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Study 318a: Cooperative Groundwater Monitoring in Santa Cruz County of Region 3 with the Central Coast Regional Water Quality Control Board

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ABSTRACT

This report summarizes findings from the continuation 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. In this phase of Study 318, 12 rural domestic water wells located in southern Santa Cruz County near Watsonville and within the Pajaro Valley Groundwater Basin were sampled during July 2024. All groundwater samples were analyzed by the California Department of Food and Agriculture's Center for Analytical Chemistry for 58 unique pesticide active ingredients (AIs) (including the analysis for the combined concentration of mefenoxam and metalaxyl) and five unique degradation products (degradates). None of the pesticides or degradation products analyzed for were detected above the laboratory reporting limit. Trace concentrations (between the reporting limit and method detection limit) were detected in two wells. One well contained trace detections of mefenoxam/metalaxyl (0.0102 parts per billion [ppb]) and methoxyfenozide (0.00574 ppb) and a second well contained a trace detection of prometryn (0.00256 ppb). All three detected chemicals (mefenoxam/metalaxyl, methoxyfenozide, prometryn) are pesticide AIs. None of the other 55 pesticide AIs or five degradates were detected in these two wells. Additionally, none of the 58 pesticide AIs or five degradates in the total analysis were detected in samples from the other 10 wells. The trace detections of mefenoxam/metalaxyl, methoxyfenozide, and prometryn were well below established pesticide drinking water quality standards. Trace detections do not trigger any regulatory processes or response but do indicate the presence of those AIs in areas surrounding the sampled wells and may suggest the need for additional monitoring there in the future. As required by Food and Agricultural Code § 13152(a)(1), DPR will also continue to conduct future groundwater monitoring of pesticide AIs in other areas of Region 3 where they have reported agricultural use.

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 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 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 (degradates). 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 rural residential properties during recent monitoring efforts became increasingly difficult for GWPP staff. Therefore, monitoring by the GWPP had become limited in certain areas of Region 3.

In recent years, GWPP met 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. One original objective of these meetings was to improve GWPP access to water wells in Region 3 for the continued monitoring of agricultural pesticides. To achieve this, Study 318 was formally initiated in 2019 as a collaborative effort between GWPP and Central Coast RWQCB staff to sample predominantly rural domestic water wells in Region 3 for agricultural pesticides. As a study task, Central Coast RWQCB staff took the lead in contacting domestic well owners in Region 3 interested in having their wells tested for certain water quality constituents (including pesticides) and scheduled those water wells for sampling. During late April/early May 2019, DPR and Central Coast RWQCB staff conducted the first phase of Study 318 by collaboratively sampling 20 water wells located in Monterey County. The second phase of Study 318 was conducted in August 2019 by collaboratively sampling 19 additional wells in San Benito and Santa Clara counties. The findings of the first and second phases of collaborative sampling under Study 318 are documented in Ruud (2022). A major goal of Study 318 is to continue to engage the assistance of the Central Coast RWQCB to expand sampling in other areas of Region 3 as an ongoing effort in the future. In early 2024, GWPP and the Central Coast RWQCB planned the third phase of sampling which was conducted in the Watsonville area of southern Santa Cruz County during August 2024.

This report summarizes the monitoring results for sampling in southern Santa Cruz County near Watsonville under 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 active ingredients (AIs) and small number of degradates in the samples; the results of the laboratory analysis of the collected groundwater samples; and comparison of detections to drinking water standards.

METHODS

Sampling Methods

GWPP staff sampled 12 wells in largely rural areas outside of Watsonville in southern Santa Cruz County during July 23-25, 2024. Groundwater samples from the wells were collected using methods described by Kocis (2020). The locations of the 12 wells are displayed in Figure 1 and geographic location information, well identification, well type, and sampling dates are listed in Table 1.

Table 1. Geographic location information, well identification, well type, and sampling dates.

