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Study 318: Cooperative Groundwater Monitoring in Region 3 with the Central Coast Regional Water Quality Control Board

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ABSTRACT

This report summarizes the findings of Study 318: groundwater sampling from water wells located in areas within the jurisdiction (Region 3) of the Central Coast Regional Water Quality Control Board. For this study, 39 unique water wells located in three different groundwater basins spanning three counties in Region 3 were sampled over two sampling events in 2019: 17 wells in the Salinas Valley Groundwater Basin in Monterey County; 19 wells in the Gilroy-Hollister Valley Groundwater Basin in San Benito and Santa Clara counties; and three wells in the Pajaro Valley Groundwater Basin in northern Monterey County. All groundwater samples were analyzed by the California Department of Food and Agriculture's Center for Analytical Chemistry for 69 pesticide active ingredients (AIs) and seven degradation products. Overall, only three pesticide AIs and one degradation product were detected in the analyzed groundwater samples. No pesticide AIs or degradation products were detected in 19 of the 39 sampled wells. In particular, the chlorthal-dimethyl (DCPA) degradation product 2,3,5,6-tetrachloroterephthalic acid (TPA) was detected in 20 wells with concentrations ranging from 0.072 to 27.6 parts per billion (ppb). All measured concentrations of TPA were below its health-protective drinking water level of 2,500 ppb. The other DCPA degradation product monomethyl tetrachloroterephthalate (MTP) was not detected in any well. Bromacil was detected in one well in the Salinas Valley Groundwater Basin at a concentration of 0.054 ppb. The bromacil detection was measured in a well located in a Ground Water Protection Area (GWPA) where bromacil is regulated as a restricted-use pesticide for agricultural, outdoor industrial, and outdoor institutional uses to protect groundwater. The bromacil detection was also significantly below its human health reference level of 197 ppb. Since the detections of TPA and bromacil were less than their respective health reference levels, no follow-up investigation of these wells by the California Department of Pesticide Regulation (DPR) is necessary at this time. As required by Food and Agricultural Code (FAC) § 13152(a)(1), DPR will continue to conduct future groundwater monitoring of DCPA, MTP, and TPA in areas of Region 3 where DCPA is used.

Additionally, a trace concentration of mefenoxam/metalaxyl was detected in one well in the Pajaro Groundwater Basin and a trace concentration of tebuthiuron was detected in one well in the Hollister-Gilroy Valley Groundwater Basin. A 'trace' detection is defined as a measured concentration between a chemical's respective method detection limit and DPR's reporting limit of 0.05 ppb. Since the trace concentrations of mefenoxam/metalaxyl and tebuthiuron are both below DPR's reporting limit, no follow-up investigation of these wells by DPR is also necessary at this time.

BACKGROUND

The California Department of Pesticide Regulation's (DPR) Groundwater Protection Program (GWPP) is mandated by the Pesticide Contamination Prevention Act (PCPA) (Food and Agricultural Code [FAC] § 13149-13152) to monitor for pesticides that have the potential to pollute groundwater based on their environmental fate properties. These pesticides are placed on the Groundwater Protection List (GWPL) (Title 3 California Code of Regulations [3CCR] § 6800). The GWPP conducts routine monitoring in California groundwater basins to determine if these pesticides have migrated to groundwater due to their agricultural use patterns.

The GWPP depends on the cooperation of public agencies and private water well users to provide them with permission to collect groundwater samples from their wells for pesticide analysis. Since the PCPA was enacted to protect California groundwater from pollution by legally used agricultural pesticides, the GWPP focuses monitoring efforts predominantly in rural agricultural areas where these pesticides are used and where underlying groundwater may be vulnerable to pollution by the pesticides or their degradation products. Due to changes in land ownership and consolidation of farming operations in agricultural areas of Region 3 over the last several decades, identifying current well owners associated with certain properties during recent monitoring efforts had become increasingly difficult for GWPP staff. Therefore, monitoring by the GWPP has become limited in certain areas of Region 3.

In recent years, the GWPP has engaged with the Central Coast Regional Water Quality Control Board (RWQCB) to exchange information and share resources about water quality issues in the basins of Region 3. Part of this ongoing effort is to improve GWPP access to water wells in Region 3 for the continued monitoring of agricultural pesticides. The Central Coast RWQCB, in partnership with Lawrence Livermore National Laboratory, planned to conduct a study to determine the age and source of nitrates in groundwater throughout Region 3. The study focused on the collection and subsequent analysis of groundwater samples obtained mostly from small public water system wells that serve rural communities. Simultaneously, the Central Coast RWQCB offered a free drinking water well testing program to Region 3 residents dependent on private water wells as their source of potable water to test for various water quality constituents. For both the nitrate study and the free drinking water well testing program, Central Coast RWQCB staff arranged access to the wells and scheduled their subsequent sampling.

In 2018, the Central Coast RWQCB invited the GWPP to participate in the sampling of the small public water system wells in Monterey County under the nitrate study and to participate in the sampling of water wells in San Benito County under the free drinking water well testing program. Sampling under the nitrate study occurred during late April and early May of 2019, while sampling under the free drinking water well testing program occurred during August of 2019. GWPP staff used this opportunity to gain access to the wells and collect groundwater samples for subsequent analysis of various pesticide active ingredients (AIs) listed in regulation on the GWPL (3CCR § 6800[a] and § 6800[b]) and other AIs registered with DPR. During both sampling events, GWPP staff accompanied Central Coast RWQCB staff to each well and collected groundwater samples to be analyzed for a large number of pesticide AIs, many of which are on the GWPL, and a small number of degradation products.

This report summarizes the monitoring results of Study 318 (Ruud, 2019). It includes a brief description of the sampling methods for collecting the groundwater samples; the analytical laboratory methods and associated quality assurance/quality control (QA/QC) standards used to measure the large suite of pesticide AIs and small number of degradation products in groundwater samples; the results of the laboratory analysis of the collected groundwater samples; and comparison of detections to health reference levels.

METHODS

Sampling Methods

GWPP staff conducted sampling under Study 318 in cooperation with Central Coast RWQCB staff in two separate sampling events in Region 3 during 2019. Geographic location information, well identification, well type, and sampling dates for the wells sampled are listed in Table 1. During the two events, GWPP staff sampled 39 wells located in and around rural agricultural areas of Monterey, San Benito, and Santa Clara counties in Region 3 (Figure 1). GWPP staff collected groundwater samples for Study 318 using methods described by Nordmark and Herrig (2011).

The first event consisted of sampling 20 water wells in Monterey County between April 29 and May 3 (Table 1). Central Coast RWQCB staff selected and scheduled sampling for the 20 wells as part of a groundwater nitrate study conducted in partnership with Lawrence Livermore National Laboratory. For the nitrate study, the focus was on sampling wells used as small water systems (i.e., those that provide potable water for 2 to 14 service connections) that serve rural communities. Domestic and irrigation wells were also considered for inclusion in the nitrate study based on their availability for sampling.

The second event consisted of sampling 18 wells in San Benito County and one well in Santa Clara County over the period of August 19-23 (Table 1). Central Coast RWQCB staff selected and scheduled sampling for the 18 wells in San Benito County as part of their free drinking water well testing program for Region 3 residents who rely on private wells as their source of potable water. The sampling of the single well in Santa Clara County was coordinated separately by GWPP staff and did not include the participation of RWQCB staff in its sampling.

Table 1. Geographic location information, well type, and sampling date of sampled wells.

County	Groundwater Basin, Subbasin[2]	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code[1]	Well Type	Sampling Date
Monterey	Salinas Valley, Upper Valley	M20S08E14	27-01	community	4/29/2019
Monterey	Salinas Valley, Upper Valley	M21S09E17	27-02	large water system	4/29/2019
Monterey	Salinas Valley, Forebay	M17S06E36	27-03	community	4/29/2019
Monterey	Salinas Valley, 180/400 Foot	M15S03E26	27-04	domestic	4/29/2019
Monterey	Salinas Valley, Forebay	M19S07E09	27-05	domestic/irrigation	4/30/2019
Monterey	Salinas Valley, 180/400 Foot	M15S03E26	27-06	domestic	4/30/2019
Monterey	Salinas Valley, Forebay	M18S06E28	27-07	irrigation	4/30/2019
Monterey	Salinas Valley, Upper Valley	M22S10E17	27-08	domestic	4/30/2019
Monterey	Salinas Valley, Forebay	M16S05E33	27-09	commercial	5/1/2019
Monterey	Salinas Valley, Forebay	M17S05E17	27-10	small water system	5/1/2019
Monterey	Salinas Valley, Eastside	M16S05E27	27-11	domestic	5/1/2019
Monterey	Salinas Valley, Eastside	M15S03E12	27-12	irrigation/small water system	5/1/2019
Monterey	Salinas Valley, 180/400 Foot	M15S03E14	27-13	small water system	5/1/2019
Monterey	Salinas Valley, Seaside	M14S02E33	27-14	domestic/small water system	5/2/2019
Monterey	Pajaro Valley	M12S02E30	27-15	domestic/small water system	5/2/2019
Monterey	Salinas Valley, Eastside	M15S04E21	27-16	irrigation	5/2/2019
Monterey	Salinas Valley, Eastside	M15S04E21	27-17	domestic/small water system	5/2/2019
Monterey	Salinas Valley, 180/400 Foot	M13S02E19	27-18	irrigation	5/2/2019
Monterey	Pajaro Valley	M12S02E25	27-19	domestic/small water system	5/3/2019
Monterey	Pajaro Valley	M12S03E30	27-20	domestic/irrigation/ small water system	5/3/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S04E36	35-01	domestic	8/19/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S04E34	35-02	domestic	8/19/2019

County	Groundwater Basin, Subbasin[2]	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code[1]	Well Type	Sampling Date
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S04E36	35-03	domestic/irrigation	8/19/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S04E36	35-04	domestic/irrigation	8/19/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S04E36	35-05	domestic	8/19/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S04E36	35-06	domestic	8/19/2019
San Benito	Gilroy-Hollister Valley, Hollister Area	M12S06E29	35-07	domestic	8/20/2019
San Benito	Gilroy-Hollister Valley, Hollister Area	M12S06E07	35-08	domestic	8/20/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M13S05E04	35-09	domestic	8/20/2019
San Benito	Gilroy-Hollister Valley, Hollister Area	M12S06E18	35-10	domestic	8/20/2019
San Benito	Gilroy-Hollister Valley, Bolsa Area	M12S05E21	35-11	domestic	8/21/2019
San Benito	Gilroy-Hollister Valley, Bolsa Area	M11S05E20	35-12	domestic/small water system	8/21/2019
San Benito	Gilroy-Hollister Valley, Hollister Area	M12S06E19	35-13	domestic/small water system	8/21/2019
San Benito	Gilroy-Hollister Valley, Hollister Area	M12S06E19	35-14	domestic/small water system	8/21/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S05E31	35-15	domestic/small water system	8/22/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S05E16	35-16	domestic/small water system	8/22/2019
San Benito	Gilroy-Hollister Valley, San Juan Bautista Area	M12S04E34	35-17	large water system	8/23/2019
San Benito	Gilroy-Hollister Valley, Hollister Area	M11S05E27	35-18	community	8/23/2019
Santa Clara	Gilroy-Hollister Valley, Llagas	M11S04E03	43-01	school	8/23/2019

[1] 'Location code' refers to a unique identifier assigned to each sampled well where the first number is the county code and the second number (after the hyphen) represents the sampling position in the sequence of sampled wells in that county.

