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Study 300: Groundwater Monitoring for DCPA and Its Degradation Products MTP and TPA

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ABSTRACT

Chlorthal-dimethyl (DCPA) is the active ingredient of a pre-emergent herbicide sold in California under the tradename Dacthal®. It is primarily used for control of annual grasses and certain broadleaved weeds in various fruit and vegetable crops and in ornamental turf. DCPA has two major degradation products: monomethyl tetrachloroterephthalate (MTP) and 2,3,5,6-tetrachloroterephthalic acid (TPA). This report summarizes the findings of Groundwater Study 300 (Study 300): groundwater sampling from water wells in California for DCPA, MTP, and TPA. The motivation and preliminary field sampling plan for Study 300 were documented in the protocol: "Study #300: Protocol for Groundwater Monitoring of DCPA and its Degradates MTP and TPA" (Ruud, 2017). For this study, 45 unique water wells located in six different groundwater basins/sub-basins spanning five counties were sampled from January 2017 through April 2018: 13 wells in the Salinas Valley Groundwater Basin in Monterey County; 18 wells in the Santa Maria River Valley Groundwater Basin in San Luis Obispo and Santa Barbara counties; five wells in the Santa Ynez River Valley Groundwater Basin in Santa Barbara County; one well in the Oxnard Aquifer Sub-basin in Ventura County; one well in the Pleasant Valley Groundwater Basin in Ventura County; and seven wells in the Coachella Valley Groundwater Basin in Riverside County. Forty-three wells were sampled once and two were sampled twice for a total of 47 groundwater samples from the 45 wells. All groundwater samples were analyzed by the California Department of Food and Agriculture's Center for Analytical Chemistry. None of the sampled wells contained detections of DCPA above the reporting limit of 0.05 parts per billion (ppb). Five wells contained detections of MTP with concentrations ranging from 0.056 to 0.13 ppb. Nineteen wells contained detections of TPA with concentrations ranging from 0.121 to 159 ppb. In particular, one well near the city of Greenfield

in the Salinas Valley contained a TPA detection of 101 ppb and three wells around the city of Guadalupe in the Santa Maria River Valley Groundwater Basin contained TPA detections of 66.5, 133, and 159 ppb. All detections were well below the health-protective drinking water level of 2,500 ppb set for TPA by the Office of Environmental Health Hazard Assessment (OEHHA, 2018).

BACKGROUND

The Pesticide Contamination Prevention Act (PCPA) is recorded in Sections 13141-13152 of the California Food and Agricultural Code (FAC). Currently, Section 13149 mandates that when a pesticide active ingredient (AI), other specified ingredient, or degradation product of a pesticide is detected in groundwater and the contamination is found to be due to legal agricultural use, the California Department of Pesticide Regulation (DPR) is required to conduct a formal review (Pesticide Detection Response Process) to determine if use of the pesticide should continue and, if so, under what conditions.

Chlorthal-dimethyl (DCPA) (tradename: Dacthal® [AMVAC, 2015]) is the AI in a number of herbicide products with historic or current use in California. DCPA has two major degradation products: monomethyl tetrachloroterephthalate (MTP) and 2,3,5,6-tetrachloroterephthalic acid (TPA). DPR conducted groundwater sampling studies between 1990 and 1997 in different areas of California where DCPA had been legally used, looking specifically for DCPA, MTP, and TPA. None of the laboratory analyses of the collected samples from those studies yielded a confirmed detection of DCPA or MTP. However, the laboratory analyses did confirm detections of TPA in samples collected in several counties (Ruud, 2017).

The PCPA was originally enacted in 1985 under Assembly Bill 2021 and was significantly revised in 2014 under Senate Bill 1117. Under the 1985 version of the PCPA (i.e., that includes the period from 1990 to 1997 when DPR's previous DCPA sampling studies were conducted), if a degradation product was detected in groundwater, the AI was only entered into the Pesticide Detection Response Process if the concentrations of the degradation product were determined to be high enough to pose a threat to public health. Although confirmed detections of TPA were found between 1990 and 1997, DPR's Medical Toxicology Branch reviewed the available toxicological data for TPA submitted by the registrant and concluded that the levels found in groundwater did not pose a threat to public health (CDPR, 1991). Consequently, DCPA was not entered into the Pesticide Detection Response Process (CDPR, 1992). A health reference level (HRL) of 70 parts per billion (ppb) (or micrograms per liter) was calculated for DCPA by the United States Environmental Protection Agency (USEPA) and adopted as an HRL for TPA and MTP (USEPA, 2008). The HRL of 70 ppb was later adopted by DPR for its monitoring of TPA in groundwater (CDPR, 2012). Since 1997, several agencies have reported detections of TPA in water wells located throughout the state but those measured TPA concentrations were all below the established HRL.

The revision of the PCPA in 2014 lifted the requirement to demonstrate a threat to public health of degradation products found in groundwater. Consequently, an AI is now entered into the Pesticide Detection Response Process when its degradation product is found in groundwater and determined to have originated from legal agricultural use of the parent AI.