County	Groundwater Basin	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code[1]	Well Type	Sampling Date
Santa Cruz	Pajaro Valley	M11S01E36	44-01	domestic	7/23/2024
Santa Cruz	Pajaro Valley	M12S01E15	44-02	domestic	7/23/2024
Santa Cruz	Pajaro Valley	M12S03E09	44-03	domestic	7/24/2024
Santa Cruz	Pajaro Valley	M11S02E17	44-04	domestic	7/24/2024
Santa Cruz	Pajaro Valley	M11S02E21	44-05	domestic	7/24/2024
Santa Cruz	Pajaro Valley	M11S02E21	44-06	domestic	7/24/2024
Santa Cruz	Pajaro Valley	M11S02E15	44-07	domestic	7/24/2024
Santa Cruz	Pajaro Valley	M11S02E16	44-08	domestic	7/25/2024
Santa Cruz	Pajaro Valley	M11S02E22	44-09	domestic	7/25/2024
Santa Cruz	Pajaro Valley	M11S02E21	44-10	domestic	7/25/2024
Santa Cruz	Pajaro Valley	M11S02E08	44-11	domestic	7/25/2024
Santa Cruz	Pajaro Valley	M11S02E08	44-12	domestic	7/25/2024

[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.

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 12 wells listed in Table 1 using two analytical methods: the GWPP Multi-Analyte Screen (EMON-SM-05-032 revision 3, CDFA, 2023a) and the Triazine Screen (EMON-SM-62.9 revision 6, CDFA, 2023b). The chemicals analyzed by the GWPP Multi-Analyte Screen and Triazine Screen are listed in Table 2.

The GWPP Multi-Analyte Screen analyzed the collected groundwater samples for 56 pesticide AIs, including six of the seven restricted-use AIs on the GWPL (3CCR § 6800[a]) and 37 AIs in 3CCR § 6800(b) of the GWPL: AIs with the potential to leach to groundwater (Table 2). The GWPP Multi-Analyte Screen also analyzed for AIBA, a degradate of bentazon. The Triazine Screen also analyzed for the same six of seven restricted-use AIs in § 6800(a) of the GWPL as the GWPP Multi-Analyte Screen; the major degradation products of atrazine, simazine, and norflurazon (i.e., ACET, DACT, DEA, and DSMN); and the AIs clothianidin, hexazinone, metribuzin, prometryn, and tebuthiuron (i.e., five AIs in 3CCR § 6800[b] of the GWPL) (Table 2). The AIs metribuzin, prometryn, and tebuthiuron are also measured by both the GWPP Multi-Analyte Screen and the Triazine Screen (Table 2).

The reporting limits for all chemicals analyzed ranged from 0.02 to 0.05 parts per billion (ppb) for the GWPP Multi-Analyte Screen and from 0.01 to 0.02 ppb for the Triazine Screen. Confirmed detections are measured concentrations above the laboratory reporting limit and trace detections are estimated concentrations by the laboratory that are below the laboratory reporting limit but above the method detection limit.

The PCPA allows a finding of an AI or a degradate in groundwater by a single analytical laboratory using a single analytical method if the method provides unequivocal identification of those chemicals (FAC § 13149[d]). This verification requirement was satisfied for this study following the standard operating procedure (SOP) by Peoples (2019). Further details about identifying methods providing unequivocal identification of a chemical are provided in Aggarwal (2012). The unequivocal determinations for the methods of the GWPP Multi-Analyte Screen and the Triazine Screen were documented in Aggarwal (2023a, 2023b), respectively.

Table 2. Pesticide AIs and degradates analyzed by the GWPP Multi-Analyte Screen (CDFA method EMON-SM-05-032 revision 3) and Triazine Screen (CDFA method EMON-SM-05-62.9 revision 6).

