L with six of the eight detections approximately half the LRL.

No follow-up sampling is recommended until concentrations above the revised LRL are reported to GWPP.

Table 23. Detections of prometryn in relation to pesticide use reported in the landscape surrounding each wellhead. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Prometryn Well Sampling and Use Information							
County	**Well**	**Well Depth (Feet)**	**Date Sampled**	**Detection (µg/L)**	**Revised LRL (µg/L)**	**Within Section (lbs)**	**Surrounding 8 Sections (lbs)**
Fresno	1014S19E29A102MZ	140	11/16/2005	0.0056	0.01	0	76
Imperial	1315S23E33H04SD	-	11/29/2007	0.0051	0.01	0	7
Kern	1525S24E31B101MZ	700	01/11/2006	0.0060	0.01	637	16,212
Kern	1525S25E10A01MD	999	01/11/2006	0.0056	0.01	0	437
Kern	1528S25E07C101MZ	600	02/27/2006	0.0087	0.01	555	11,565
Merced	2409S11E10M101MZ	-	06/30/2010	0.0065	0.01	2,011	12,271
Riverside	3308S01W05P01SD	250	05/27/2004	0.0081	0.01	0	0
			04/23/2014	0	0.01		
Ventura	5604N18W29F01SD	285	06/06/2007	0.0050	0.01	49	0

Table 24. Detection of prometryn in relation to other residues measured in a well sampled in Riverside County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Riverside: Well 3308S01W05P01SD: Depth 250 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 5/27/2004				
Prometryn	0.0081	0.01	0	0
Atrazine	0.0072	0.008	0	0
Deethylatrazine	0.005	0.014	-	-
Diuron	-	-	0	387
3,4-Dichloroaniline	0.0085	0.006	-	-
Prometon	0.0071	0.012	0	0
Simazine	0.0165	0.01	0	1,293
Terbuthylazine	0.006	0.009	0	0
Sampled 4/23/2014				
Prometryn	0	0.01	0	0
Atrazine	0	0.008	0	0
Deethylatrazine	0	0.014	-	-
Bromacil	0	0.06	0	291
Diuron	0	0.04	0	452
Prometon	0	0.012	0	0
Simazine	0	0.01	0	1,922
Deethylsimazine	0	0.08	-	-
Terbuthylazine	0	0.009	0	0

Figure 16. Landscape surrounding the wellhead with a reported detection of prometryn in Riverside County.

Propanil: USGS Parameter Code 82679

Pesticide use and landscape analysis: Residue of propanil was reported in a well sampled in Butte County with a concentration above the revised LRL (Table 25). The landscape surrounding the wellhead is dominated by rice production (Figure 17). Products containing propanil are used in rice production to control weed growth. Propanil use in the section where the detection occurred and in the surrounding eight sections was substantial, indicating potential for its movement to groundwater and for detection of its residues in the well water sample. Bentazon and molinate are also rice herbicides and they were also detected in the sample. Thiobencarb, another rice herbicide, had no residue reported in the sample despite heavy use in the area. Logically, if propanil is a potential groundwater contaminant, similar amounts of use in other rice growing areas should have also resulted in detections in other wells. Bentazon, though no longer registered for use on rice, is a known groundwater contaminant: its residues in groundwater are known to result from historic use to control weeds in rice. Bentazon residues at concentrations greater than the revised LRL were measured in eight other wells in Butte County, ten wells in Colusa County, ten wells in Glenn County, one well in Placer County, one well in Sutter County, and three wells in Yuba County. All of these wells are located in areas dominated by rice production. Total amounts of chemicals used on rice from 1990 to 2005 in the sections of land in which these 34 wells were located were 348,050 lbs molinate, 215,615 lbs propanil, 159,125 lbs thiobencarb, and 10,042 lbs triclopyr. No residues of propanil, triclopyr, or thiobencarb were reported in these samples; and the only well with a molinate residue was the well in question in Butte County with the reported detection of propanil residue.

Additional evidence for the low potential of propanil to move to groundwater is provided by GWPP's targeted sampling of wells for pesticides used in rice production areas. A study conducted in 2013 included propanil in the chemical analysis at a reporting limit of 0.05 µg/L where 165 wells were sampled, including the well in question located in Butte County (CDPR, 2020b). Despite the increasing use of propanil over time, no propanil, triclopyr, molinate, or thiobencarb residues were detected. Analysis of bentazon residues was not included in that study.

Recommendation: Agricultural use does not appear to be a likely source of the propanil detection due to:

- No detection in other wells sampled in rice growing areas where residues of bentazon were detected. Detection of bentazon indicates a hydrologic connection between water used in rice culture and water sampled in wells.
- No detection in targeted studies conducted by the GWPP.

These findings, taken together, indicate that the agricultural use was not the source of the reported propanil detection.

Follow-up sampling did not verify the detection; therefore, no further action is recommended.