[2] The San Juan Bautista, Bolsa, and Hollister area subbasins are now part of the North San Benito Subbasin of the Gilroy-Hollister Valley Groundwater Basin.

Analytical Methods

Chemical analysis of groundwater samples was performed by the California Department of Food and Agriculture's (CDFA) Center for Analytical Chemistry (CAC). CDFA's CAC analyzed samples collected from the wells listed in Table 1 using three analytical methods: 1) the GWPP Multi-Analyte Screen (EM-SM-05-032, CDFA, 2013), 2) the DCPA Screen (EMON-SM-05-040, CDFA, 2016), and 3) the Surface Water Protection Program [SWPP] Multi-Analyte Screen (EMON-SM-05-037, CDFA, 2017). The chemicals analyzed for by the GWPP Multi-Analyte Screen and DCPA Screen are listed in Table 2a and the chemicals analyzed for by the SWPP Multi-Analyte Screen are listed in Table 2b.

The GWPP Multi-Analyte Screen analyzes for 44 pesticide AIs, including six of the seven restricted-use AIs on the GWPL (3CCR § 6800[a]) and 29 AIs in 3CCR § 6800(b) of the GWPL: AIs with the potential to leach to groundwater (Table 2a). The SWPP Multi-Analyte Screen analyzes for 29 pesticide AIs or degradates, including 8 AIs in 3CCR § 6800(b) of the GWPL (Table 2b).

DCPA is an accepted common name for the pesticide AI chlorthal-dimethyl. DCPA has two major degradation products: monomethyl tetrachloroterephthalate (MTP) and 2,3,5,6-tetrachloroterephthalic acid (TPA) (Table 2a). Analysis of DCPA, MTP, and TPA was included in Study 318 because of the significant use of DCPA as an herbicide in Region 3 over the last several decades and the subsequent finding of numerous detections of TPA in wells throughout the region in past sampling studies (Ruud, 2017; 2018; 2021).

The reporting limit for all chemicals analyzed for by the GWPP Multi-Analyte Screen and DCPA Screen was 0.05 parts per billion (ppb). The reporting limits of the chemicals analyzed for by the SWPP Multi-Analyte Screen ranged from 0.01 to 0.02 ppb and are listed for each chemical in Table 2b. A 'trace' detection is defined as a measured concentration between a chemical's respective method detection limit and its reporting limit.

The PCPA allows a finding of an AI or a degradation product in groundwater by a single analytical laboratory using a single analytical method if the method provides unequivocal identification of those chemicals (FAC § 13149[d]). Peoples (2019) updated the previous standard operating procedure (SOP) (Segawa, 1995) to reflect this verification requirement. Although the previous SOP (Segawa, 1995) had not yet been updated at the time Study 318 was conducted, the verification requirement documented by Peoples (2019) was nevertheless followed in this study. Further details about identifying methods providing unequivocal identification of a chemical are provided in Aggarwal (2012). An unequivocal determination was conducted for each of the three methods (Aggarwal, 2016; 2017; 2019).

Table 2a. Pesticides and degradates analyzed by the GWPP Multi-Analyte and DCPA screens (CDFA methods EMON-SM-05-032 and EMON-SM-05-040). The reporting limit for all analytes was 0.05 parts per billion (ppb).

GWPP Multi-Analyte Screen (LCMS Method)		**GWPP Multi-Analyte Screen (GCMS Method)**	**DCPA Screen**
EMON-SM-05-032		**EMON-SM-05-032**	**EMON-SM-05-040**
Atrazine[1]	Linuron[2]	Clomazone[2]	DCPA
Azinphos-methyl	Mefenoxam/Metalaxyl[2,3]	Dichloran[2]	MTP
Azoxystrobin[2]	Methiocarb[2]	Dichlobenil[2]	TPA
Bensulide[2]	Metolachlor[2,4]	Disulfoton	
Bromacil[1]	Metribuzin[2]	Ethoprophos[2,4]	
Carbaryl[2]	Napropamide[2]	Ethyl parathion	
Carbofuran	Norflurazon[1]	Fonofos	
Diazinon[2]	Oryzalin[2]	Malathion[2]	
Dimethenamide[2]	Prometon[1]	Methyl parathion	
Dimethoate[2]	Simazine[1]	Phorate[2]	
Diuron[1]	Tebuthiuron[2]	Piperonyl butoxide	
Ethofumesate[2]	Thiamethoxam[2]	Prometryn[2]	
Fenamiphos	Thiobencarb[2]	Propanil[2]	
Fludioxonil[2]	Uniconazole	Triallate[2]	
Imidacloprid[2]			

[1]Restricted-use AIs in 3CCR § 6800(a) of the Groundwater Protection List.
[2]AIs in 3CCR § 6800(b) of the Groundwater Protection List: AIs with the potential to leach to groundwater.
[3]Mefenoxam and metalaxyl are stereoisomers. The analytical method cannot differentiate the two analytes.
[4]Analytes that are included in both the GWPP and SWPP Multi-Analyte screens (EMON-SM-05-032 and EMON-SM-05-037).

Table 2b. Pesticides and degradates analyzed by the SWPP Multi-Analyte Screen (CDFA method EMON-SM-05-037).

SWPP Multi-Analyte Screen (LCMS Method)	
EMON-SM-05-037	
Analyte	**Reporting Limit (ppb)**
Abamectin	0.02
Chlorantraniliprole[1]	0.02
Chlorpyrifos	0.02
Cyprodinil[1]	0.02
Diflubenzuron	0.02
Ethoprophos[1,2]	0.02
Etofenprox	0.02
Hexazinone[1]	0.02
Indoxacarb	0.02
Isoxaben[1]	0.02
Kresoxim-methyl	0.02
Methidathion	0.02
Methomyl[1]	0.02
Methoxyfenozide	0.02
Oxadiazon	0.02
Propargite	0.02
Propiconazole[1]	0.02
Pyraclostrobin[1]	0.02
Pyriproxyfen	0.015
Quinoxyfen	0.02
Metolachlor[1,2]	0.02
Tebufenozide	0.02
Trifloxystrobin	0.02
Fipronil	0.01
Fipronil Amide	0.01
Fipronil Sulfide	0.01
Fipronil Sulfone	0.01
Desulfinyl Fipronil	0.01
Desulfinyl Fipronil Amide	0.01

[1]AIs in 3CCR § 6800(b) of the Groundwater Protection List: AIs with the potential to leach to groundwater.
[2]Analytes that are included in both EMON-SM-05-032 and EMON-SM-05-037.

Quality Assurance and Quality Control

CDFA's CAC analyzed quality control (QC) samples with every set of samples to assess laboratory precision. Peoples (2019) specifies the procedures followed for QC despite this study predating the official update of that SOP. During sample analysis for each extraction set (i.e., a group of samples extracted and processed as a batch), the laboratory simultaneously analyzed a laboratory matrix-blank and a QC matrix-spike. The laboratory matrix-blank is a sample of analyte-free groundwater collected from a well in the Sierra foothills. The QC matrix-spike consists of the same source of analyte-free groundwater fortified (spiked) with all analytes on each screen. The QC matrix-spike results were evaluated by laboratory chemists, CDFA's CAC Quality Assurance (QA) Program, and the Environmental Monitoring Branch (EM) QA Officer to ensure analytical integrity. The evaluation included comparing the QC matrix-spike recoveries to control limits set at 3-times the standard deviation of the method validation data for each analyte fortified. Recoveries from the QC were used to assess and monitor ongoing sample analysis and minor variation was expected. The EM QA Officer also submitted blind spikes to the laboratory disguised as field samples per the SOP described by Ganapathy (2005), where the blind spike consists of the analyte-free groundwater (matrix-blank sample) fortified with the chosen analytes. In addition to laboratory QC, samples containing deionized water (field blanks) were collected simultaneously with field samples per Peoples (2019) and were analyzed to confirm the validity of detections when deemed necessary (Richardson, 2011).

RESULTS AND DISCUSSION

Sample Analysis Results

<u>DCPA Screen Results</u>

Laboratory-measured concentrations of DCPA, MTP, and TPA (DCPA Screen) in groundwater samples from each of the 39 sampled wells are listed in Table 3. Of the 39 wells sampled, 20 wells had detections of the DCPA degradation product TPA with concentrations ranging from 0.072 to 27.6 ppb. All measured concentrations of TPA were below the health-protective drinking water level of 2,500 ppb set for TPA by the Office of Environmental Health Hazard Assessment (OEHHA, 2018). Since the detections of TPA were less than their health reference level, no follow-up investigation of these wells by DPR is necessary at this time. As required by FAC § 13152(a)(1), DPR will continue to conduct future groundwater monitoring of DCPA, MTP, and TPA in areas of Region 3 where DCPA is used (Sanders, 2018). The detections are summarized by county in Table 4 and are briefly described by location within each groundwater basin in the following sections.