GWPP Multi-Analyte Screen (LCMS Method)		**GWPP Multi-Analyte Screen (GCMS Method)**	**Triazine Screen**
EMON-SM-05-032 Rev 3		**EMON-SM-05-032 Rev 3**	**EMON-SM-05-62.9 Rev 6**
AIBA[6]	Isoxaben[2]	Benfluralin	ACET[5]
Alachlor[2]	Linuron[2]	Clomazone[2]	Atrazine[1,4]
Atrazine[1,4]	Mefenoxam/Metalaxyl[2,3]	Dichlobenil[2]	Bromacil[1,4]
Azinphos-methyl	Methiocarb[2]	Dichloran[2]	Clothianidin[2]
Azoxystrobin[2]	Methomyl[2]	Disulfoton	DACT[7]
Bensulide[2]	Methoxyfenozide	EPTC[2]	DEA[8]
Bromacil[1,4]	Metolachlor[2]	Ethoprophos[2]	DSMN[9]
Carbaryl[2]	Metribuzin[2,4]	Fonofos	Diuron[1,4]
Carbofuran	Myclobutanil[2]	Malathion[2]	Hexazinone[2]
Chlorantraniliprole[2]	Napropamide[2]	Parathion Ethyl	Metribuzin[2,4]
Cyprodinil[2]	Norflurazon[1,4]	Parathion Methyl	Norflurazon[1,4]
Diazinon[2]	Oryzalin[2]	Phorate[2]	Prometon[1,4]
Dimethenamid[2,10]	Prometon[1,4]	Piperonyl butoxide	Prometryn[2,4]
Dimethoate[2]	Propiconazole[2]	Prometryn[2,4]	Simazine[1,4]
Diuron[1,4]	Pyraclostrobin[2]	Propanil[2]	Tebuthiuron[2,4]
Ethofumesate[2]	Simazine[1,4]	Triallate[2]	
Fenamiphos	Tebuthiuron[2,4]		
Fludioxonil[2]	Thiamethoxam[2]		
Flupyradifurone	Thiobencarb[2]		
Flutriafol	Uniconazole		
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 in both the GWPP Multi-Analyte Screen (EMON-SM-05-032 revision 3) and Triazine Screen (EMON-SM-05-62.9 revision 6).

[5]ACET: deethyl-simazine or deisopropyl-atrazine; degradate of atrazine and simazine.

[6]AIBA: 2-amino-*N*-isopropylbenzamide; degradate of bentazon.

[7]DACT: diaminochlorotriazine; degradate of simazine.

[8]DEA: deethyl-atrazine; degradate of atrazine.

[9]DSMN: desmethyl-norflurazon; degradate of norflurazon.

[10]Dimethenamid-P is the herbicidally active enantiomer in dimethenamid and is the chemical form listed in 3CCR § 6800(b) of the Groundwater Protection List.

Quality Assurance and Quality Control

CDFA's CAC analyzed continuing quality control (QC) samples with every set of samples to assess laboratory precision per Peoples (2019). 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 continuing QC matrix-spike consists of the same source of analyte-free groundwater fortified (spiked) with all analytes on each screen. The continuing 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 3-times the standard deviation of the method validation data for each analyte fortified. Recoveries from the continuing 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

GWPP Multi-Analyte Screen Results

For the 12 sampled wells, only the pesticide AIs mefenoxam/metalaxyl and methoxyfenozide in the GWPP Multi-Analyte Screen were detected in a single well (location code 44-02) at trace levels of 0.0102 and 0.00574 ppb, respectively (Table 3). None of the other 54 pesticide AIs or the degradate AIBA in the GWPP Multi-Analyte Screen were detected in this well. Additionally, none of the 56 pesticide AIs or the degradate AIBA in the GWPP Multi-Analyte Screen were detected in groundwater samples from the other 11 wells.

Table 3. GWPP Multi-Analyte Screen (EMON-SM-05-032) analytical results for wells with detectable residues.

Sample Number	Sample Code[1]	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code	Sample Date	Detected Analyte	Measured Concentration (ppb)
61	P	M12S01E15	44-02	7/23/2024	mefenoxam/ metalaxyl	Trace (0.0102)
61	P	M12S01E15	44-02	7/23/2024	methoxyfenozide	Trace (0.00574)
50	P	M11S02E21	44-10	7/25/2024	prometryn	Trace (0.00256)

[1]P = primary sample

All 12 wells sampled in this study are located in the Pajaro Valley Groundwater Basin (DWR, 2004) which spans the northern region of Monterey County and a southern area of Santa Cruz County (Figure 1). The DPR Pesticide Use Reporting (PUR) database was checked for recent historical use of the two pesticide AIs detected in the sampling event (DPR, 2025a). The trace detections of mefenoxam/metalaxyl and methoxyfenozide occurred in a well (location code 44-02) located in the extreme northeastern corner of section M12S01E15 (Figure 1). Although no agricultural use of mefenoxam, metalaxyl, or methoxyfenozide was reported to have occurred strictly within the boundaries of section M12S01E15 between 2005 and 2020, moderate use of mefenoxam and methoxyfenozide did occur nearby in the adjacent sections of M12S01E10, M12S01E11, and M12S01E14 (DPR, 2025a). No agricultural use of metalaxyl, however, was reported in those same sections (DPR, 2025a).