Groundwater Study 300 (Study 300) was planned and conducted to assess current concentrations of DCPA, MTP, and TPA in water wells located in regions where historical agricultural use of DCPA had been relatively high and where detections of TPA had been found in previous studies. A subsequent analysis of historic and current detections of DCPA, MTP, and TPA in groundwater as occurrences of non-point source contamination due to legal agricultural use of DCPA was presented in a separate report entitled "Legal Agricultural Use Determination for DCPA Degradate Detections in California" (Ruud, 2018). The determination that the degradate TPA was found in groundwater due to legal agricultural use of DCPA formed the basis for entering DCPA into the Pesticide Detection Response Process in March 2018 per the 2014 revisions to the PCPA (CDPR, 2018a). In August 2018, a public hearing was conducted to formally review the continued use of DCPA in agricultural products registered for use in California (CDPR, 2018b). In December 2018, the Director of DPR concurred with the findings and recommendations of the formal review subcommittee that MTP and TPA had not polluted and do not threaten to pollute the groundwater of the state (CDPR, 2018c). Subsequently, the use of registered DCPA agricultural products was allowed to continue in California. DPR was required to continue monitoring for MTP and TPA to assess concentrations of those constituents in groundwater relative to a health-protective drinking water level of 2,500 ppb set for DCPA, MTP, and TPA by the Office of Environmental Health Hazard Assessment (OEHHA) as part of the formal review process (OEHHA, 2018).

This report summarizes the monitoring results of Study 300 that were used to inform the aforementioned Pesticide Detection Response Process for DCPA. It includes a brief description of the sampling methods for collecting the groundwater samples; the analytical laboratory method and associated quality assurance/quality control (QA/QC) standards used to measure DCPA, MTP, and TPA in groundwater samples; and the results of the laboratory analysis of the collected groundwater samples.

METHODS

Sampling Methods

The field sampling plan documented in the protocol (Ruud, 2017) included the identification of potential areas from which to choose wells to sample for DCPA, MTP, and TPA. Using Pesticide Use Reporting (PUR) data, five different regions in California were identified as having significant DCPA use between the years 2000 and 2010 (CDPR, 2019a). Each of the five regions included one or more groundwater basins or sub-basins. The protocol also included a map displaying the locations in California with confirmed detections of TPA from sampling that occurred from 1990 through 1997 (CDPR, 2019b). For Study 300, DPR's Groundwater Protection Program (GWPP) collected samples at 45 unique water wells located in six different groundwater basins/sub-basins spanning five counties from January 2017 through April 2018. Forty-three of the 45 wells were sampled once and two of the 45 wells were sampled twice for a total of 47 groundwater samples from the 45 wells. GWPP staff collected samples from the wells using methods described in Standard Operating Procedure (SOP) FSWA001.02 (Nordmark and Herrig, 2011). Geographic location information, well type, and the sampling date(s) for each of the 45 wells are listed in Table 1.

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

County	Groundwater Basin/Sub-basin	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code[1]	Well Type	Sampling Date
Monterey	Salinas Valley/Eastside	M15S04E22	27-01	domestic	1/9/2017
Monterey	Salinas Valley/Forebay	M19S07E05	27-02**	domestic	1/10/2017
Monterey	Salinas Valley/Eastside	M16S05E18	27-03	agricultural	1/11/2017
Monterey	Salinas Valley/Forebay	M18S06E09	27-04	domestic	1/12/2017
Monterey	Salinas Valley/Forebay	M17S06E32	27-05	domestic	1/12/2017
Monterey	Salinas Valley/Forebay	M19S06E01	27-06*	domestic	1/12/2017
Monterey	Salinas Valley/Forebay	M18S06E23	27-07	domestic	1/12/2017
Monterey	Salinas Valley/Eastside	M14S03E35	27-08	agricultural	5/22/2017
Monterey	Salinas Valley/Forebay	M18S06E36	27-09	municipal	5/23/2017
Monterey	Salinas Valley/Forebay	M18S07E31	27-10	municipal	5/23/2017
Monterey	Salinas Valley/Forebay	M19S07E05	27-11**	domestic	5/24/2017