<u>GWPP Multi-Analyte Screen Results</u>

For the 39 sampled wells, only three analytes in the GWPP Multi-Analyte Screen were detected — bromacil, mefenoxam/metalaxyl, and tebuthiuron. These detections are summarized in Table 5. Bromacil was detected in one well in the Salinas Valley Groundwater Basin at a concentration of 0.054 ppb. The bromacil detection was measured in a well located in a Ground Water Protection Area (GWPA) (3CCR § 6487.3-6487.5) at a concentration below its human health reference level of 197 ppb (Brown et al., 2021). Since the concentration of the bromacil detection was less than its health reference level, no follow-up investigation by DPR is necessary at this time. Additionally, a trace concentration of mefenoxam/metalaxyl was detected in one well in the Pajaro Groundwater Basin and a trace concentration of tebuthiuron was detected in one well in the Hollister-Gilroy Valley Groundwater Basin. Since the trace concentrations of mefenoxam/metalaxyl and tebuthiuron are both below DPR's reporting limit of 0.05 ppb, no follow-up investigation of these wells by DPR is necessary at this time. The bromacil detection is summarized by county in Table 4 and the detections are briefly described by location within each groundwater basin in the following sections.

SWPP Multi-Analyte Screen Results

No analytes in the SWPP Multi-Analyte Screen were detected in any of the 39 sampled wells.

Table 3. DCPA Screen (EMON-SM-05-040) analytical results for all wells sampled.

Sample Number	Sample Code[1]	County	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code	Sample Date	DCPA (ppb)	MTP (ppb)	TPA (ppb)
01	P	Monterey	M20S08E14	27-01	4/29/2019	ND	ND	ND
07	P	Monterey	M21S09E17	27-02	4/29/2019	ND	ND	17.9
12	FB	Monterey	M21S09E17	27-02	4/29/2019	ND	ND	ND
13	P	Monterey	M17S06E36	27-03	4/29/2019	ND	ND	ND
19	P	Monterey	M15S03E26	27-04	4/29/2019	ND	ND	ND
25	P	Monterey	M19S07E09	27-05	4/30/2019	ND	ND	0.086
30	FB	Monterey	M19S07E09	27-05	4/30/2019	ND	ND	ND
31	P	Monterey	M15S03E26	27-06	4/30/2019	ND	ND	0.272
36	FB	Monterey	M15S03E26	27-06	4/30/2019	ND	ND	ND
37	P	Monterey	M18S06E28	27-07	4/30/2019	ND	ND	3.52
42	FB	Monterey	M18S06E28	27-07	4/30/2019	ND	ND	ND
43	P	Monterey	M22S10E17	27-08	4/30/2019	ND	ND	ND
49	P	Monterey	M16S05E33	27-09	5/1/2019	ND	ND	22.6
54	FB	Monterey	M16S05E33	27-09	5/1/2019	ND	ND	ND
55	P	Monterey	M17S05E17	27-10	5/1/2019	ND	ND	ND
61	P	Monterey	M16S05E27	27-11	5/1/2019	ND	ND	1.06
66	FB	Monterey	M16S05E27	27-11	5/1/2019	ND	ND	ND
67	P	Monterey	M15S03E12	27-12	5/1/2019	ND	ND	0.736
72	FB	Monterey	M15S03E12	27-12	5/1/2019	ND	ND	ND
73	P	Monterey	M15S03E14	27-13	5/1/2019	ND	ND	ND
79	P	Monterey	M14S02E33	27-14	5/2/2019	ND	ND	0.113
84	FB	Monterey	M14S02E33	27-14	5/2/2019	ND	ND	ND
85	P	Monterey	M12S02E30	27-15	5/2/2019	ND	ND	9.46
90	FB	Monterey	M12S02E30	27-15	5/2/2019	ND	ND	ND
91	P	Monterey	M15S04E21	27-16	5/2/2019	ND	ND	20.8
96	FB	Monterey	M15S04E21	27-16	5/2/2019	ND	ND	ND
97	P	Monterey	M15S04E21	27-17	5/2/2019	ND	ND	ND
103	P	Monterey	M13S02E19	27-18	5/2/2019	ND	ND	ND
109	P	Monterey	M12S02E25	27-19	5/3/2019	ND	ND	ND
115	P	Monterey	M12S03E30	27-20	5/3/2019	ND	ND	ND

Sample Number	Sample Code[1]	County	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code	Sample Date	DCPA (ppb)	MTP (ppb)	TPA (ppb)
300	P	San Benito	M12S04E36	35-01	8/19/2019	ND	ND	0.072
304	FB	San Benito	M12S04E36	35-01	8/19/2019	ND	ND	ND
306	P	San Benito	M12S04E34	35-02	8/19/2019	ND	ND	0.494
310	FB	San Benito	M12S04E34	35-02	8/19/2019	ND	ND	Trace
312	P	San Benito	M12S04E36	35-03	8/19/2019	ND	ND	1.41
316	FB	San Benito	M12S04E36	35-03	8/19/2019	ND	ND	ND
324	P	San Benito	M12S04E36	35-04	8/19/2019	ND	ND	0.471
328	FB	San Benito	M12S04E36	35-04	8/19/2019	ND	ND	ND
318	P	San Benito	M12S04E36	35-05	8/19/2019	ND	ND	0.979
322	FB	San Benito	M12S04E36	35-05	8/19/2019	ND	ND	Trace
330	P	San Benito	M12S04E36	35-06	8/19/2019	ND	ND	3.97
334	FB	San Benito	M12S04E36	35-06	8/19/2019	ND	ND	ND
336	P	San Benito	M12S06E29	35-07	8/20/2019	ND	ND	ND
342	P	San Benito	M12S06E07	35-08	8/20/2019	ND	ND	ND
348	P	San Benito	M13S05E04	35-09	8/20/2019	ND	ND	ND
354	P	San Benito	M12S06E18	35-10	8/20/2019	ND	ND	ND
360	P	San Benito	M12S05E21	35-11	8/21/2019	ND	ND	1.81
364	FB	San Benito	M12S05E21	35-11	8/21/2019	ND	ND	Trace
366	P	San Benito	M11S05E20	35-12	8/21/2019	ND	ND	ND
372	P	San Benito	M12S06E19	35-13	8/21/2019	ND	ND	ND
378	P	San Benito	M12S06E19	35-14	8/21/2019	ND	ND	ND
384	P	San Benito	M12S05E31	35-15	8/22/2019	ND	ND	0.469
390	P	San Benito	M12S05E16	35-16	8/22/2019	ND	ND	ND
398	P	San Benito	M12S04E34	35-17	8/23/2019	ND	ND	0.102
408	P	San Benito	M11S05E27	35-18	8/23/2019	ND	ND	ND
402	P	Santa Clara	M11S04E03	43-01	8/23/2019	ND	ND	27.6

[1]P = primary sample, FB = field blank sample
ND = not detected below the method detection limit
Trace = positive result between the method detection limit and the reporting limit
Note: Trace concentrations of TPA were detected in three FB samples

Table 4. Summary by county of pesticide or degradate detections above the reporting limit.

County	Number of Wells Sampled	Number of Wells with Detections	Pesticides or Degradates Detected
Monterey	20	10	TPA, bromacil
San Benito	18	9	TPA
Santa Clara	1	1	TPA

Table 5. GWPP Multi-Analyte Screen (EMON-SM-05-032) analytical results for wells with detectable residues.

Sample Number	Sample Code[1]	County	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code	Sample Date	Detected Analyte	Measured Concentration (ppb)
80	P	Monterey	M14S02E33	27-14	5/2/2019	bromacil	0.054
86	P	Monterey	M12S02E30	27-15	5/2/2019	mefenoxam/ metalaxyl	Trace
385	P	San Benito	M12S05E31	35-15	8/22/2019	tebuthiuron	Trace

[1]P = primary sample

Salinas Valley Groundwater Basin

The northern portion of the Salinas Valley Groundwater Basin is located in Monterey County and includes the Upper Valley Aquifer Subbasin (Figure 2; CDWR, 2004a), the Forebay Aquifer Subbasin (Figure 3; CDWR, 2004b), the Seaside Area Subbasin (Figure 4; CDWR, 2004c), the 180/400 Foot Aquifer Subbasin (Figure 5; CDWR, 2004d), and the Eastside Aquifer Subbasin (Figure 6; CDWR, 2004e). GWPP staff collected samples at 17 wells in the five subbasins from April 29 through May 2, 2019 (Table 1). The sampled wells were of the following types: domestic, small water system, large water system, community, commercial, or irrigation (Table 1).

Nine of the 17 wells had detections of TPA ranging in concentration from 0.086 to 22.6 ppb (Table 3). A single detection of bromacil with a measured concentration of 0.054 ppb (Table 5) was found in a domestic-small water system well (location code 27-14) in the Seaside Area Subbasin west of the city of Salinas (Figure 4). No other analytes were detected in the 17 sampled wells. The DPR Pesticide Use Reporting (PUR) database contained no reported use of bromacil between 1990 and 2019 in section M14S02E33 where the bromacil detection was measured in the sampled well (CDPR, 2022a). Section M14S02E33 is also a GWPA where bromacil is regulated as a restricted-use pesticide for agricultural, outdoor industrial, and outdoor institutional uses to protect groundwater. The most recent application of bromacil in the nearest section to M14S02E33 occurred in 1996 in section M14S02E23 (i.e., 48 pounds of bromacil applied to a 24-acre field) (CDPR, 2022a). Although bromacil is known to be both persistent and mobile in the subsurface, it is difficult to assess whether use in section M14S02E23, unreported outdoor industrial or institutional use (e.g., rights of way) in the region, or legacy use (i.e., bromacil use prior to 1986) in other nearby areas is the source of the bromacil detected in the well in section M14S02E33 (Table 5). The bromacil detection in section M14S02E33 was significantly below the human health reference level of 197 ppb and no follow-up investigation of this detection by DPR is necessary at this time.

Pajaro Valley Groundwater Basin

The Pajaro Valley Groundwater Basin (CDWR, 2004f) spans the northern region of Monterey County and a southern part of Santa Cruz County (Figure 7). GWPP staff collected samples at three wells located in the basin over the sampling period of May 2-3, 2019 (Table 1). One well (location code 27-15) had both a detection of TPA at a concentration of 9.46 ppb (Table 3) and a trace detection of mefenoxam/metalaxyl (Table 5 and Figure 7). No other analytes were detected in the three sampled wells.

Gilroy-Hollister Valley Groundwater Basin

The Gilroy-Hollister Valley Groundwater Basin (CDWR, 2004g) includes the North San Benito Subbasin[1] in northern San Benito County and the Llagas Subbasin in southern Santa Clara County (Figure 1). During 2019, GWPP staff collected samples at ten wells in the San Juan Bautista Area Subbasin (Figure 8), two wells in the Bolsa Area Subbasin (Figure 9), and six wells in the Hollister Area Subbasin (Figure 10) over the sampling period of August 19-23 and at one well in the Llagas Subbasin (Figure 11) on August 23 (Table 1).