Triazine Screen Results

For the 12 sampled wells, only the pesticide AI prometryn in the Triazine Screen was detected in a single well (location code 44-10) at a trace level of 0.00256 ppb (Table 3). None of the other 10 pesticide AIs or four degradates in the Triazine Screen were detected in this well. Additionally, none of the 11 pesticide AIs or four degradates in the Triazine Screen were detected in groundwater samples from the other 11 wells. It is worth noting that prometryn is also analyzed for by the GWPP Multi-Analyte Screen but was not detected even at a trace level by that method. The method detection limit for prometryn in the Triazine Screen is 0.00251 ppb whereas its method detection limit in the GWPP Multi-Analyte Screen is 0.006 ppb. The estimated concentration of 0.00256 ppb by the Triazine Screen is slightly greater than its method detection limit of 0.00251 ppb and less than the method detection limit of 0.006 ppb for prometryn by the GWPP Multi-Analyte Screen.

The well (location code 44-10) with the trace detection of prometryn is located near the center of section M11S02E21 (Figure 1). Unlike mefenoxam and methoxyfenozide, no agricultural use of prometryn was reported in section M11S02E21 or in any surrounding sections (i.e., sections M11S02E15, M11S02E16, M11S02E17, M11S02E20, M11S02E22, M11S02E27, M11S02E28, M11S02E29) between 2005 and 2020 (DPR, 2025a).

Overall, the trace detections of mefenoxam/metalaxyl, methoxyfenozide, and prometryn were well below their established pesticide drinking water quality standards (i.e., United States Environmental Protection Agency [USEPA] Chronic or Acute Human Health Benchmarks for Pesticides [HHPBs]) of 3,000, 600, and 200 ppb, respectively (DPR, 2024). The Groundwater Pesticide Detection Response Process is not triggered by trace detections and no immediate follow-up investigation of these wells by GWPP is necessary at this time. Trace detections do indicate the presence of those AIs in areas surrounding the sampled wells and may suggest the need for additional monitoring there in the future. As required by FAC § 13152(a)(1), DPR will also continue to conduct future groundwater monitoring of pesticide AIs in other areas of Region 3 where they have reported agricultural use.

All results from the CDFA CAC laboratory analysis of the samples collected from the 12 wells under Study 318 have been entered into DPR's Well Inventory Database (DPR, 2025b).

Quality Assurance and Quality Control Results

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

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 (Table 2). Two QC matrix-spikes were analyzed along with two sets of samples using LCMS for the GWPP Multi-Analyte Screen. All 41 analytes in the LCMS portion were spiked at 0.1 ppb in the QC matrix-spikes and the recoveries ranged from 41 to 142%. Recoveries of 31 of the 41 analytes were within their control limits whereas recoveries of the other 10 analytes were above or below their respective control limits. With respect to the two matrix-spikes of mefenoxam/metalaxyl, which was detected at a trace concentration in the well with location code 44-02, both recoveries were within control limits. For the two matrix-spikes of methoxyfenozide, which was also detected at a trace concentration in the well with location code 44-02, one recovery was within control limits whereas the other recovery was above the upper control limit. The two atrazine-d5 surrogate recoveries and the two imidacloprid-d4 surrogate recoveries in the QC matrix-spikes for the LCMS were within their respective control limits. With respect to the field samples, 7 of the 14 atrazine-d5 surrogate recoveries from the 14 analyzed samples (12 primary field samples, 1 backup field sample, 1 field blank) were outside control limits. However, all 14 imidacloprid-d4 surrogate recoveries from the 14 analyzed samples (12 primary field samples, 1 backup field sample, 1 field blank) were within control limits. One QC matrix-spike was also analyzed along with one set of samples using GCMS for the GWPP Multi-Analyte Screen. All 16 analytes were spiked at 0.1 ppb for the QC matrix-spike. The recoveries ranged from 75.6 to 135% with all analyte recoveries within their respective control limits.