Table 25. Detection of propanil and triclopyr in relation to other residues measured in a well sampled in Butte County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Butte: Well 0420N02E09M01MD: Depth 554 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 6/13/2006				
Propanil	0.097	0.014	5,017	35,218
Triclopyr	0.12	0.08	563	2,141
Bentazon	0.09	0.06	Historical	-
Diuron	0	0.04	0	189
3,4-Dichloroaniline	0.541	0.006	-	-
Molinate	0.02	0.008	31,980	105,903
Thiobencarb	0	0.01	13,964	40,769

Figure 17. Landscape surrounding the wellhead with reported detections of propanil and triclopyr in Butte County.

Terbuthylazine: USGS Parameter Code 04022

Pesticide use and landscape analysis: Two detections of terbuthylazine were reported, one in Monterey County and a second in Riverside County (Tables 26, and 24, respectively). Terbuthylazine is registered as a biocide to control growth in devices such as water coolers and water condensers and in areas such as ornamental ponds.

The terbuthylazine detection in the Riverside County well was accompanied by detections of six other chemical residues. The concentration of terbuthylazine was below the revised LRL. As discussed in the prometryn-specific section concerning this same well water sample, residues of terbuthylazine were not detected in subsequent samples (Table 24). Also, the landscape to the north, east, and south of the wellhead is foothills and the well appears to be in a naturally vegetated catchment for runoff water (Figure 16). Use of terbuthylazine was not reported around the wellhead.

For the reported detection in Monterey County, the well is in an urbanized area with agriculture to the east (Figure 18). No use of terbuthylazine was reported in the area surrounding the wellhead (Table 26). Some use of imidacloprid and the known groundwater contaminant simazine, was reported in the area surrounding the wellhead but there were no concomitant detections.

Recommendation: Agricultural use does not appear to be the source for the detections of terbuthylazine due to:

- The uses of terbuthylazine are not conducive for movement to groundwater because applications are made to closed systems such as water coolers and condensers, or to ornamental ponds that are constructed to retain water.
- No use was reported in the landscape surrounding the wellheads.
- The concentration was below the revised LRL for the Riverside County sample.
- No residues detected in subsequent sampling in the Riverside County well.

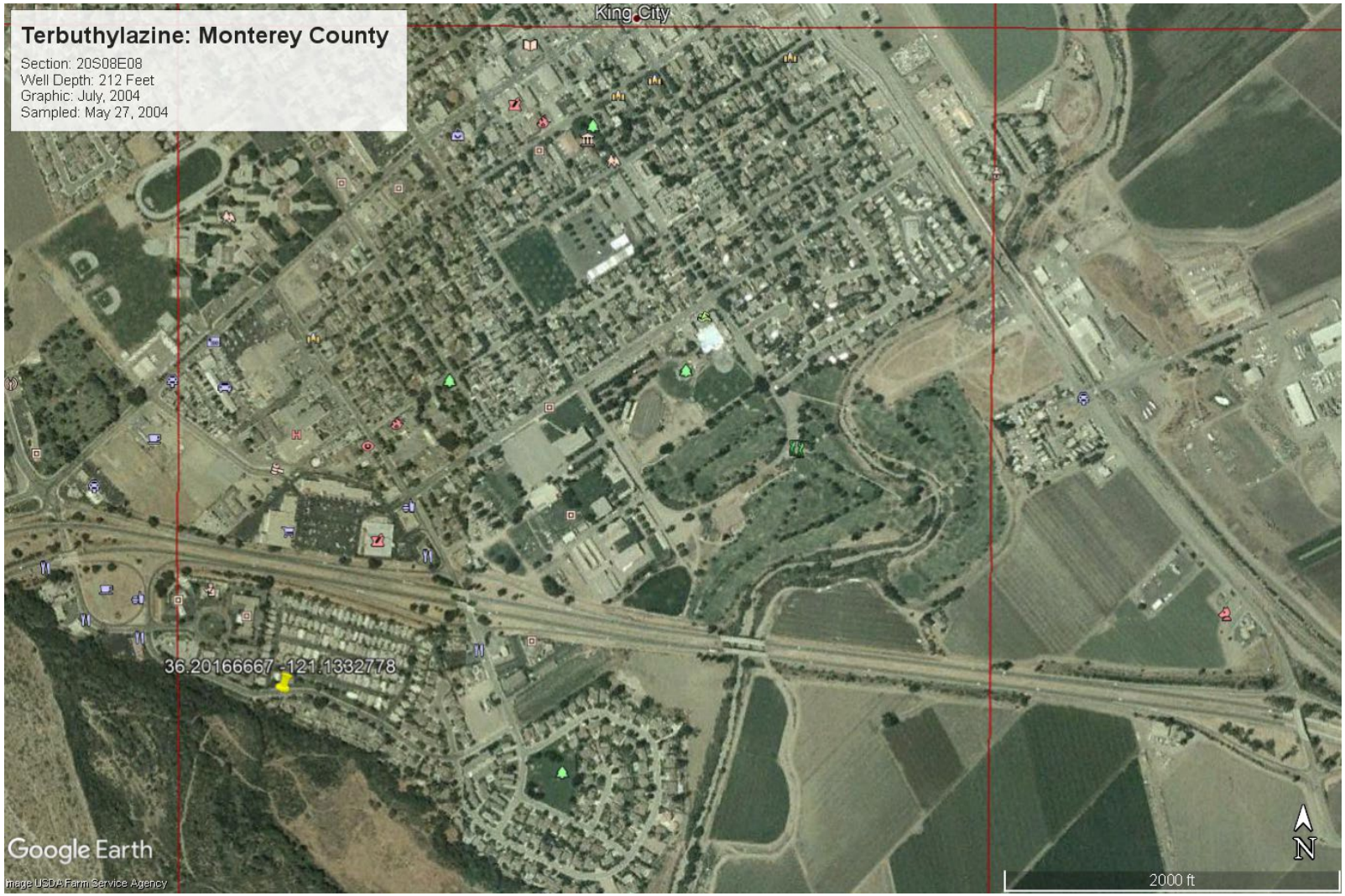
These findings, taken together, indicate that agricultural use was not the source of the two reported terbuthylazine detections.