Eight of the ten wells in the San Juan Bautista Area Subbasin (Figure 8) had detectable residues of TPA ranging in concentration from 0.072 to 3.97 ppb (Table 3) and one well near the city of San Juan Bautista (location code 35-15) had a trace detection of tebuthiuron (Table 5). One well in the Bolsa Area Subbasin (well location 35-11) had a detectable residue of TPA at a concentration of 1.81 ppb (Figure 9 and Table 3). Six wells were sampled in the Hollister Area Subbasin (Figure 10), and no analytes were detected in those samples.

The lone sampled well in the Llagas Subbasin (Figure 11) had a TPA detection at a concentration of 27.6 ppb (Table 3). No other analytes were detected in the 19 sampled wells in the Gilroy-Hollister Valley Groundwater Basin.

Quality Assurance and Quality Control Results

For this study, the laboratory matrix-blank results were all non-detects. The QC and blind spike results for the analysis of the DCPA Screen, GWPP Multi-Analyte Screen, and SWPP Multi-Analyte Screen are summarized in this section. QC data for all analytes are available upon request.

[1] The North San Benito Subbasin is a new subbasin designation that encompasses the formerly named San Juan Bautista, Bolsa, and Hollister area subbasins shown on Figure 1. In this report, sampling results will be presented with respect to the areas of the former San Juan Bautista, Bolsa, and Hollister area subbasins displayed on Figures 8, 9, and 10, respectively.

DCPA Screen QC Samples

The QC data for the DCPA Screen is summarized in Table 6. Six matrix-spikes with DCPA, MTP, and TPA were analyzed along with 39 sets of samples with the DCPA Screen. DCPA, MTP, and TPA were all spiked at 0.2 ppb. The average recovery of DCPA, MTP, and TPA was 66, 84.2, and 82.1%, respectively. The associated standard deviation of the recovery of DCPA, MTP, and TPA was 7.8, 9.2, and 11.9%, respectively. One recovery of DCPA (55%) was below its lower control limit. All other recoveries of DCPA, MTP, and TPA were within their respective control limits.

Table 6. Quality control data for the DCPA Screen from the CDFA laboratory.

Analysis Date	Analyte	Spike Level (ppb)	% Recovery	Control Limited Exceeded?
5/7/2019	DCPA	0.200	68.5	No
	MTP	0.200	97.0	No
	TPA	0.200	102	No
5/9/2019	DCPA	0.200	55.0	Yes
	MTP	0.200	76.0	No
	TPA	0.200	80.0	No
5/15/2019*	DCPA	0.200	N/A	N/A
	MTP	0.200	N/A	N/A
	TPA	0.200	80.0	No
8/23/2019	DCPA	0.200	68.5	No
	MTP	0.200	87.0	No
	TPA	0.200	67.0	No
8/26/2019	DCPA	0.200	66.5	No
	MTP	0.200	78.5	No
	TPA	0.200	75.5	No
8/28/2019	DCPA	0.200	60.0	No
	MTP	0.200	74.5	No
	TPA	0.200	76.0	No
9/25/2019	DCPA	0.200	77.5	No
	MTP	0.200	92.0	No
	TPA	0.200	94.0	No
Mean (SD**)	DCPA		66.0% (7.8%)	
	MTP		84.2% (9.2%)	
	TPA		82.1% (11.9%)	
Control Limits	DCPA		57.4 – 84.4%	
	MTP		73.3 – 115%	
	TPA		48.5 – 104%	

*Recoveries were not analyzed (N/A) for DCPA and MTP on 5/15/2019.

**SD: Standard deviation (values in parenthesis).

GWPP Multi-Analyte Screen QC Samples

For the GWPP Multi-Analyte Screen, QC matrix-spikes were extracted and split to be analyzed along with sets of samples for both the liquid chromatography mass spectrometry (LCMS) and gas chromatography mass spectrometry (GCMS) instruments. Four QC matrix-spikes were analyzed along with two sets of samples using LCMS for the GWPP Multi-Analyte Screen. All 29 analytes in the LCMS portion were spiked at 0.2 ppb in the QC matrix-spikes and the recoveries ranged from 59.5 to 110%. One recovery of bromacil (75%) and one recovery of dimethoate (72%) were slightly below their respective lower control limits. The other 27 analytes were within their respective control limits. Four QC matrix-spikes were also analyzed along with two sets of samples using GCMS for the GWPP Multi-Analyte Screen. All 14 analytes were spiked at 0.1 ppb for both QC matrix-spikes. The recoveries ranged from 59.5 to 122% with all analyte recoveries within their respective control limits.

SWPP Multi-Analyte Screen QC Samples

For the SWPP Multi-Analyte Screen, QC matrix-spikes were extracted and split to be analyzed along with sets of samples for the LCMS instrument. Four QC matrix-spikes were analyzed along with two sets of samples using LCMS for the SWPP Multi-Analyte Screen. All 29 analytes were spiked at 0.2 ppb in the QC matrix-spikes and the recoveries ranged from 74.8 to 118%. One recovery of ethoprophos (101%) was above its upper control limit. The other 28 analytes were within their respective control limits.

Blind Spikes

A blind spike is a matrix-blank sample spiked by a different chemist than the chemist extracting and analyzing that screen. A total of four blind spikes for select analytes were submitted and the analytes, spike levels, and recovery results are presented in Table 7. Two of the blind spikes were submitted during the analysis of samples from the April 29 through May 3 sampling event and the other two blind spikes were submitted during the analysis of samples from the August 19 through 23 sampling event (Table 7). As seen in Table 7, the recoveries of all the analytes measured in the blind spike samples were within their respective control limits.

Table 7. Blind spike levels and recoveries.

Sample Number	Analysis Date	Analysis Screen	Analyte	Spike Level (ppb)	Result (ppb)	Recovery (%)	Control Limit Exceeded?
182	5/9/2019	GWPP Multi-Analyte	fludioxonil	0.20	0.206	103	No
			imidacloprid	0.15	0.148	98.7	No
			prometryn	0.25	0.210	84.0	No
181	5/9/2019	DCPA	DCPA	0.10	0.065	65.0	No
			MTP	0.20	0.184	92.0	No
			TPA	0.15	0.136	90.7	No
416	8/26/2019	SWPP Multi-Analyte	cyprodinil	0.05	0.053	106	No
			propiconazole	0.08	0.086	108	No
			tebufenozide	0.10	0.088	88.0	No
			trifloxystrobin	0.15	0.118	78.7	No
415	8/26/2019	GWPP Multi-Analyte	dichlobenil	0.20	0.144	87.5	No
			triallate	0.15	0.250	99.3	No

CONCLUSIONS

This report summarizes the findings of Study 318: groundwater sampling from water wells located in areas within the Region 3 jurisdiction of the Central Coast RWQCB. For this study, 39 unique water wells located in three different groundwater basins spanning three counties were sampled over two sampling events in 2019: 17 wells in the Salinas Valley Groundwater Basin in Monterey County; 19 wells in the Gilroy-Hollister Valley Groundwater Basin in San Benito and Santa Clara counties; and three wells in the Pajaro Valley Groundwater Basin in northern Monterey County. All results from the CDFA laboratory analysis of groundwater samples collected from the 39 wells under Study 318 have been entered into the DPR Well Inventory Database (CDPR, 2022b).

Overall, TPA was detected in 20 wells with concentrations ranging from 0.072 to 27.6 ppb. All measured concentrations of TPA were below the health-protective drinking water level of 2,500 ppb set for TPA by OEHHA (2018). Bromacil was detected in one well in the Salinas Valley Groundwater Basin at a concentration of 0.054 ppb. The bromacil detection was measured in a well located in a GWPA where bromacil is regulated as a restricted-use pesticide for agricultural, outdoor industrial, and outdoor institutional uses to protect groundwater. The bromacil detection was also significantly below its human health reference level of 197 ppb (Brown et al., 2021). Since the detections of TPA and bromacil were less than their respective health reference levels, no follow-up investigation of these wells by DPR is necessary at this time. As required by FAC § 13152(a)(1), DPR will continue to conduct future groundwater monitoring of DCPA, MTP, and TPA in areas of Region 3 where DCPA is used (Sanders, 2018).

Additionally, a trace concentration of mefenoxam/metalaxyl was detected in one well in the Pajaro Groundwater Basin and a trace concentration of tebuthiuron was detected in one well in the Hollister-Gilroy Valley Groundwater Basin. Since the trace concentrations of mefenoxam/metalaxyl and tebuthiuron are both below DPR's reporting limit of 0.05 ppb, no follow-up investigation of these wells by DPR is necessary at this time.