Triazine Screen QC Samples

Six QC matrix-spikes, two pairs of duplicates, were analyzed along with three sets of samples for the Triazine Screen. All analytes were spiked at 0.2 ppb and the recoveries for the 15 analytes ranged from 62 to 109.5%. Overall, 84% of the recoveries for the 90 analyses of the 15 analytes (i.e., 15 analytes multiplied by 6 QC matrix-spikes) were within control limits. In particular, one recovery of prometryn in the six matrix-spikes was below the lower control limit. To save resources, the sets were not reanalyzed. Two of the six propazine surrogate recoveries in the QC matrix-spikes were below their lower control limit. With respect to the field samples, 12 of the propazine surrogate recoveries from the 14 analyzed samples (12 primary field samples, 1 backup field sample, 1 field blank) were below their lower control limit.

Blind Spikes

A blind spike is a matrix-blank sample spiked by a different chemist than the chemist extracting and analyzing that screen. A blind spike for select analytes was submitted for the GWPP Multi-Analyte Screen and for the Triazine Screen. The selected analytes, spike levels, and recovery results for the two blind spikes are presented in Table 4. For the GWPP Multi-Analyte Screen blind spike, only the recovery for flupyradifurone was outside its control limit (Table 4). On the other hand, the recoveries for all analytes in the Triazine Screen blind spike (i.e., including the propazine surrogate) were below their respective lower control limits (Table 4). As seen in Table 4, however, the measured concentrations of flupyradifurone and the five Triazine Screen analytes (excluding the propazine surrogate) in the blind spike samples (i.e., each spiked to a concentration of 0.1 ppb in the blind spike sample) ranged from 0.0535 to 0.0711 ppb. For contrast, the laboratory reporting limit for flupyradifurone, atrazine, clothianidin, diuron, and norflurazon is 0.02 ppb, whereas the reporting limit for DSMN is 0.01 ppb.

Table 4. Blind spike levels and recoveries.

Sample Number	Analysis Date	Analysis Screen	Analyte	Spike Level (ppb)	Result (ppb)	Recovery (%)	Control Limit Exceeded?
13	8/8/2024	GWPP Multi-Analyte	chlorantraniliprole	0.1	0.0738	73.8	No
			flupyradifurone	0.1	0.0711	71.1	Yes
			fludioxonil	0.15	0.109	72.7	No
			thiamethoxam	0.1	0.0822	82.2	No
			methoxyfenozide	0.15	0.121	80.7	No
			atrazine-d5 (Surrogate)	0.1	0.0942	94.2	No
			imidacloprid-d4 (Surrogate)	0.1	0.0931	93.1	No
14	8/9/2024	Triazine	atrazine	0.1	0.0578	57.8	Yes
			clothianidin	0.1	0.0535	53.5	Yes
			DSMN	0.1	0.0609	60.9	Yes
			diuron	0.1	0.0561	56.1	Yes
			norflurazon	0.1	0.0595	59.5	Yes
			propazine (Surrogate)	0.2	0.13	65.0	Yes

CONCLUSIONS

This report summarizes findings from the continuation of Study 318: groundwater sampling from water wells located in areas within the jurisdiction (Region 3) of the Central Coast RWQCB. In this phase of Study 318, 12 domestic water wells located in southern Santa Cruz County near Watsonville and within the Pajaro Valley Groundwater Basin were sampled during July 2024. The groundwater samples were analyzed by the CDFA's CAC for 58 unique pesticide AIs (including the analysis for the combined concentration of mefenoxam and metalaxyl) and five unique degradates. All results from the CDFA CAC laboratory analysis of the samples collected from the 12 wells under Study 318 were entered into DPR's Well Inventory Database.

Overall, one well (location code 44-02) contained trace detections of mefenoxam/metalaxyl (0.0102 ppb) and methoxyfenozide (0.00574 ppb) and a second well (location code 44-10) contained a trace detection of prometryn (0.00256 ppb). Confirmed detections are measured concentrations above the laboratory reporting limit and trace detections are estimated concentrations by the laboratory that are below the laboratory reporting limit but above the method detection limit. All three detected chemicals (mefenoxam/metalaxyl, methoxyfenozide, prometryn) are pesticide AIs. None of the other 55 pesticide AIs or five degradates in the analysis were detected in these two wells. Additionally, none of the 58 pesticide AIs or five degradates in the total analysis were detected in samples from the other 10 wells.