No follow-up sampling is recommended.

Table 26. Detection of terbuthylazine in relation to analysis of other residues in a well sampled in Monterey County. (LRL = long-term reporting limit; reported pesticide use was summed from 1990 until one year prior to the reported detection)

Monterey: Well 2720S08E08M01MD: Depth 212 Feet				
	Water Sample		Amount Used	
Chemical Degradate	Concentration (µg/L)	Revised LRL (µg/L)	Within Section (lbs)	Surrounding 8 Sections (lbs)
Sampled 08/02/2005				
Terbuthylazine	0.01	0.009	0	0
Diuron	0	0.04	36	0
3,4-Dichloroaniline	0	0.006	-	-
Imidacloprid	0	0.02	43	1,799
Simazine	0	0.01	0	1,354
Deethylsimazine	0	0.08	-	-

Figure 18. Landscape surrounding the wellhead with a reported detection of terbuthylazine in Monterey County.



Triclopyr: USGS Parameter Code 49235

Pesticide use and landscape analysis: Residue of triclopyr was reported in a well sampled in Butte County with the concentration above the revised LRL (Table 25). This well also had a reported detection of propanil. The landscape surrounding the wellhead is dominated by rice production (Figure 17). Products containing triclopyr are used in rice production to control weed growth. Reported use of triclopyr in and around the site of the detection was sufficient for potential residue movement to groundwater and possible measurement in a well water sample. Bentazon and molinate are also rice herbicides and their residues were detected in the sample. Thiobencarb, another rice herbicide, had no residue reported in the sample. Logically, if triclopyr is a potential groundwater contaminant, similar amounts of use in other rice growing areas should have also resulted in detections in other wells. Bentazon, though no longer registered for use on rice, is a known groundwater contaminant: its residues in groundwater are known to result from historic use to control weeds in rice. Bentazon residues at concentrations greater than the revised LRL were measured in eight other wells in Butte County, ten wells in Colusa County, ten wells in Glenn County, one well in Placer County, one well in Sutter County, and three wells in Yuba County. All of these wells are located in areas dominated by rice production. Total amounts of chemicals used on rice from 1990 to 2005 in the sections of land in which these 34 wells were located were 348,050 lbs molinate, 215,615 lbs propanil, 159,125 lbs thiobencarb, and 10,042 lbs triclopyr. No residues of propanil, triclopyr, or thiobencarb were reported in these samples. The only well with a molinate residue was the well in question in Butte County with the reported detection of triclopyr residue.

Additional evidence for the low potential of triclopyr to move to groundwater is provided by GWPP's targeted sampling of wells for pesticides used in rice production areas. A study conducted in 2013 included triclopyr in the chemical analysis at a reporting limit of 0.05 µg/L where 165 wells were sampled, including the well in question in Butte County (CDPR, 2020b). Even though use of triclopyr has increased over time, no triclopyr, propanil, molinate, or thiobencarb residues were detected. Analysis of bentazon residues was not included in that study.

Recommendation: Agricultural use does not appear to be a likely source of the triclopyr detection due to:

- No detection in other wells sampled in rice growing areas where residues of bentazon were detected. Detection of bentazon indicates a hydrologic connection between water used in rice culture and water sampled in wells.
- No detection in targeted studies conducted by GWPP.

These findings, taken together, indicate that agricultural use was not the source of the reported triclopyr detection.

Follow-up sampling did not verify the detection; therefore, no further action is recommended.

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