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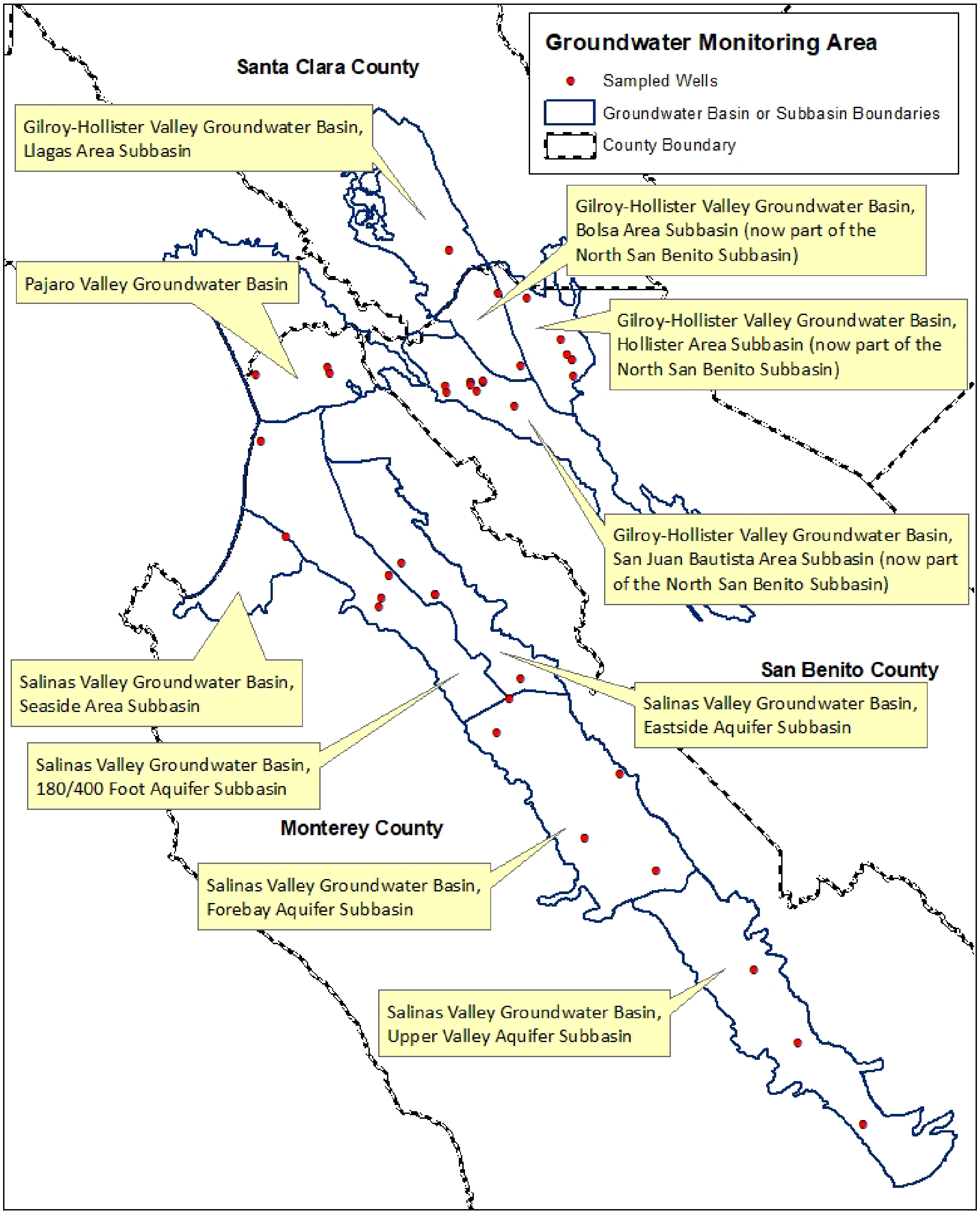

Figure 1. Regional area of groundwater monitoring under Study 318.

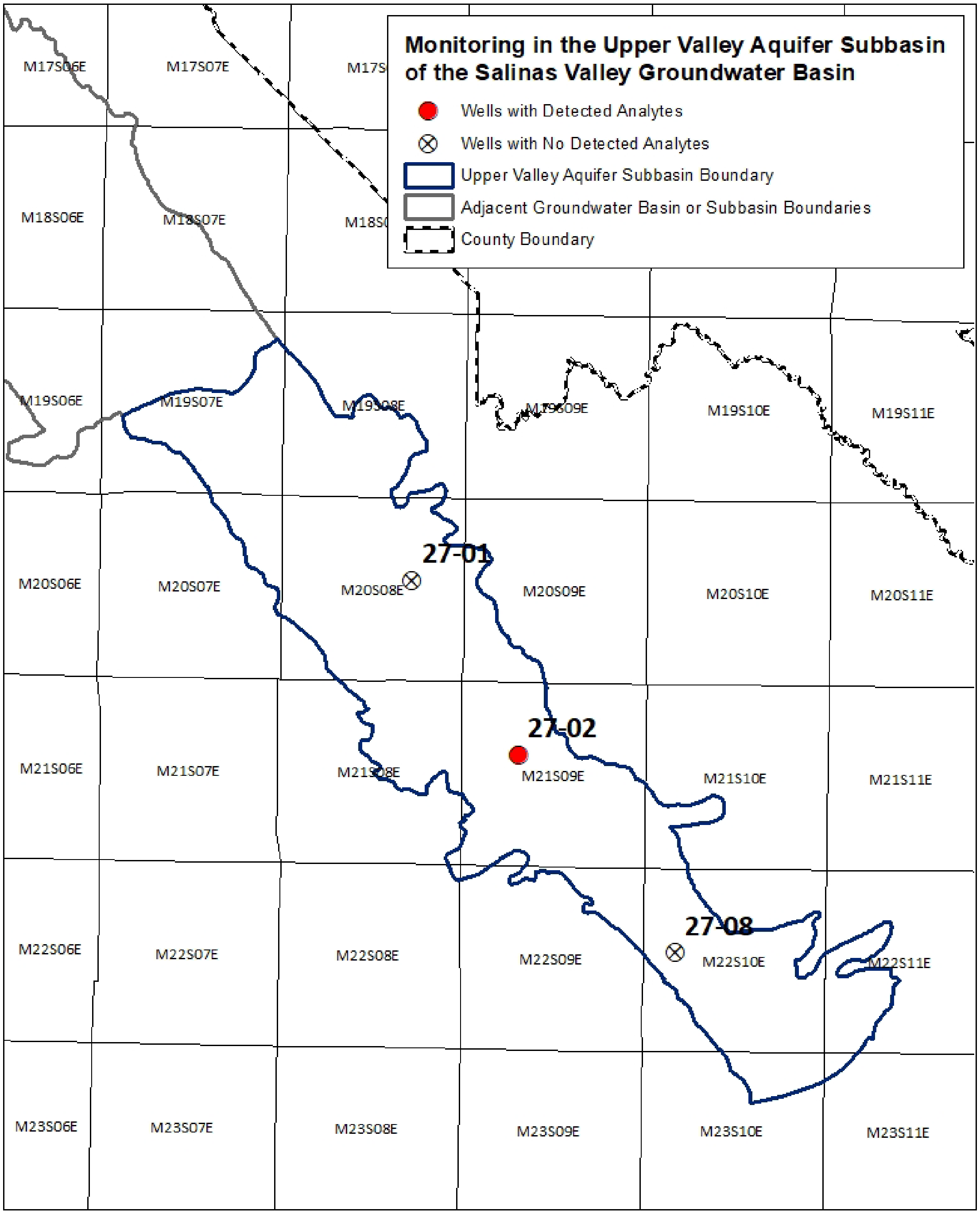

Figure 2. Locations of wells sampled in the Upper Valley Aquifer Subbasin of the Salinas Valley Groundwater Basin (CDPR, 2022b).

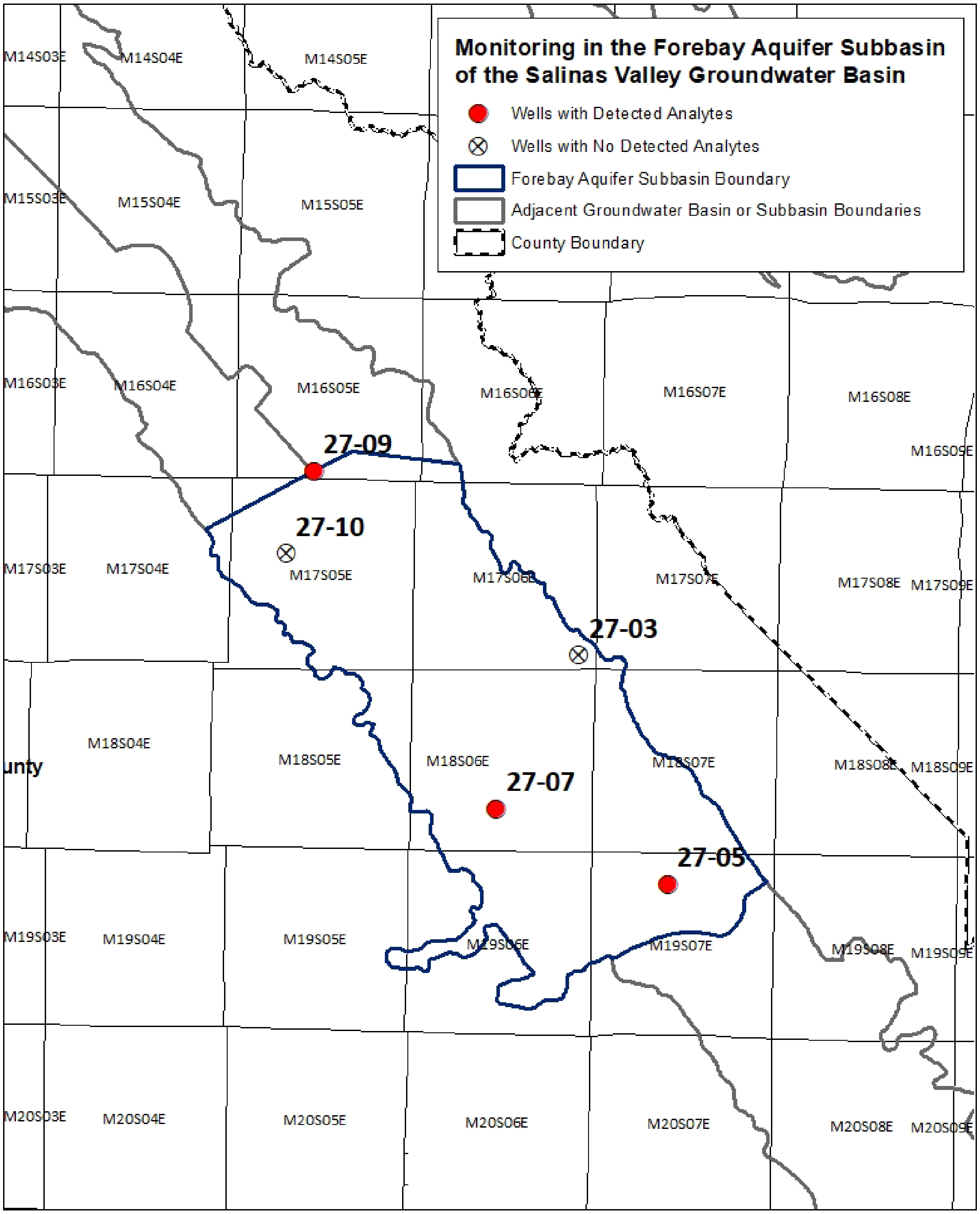

Figure 3. Locations of wells sampled in the Forebay Aquifer Subbasin of the Salinas Valley Groundwater. Basin (CDPR, 2022b).