The trace detections of mefenoxam/metalaxyl, methoxyfenozide, and prometryn were well below established pesticide drinking water quality standards. No immediate follow-up investigation of these wells by GWPP is necessary at this time. DPR will also continue to conduct future groundwater monitoring of pesticide AIs in other areas of Region 3 where they have reported agricultural use.

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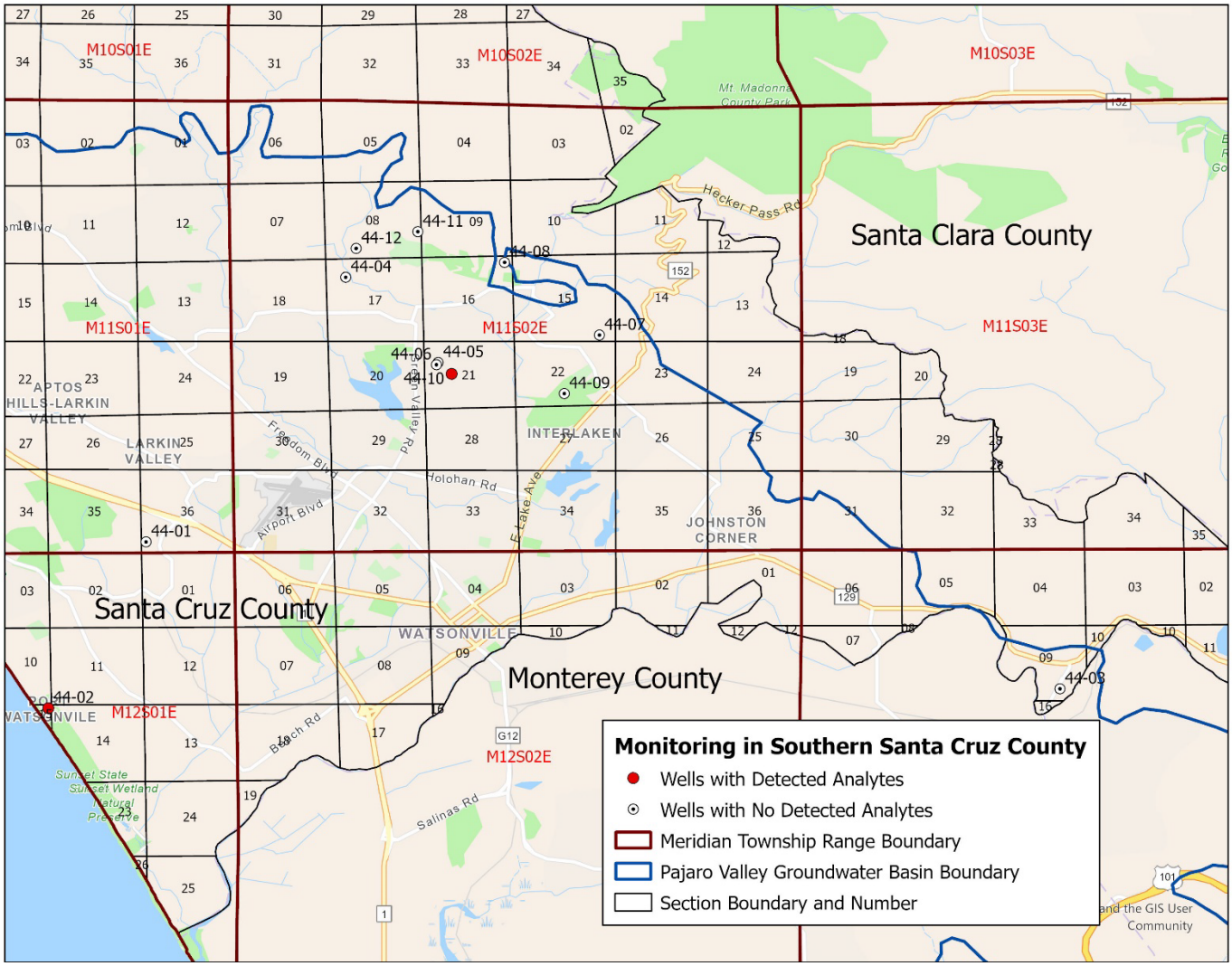

Figure 1. Locations of rural domestic water wells sampled in southern Santa Cruz County near Watsonville (DPR, 2025b).