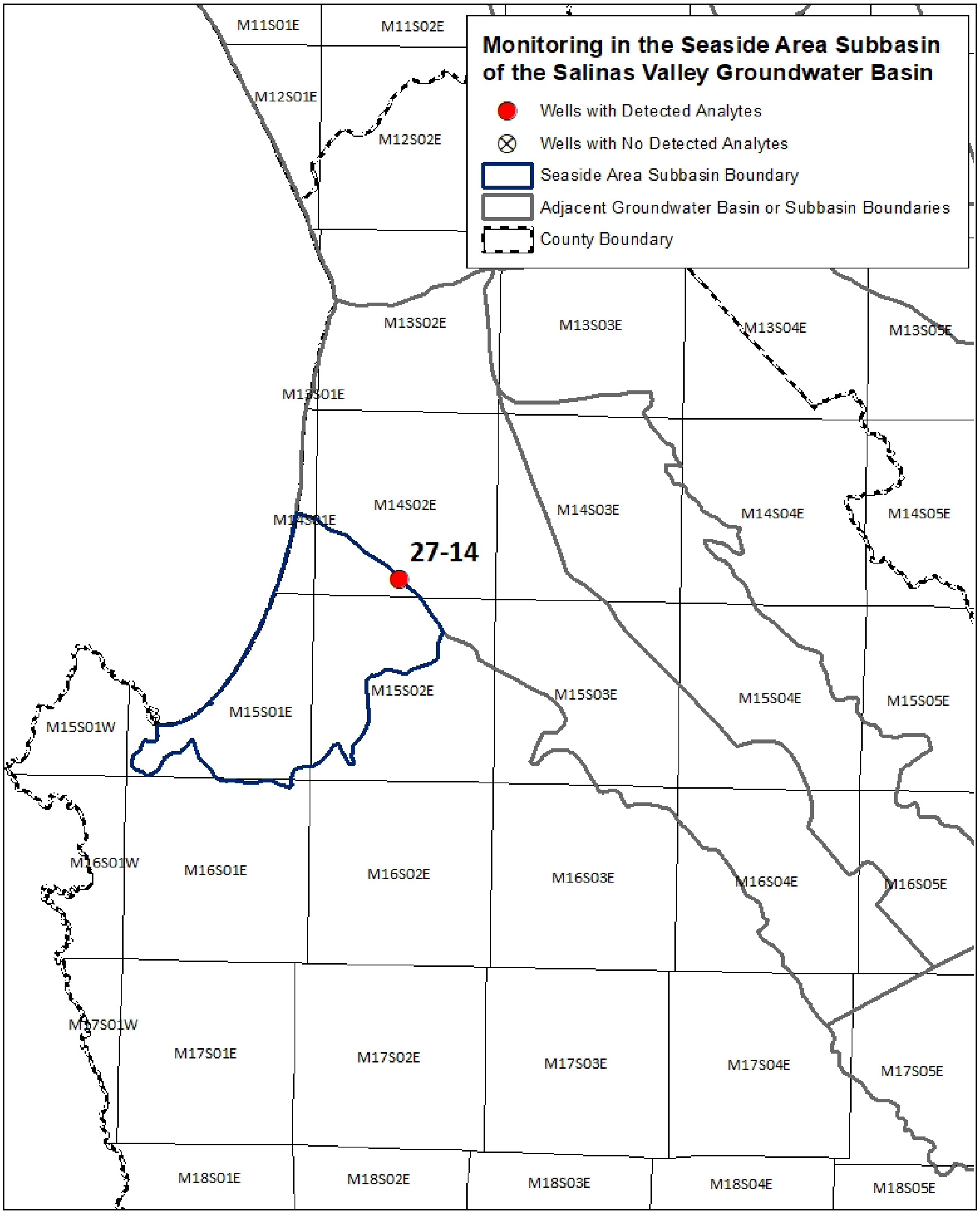

Figure 4. Locations of wells sampled in the Seaside Area Subbasin of the Salinas Valley Groundwater (CDPR, 2022b).

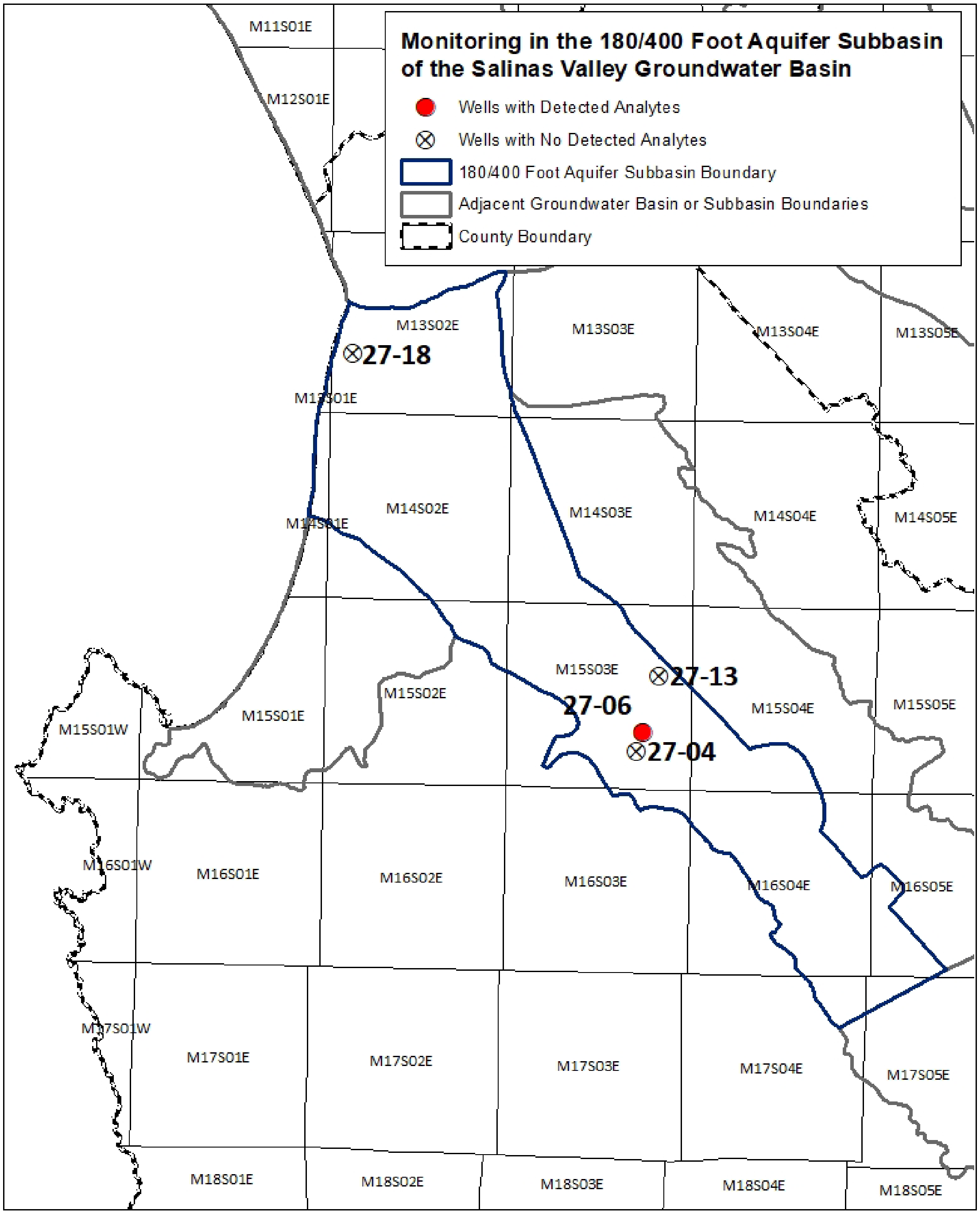

Figure 5. Locations of wells sampled in the 180/400 Foot Aquifer Subbasin of the Salinas Valley Groundwater (CDPR, 2022b).

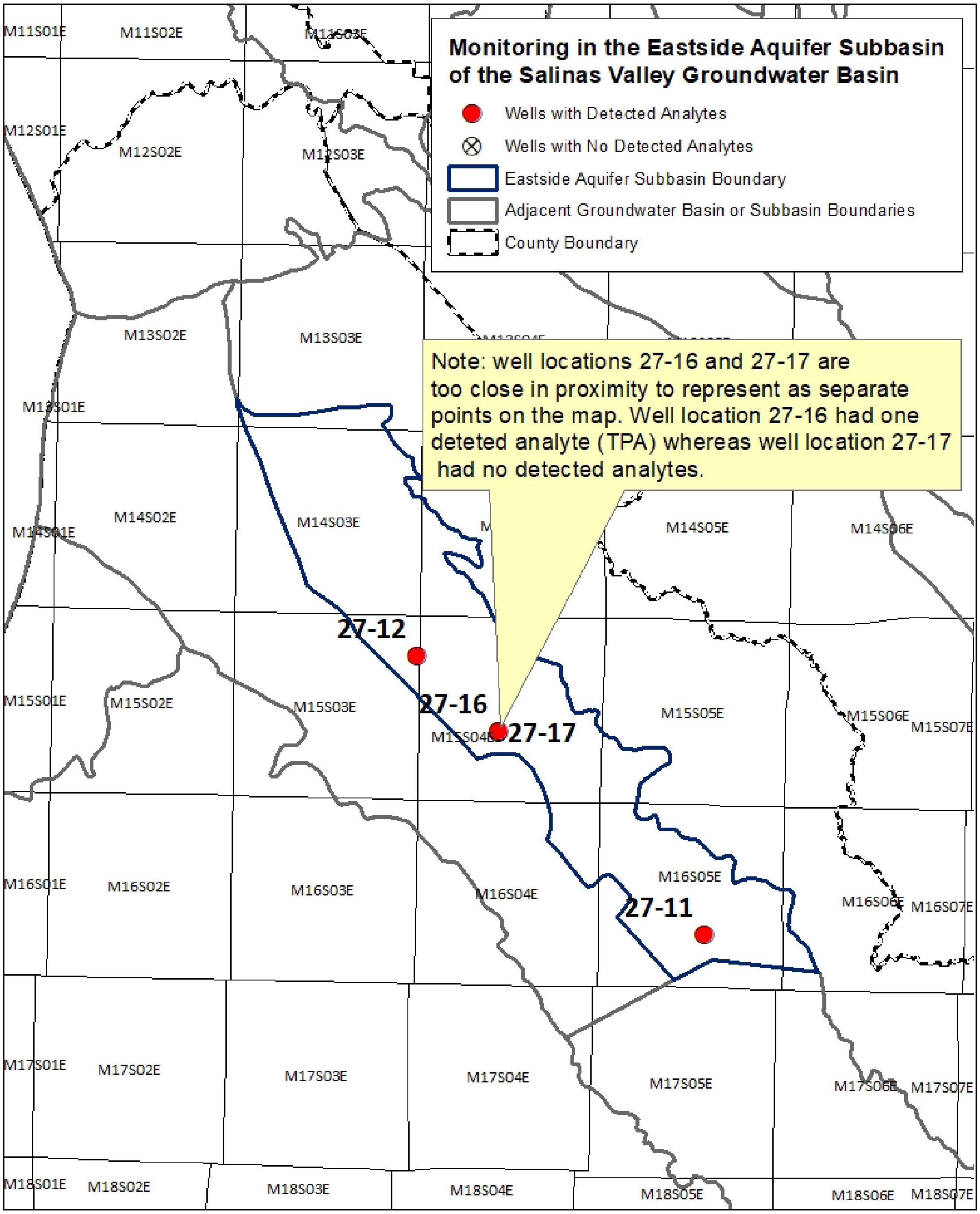

Figure 6. Locations of wells sampled in the Eastside Aquifer Subbasin of the Salinas Valley Groundwater (CDPR, 2022b).

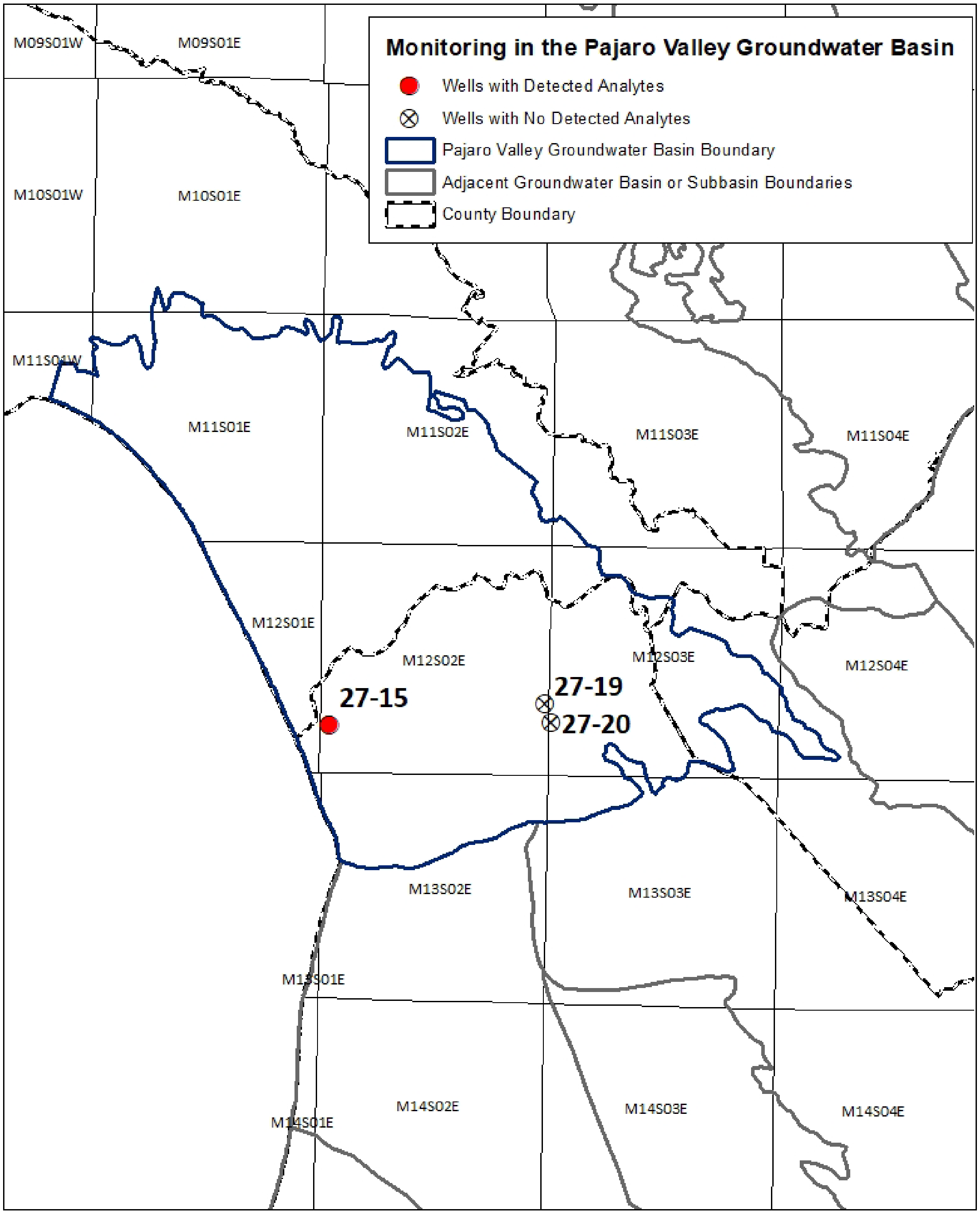

Figure 7. Locations of wells sampled in the Pajaro Valley Groundwater Basin (CDPR, 2022b).

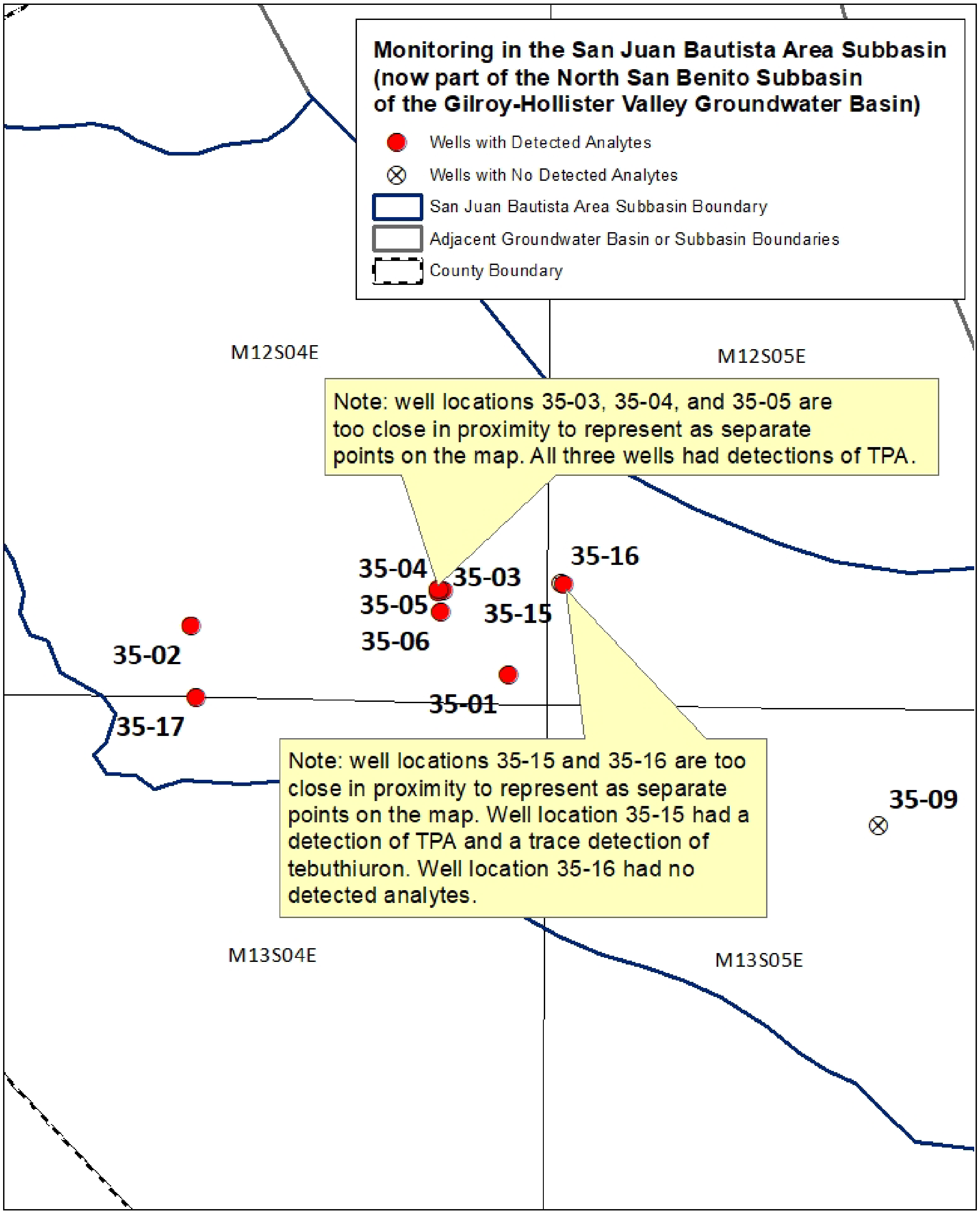

Figure 8. Locations of wells sampled in the San Juan Bautista Area Subbasin (now part of the North San Benito Subbasin) of the Gilroy-Hollister Valley Groundwater Basin (CDPR, 2022b).

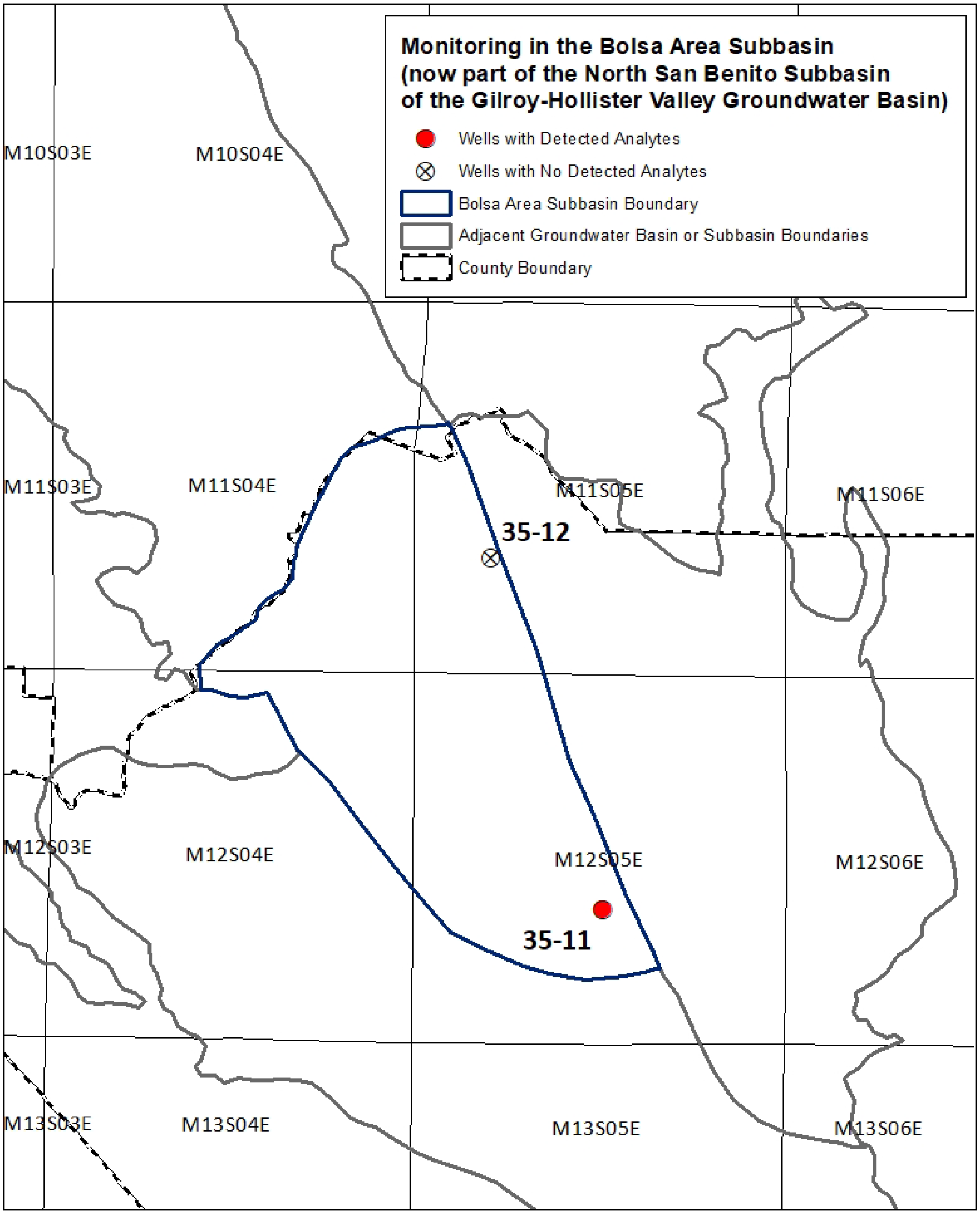

Figure 9. Locations of wells sampled in the Bolsa Area Subbasin (now part of the North San Benito Subbasin) of the Gilroy-Hollister Valley Groundwater Basin (CDPR, 2022b).

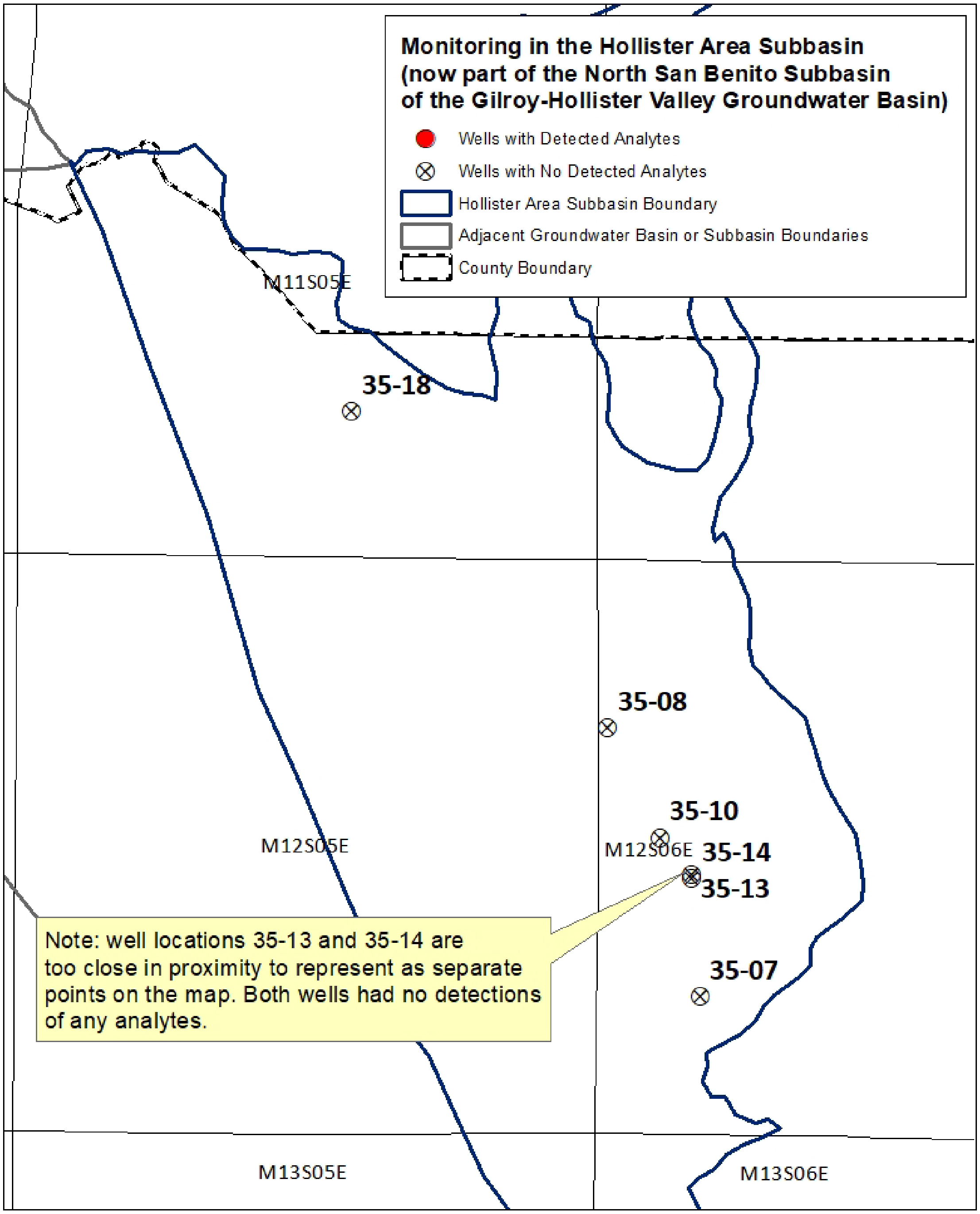

Figure 10. Locations of wells sampled in the Hollister Area Subbasin (now part of the North San Benito Subbasin) of the Gilroy-Hollister Valley Groundwater Basin (CDPR, 2022b).

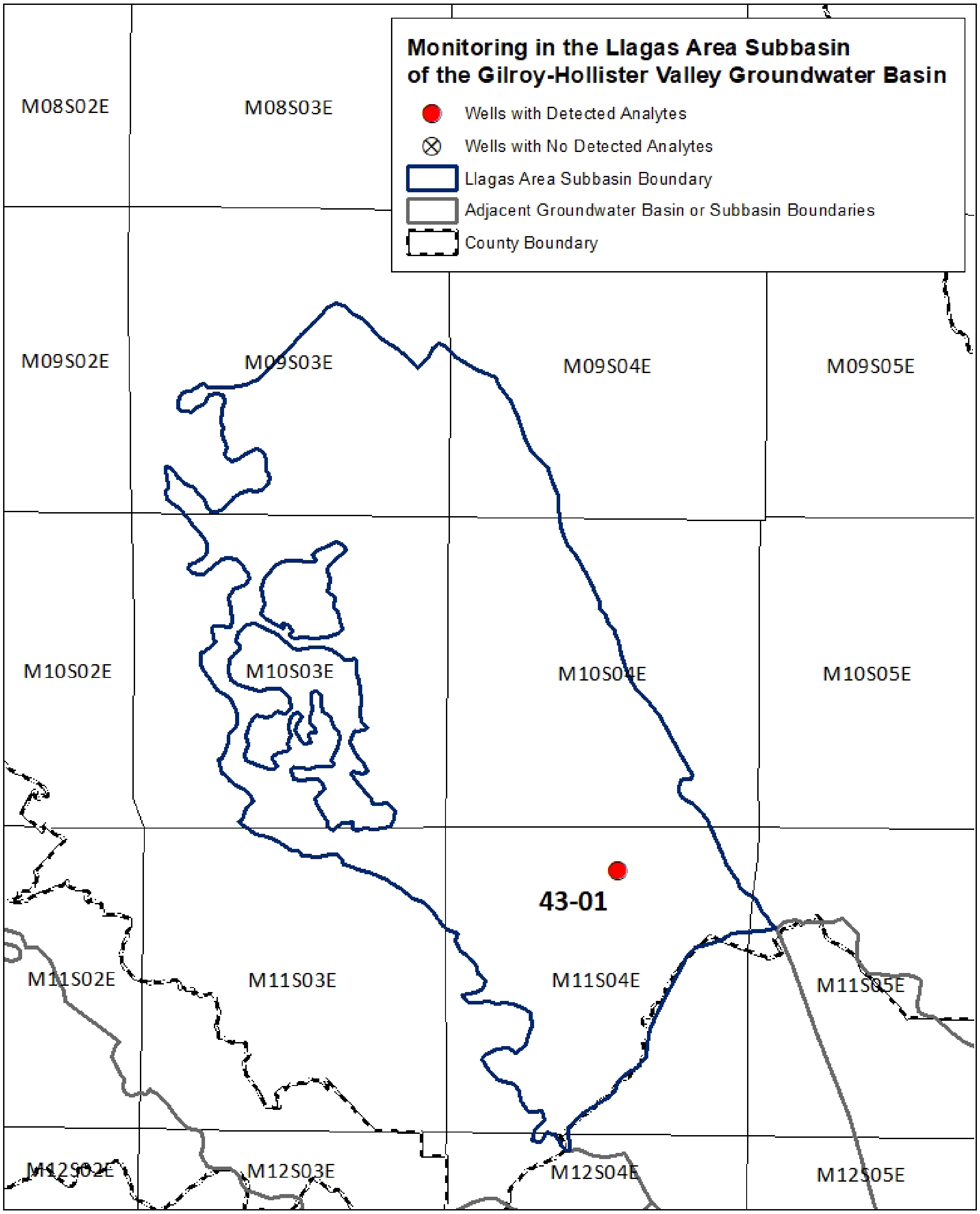

Figure 11. Locations of wells sampled in the Llagas Area Subbasin of the Gilroy-Hollister Valley Groundwater Basin (CDPR, 2022b).