County	Groundwater Basin/Sub-basin	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code[1]	Well Type	Sampling Date
Monterey	Salinas Valley/Forebay	M19S06E01	27-12*	domestic	5/24/2017
Monterey	Salinas Valley/Eastside	M15S04E16	27-13	agricultural	5/24/2017
Monterey	Salinas Valley/Eastside	M15S04E17	27-14	agricultural	5/25/2017
Monterey	Salinas Valley/Eastside	M15S03E02	27-15	municipal	6/15/2017
San Luis Obispo	Santa Maria River Valley	M32S13E01	40-01	domestic	10/11/2017
San Luis Obispo	Santa Maria River Valley	M32S14E18	40-02	domestic	10/11/2017
Santa Barbara	Santa Ynez River Valley	S06N32W06	42-01	domestic	10/9/2017
Santa Barbara	Santa Ynez River Valley	S07N33W27	42-02	domestic	10/9/2017
Santa Barbara	Santa Ynez River Valley	S07N34W35	42-03	domestic	10/9/2017
Santa Barbara	Santa Maria River Valley	S10N34W18	42-04	domestic	10/10/2017
Santa Barbara	Santa Maria River Valley	S10N34W17	42-05	domestic	10/10/2017
Santa Barbara	Santa Maria River Valley	S10N35W09	42-06	municipal	10/12/2017
Santa Barbara	Santa Maria River Valley	S10N35W09	42-07	municipal	10/12/2017
San Luis Obispo	Santa Maria River Valley	M32S13E12	40-51	domestic	11/28/2017
San Luis Obispo	Santa Maria River Valley	M32S13E13	40-52	domestic	11/28/2017
San Luis Obispo	Santa Maria River Valley	M32S13E28	40-53	domestic	11/28/2017
San Luis Obispo	Santa Maria River Valley	M32S13E32	40-54	domestic	11/28/2017
San Luis Obispo	Santa Maria River Valley	S11N35W26	40-55	agricultural	11/28/2017
Santa Barbara	Santa Maria River Valley	S10N35W09	42-61	domestic	11/28/2017
Santa Barbara	Santa Maria River Valley	S10N35W23	42-62	domestic	11/28/2017
Santa Barbara	Santa Maria River Valley	S09N33W02	42-63	domestic	11/28/2017
Santa Barbara	Santa Ynez River Valley	S07N35W25	42-64	domestic	11/29/2017
Santa Barbara	Santa Ynez River Valley	S07N35W24	42-65	domestic	11/29/2017
Santa Barbara	Santa Maria River Valley	S09N34W08	42-71	domestic	11/29/2017

County	Groundwater Basin/Sub-basin	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code[1]	Well Type	Sampling Date
Santa Barbara	Santa Maria River Valley	S10N35W08	42-72	domestic	11/29/2017
Santa Barbara	Santa Maria River Valley	S10N35W10	42-73	domestic	11/29/2017
Santa Barbara	Santa Maria River Valley	S10N34W17	42-74	agricultural	11/30/2017
Riverside	Coachella Valley	S07S07E01	33-01	domestic	3/20/2018
Riverside	Coachella Valley	S07S08E04	33-02	domestic	3/20/2018
Riverside	Coachella Valley	S07S08E02	33-03	domestic	3/20/2018
Riverside	Coachella Valley	S08S08E13	33-14	domestic	3/21/2018
Riverside	Coachella Valley	S08S08E02	33-15	domestic	3/21/2018
Riverside	Coachella Valley	S07S09E26	33-16	domestic	3/21/2018
Riverside	Coachella Valley	S07S08E01	33-17	small public water system	3/22/2018
Ventura	Santa Clara River Valley/Oxnard Aquifer	S01N21W21	56-01	domestic/ agricultural	4/3/2018
Ventura	Pleasant Valley	S01N21W02	56-02	domestic	4/4/2018

[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.

* Location codes 27-06 and 27-12 refer to the same well (M19S06E01) sampled on two different dates.

**Location codes 27-02 and 27-11 refer to the same well (M19S07E05) sampled on two different dates.

Analytical Methods

Chemical analysis of groundwater samples collected under Study 300 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 for DCPA, MTP, and TPA using method EMON-SM-05-040 (DCPA Screen) (CDFA, 2016). 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]). SOP QAQC001.01 (Peoples, 2019) updated the previous SOP QAQC001.00 (Segawa, 1995) to reflect this verification requirement. Although SOP QAQC001.00 (Segawa, 1995) had not yet been updated at the time Study 300 was conducted, this verification requirement (as documented in SOP QAQC001.01 [Peoples, 2019]) was nevertheless followed in this study. The criterion to identify methods providing unequivocal identification of a chemical are further provided in Aggarwal (2012). Unequivocal identification of EMON-SM-05-040 was established and documented in Aggarwal (2017). The method detection limits for DCPA, MTP, and TPA using method EMON-SM-05-040 were 0.00629, 0.0155, and 0.0313 ppb, respectively (CDFA, 2016). The reporting limit for all chemicals in Table 2 was 0.05 ppb. A ‘trace’ detection is defined as a measured concentration between a method’s detection limit and the reporting limit of 0.05 ppb.

Table 2. Pesticides and degradates included in CDFA laboratory screens.

Multi-Analyte Screen* (LCMS Method)		**Multi-Analyte Screen* (GCMS Method)**	**Triazine Screen***	**DCPA Screen**
EMON-SM-05-032		**EMON-SM-05-032**	**EMON-SM-62.9**	**EMON-SM-05-040**
Atrazine**	Linuron	Clomazone	ACET[2]	DCPA
Azinphos-methyl	Mefenoxam/ Metalaxyl[1]	Dichloran	Atrazine**	MTP
Azoxystrobin	Methiocarb	Dichlobenil	Bromacil**	TPA
Bensulide	Metolachlor	Disulfoton	DACT[3]	
Bromacil**	Metribuzin	Ethoprophos	DEA[4]	
Carbaryl	Napropamide	Ethyl parathion	Diuron**	
Carbofuran	Norflurazon**	Fonofos	DSMN[5]	
Diazinon	Oryzalin	Malathion	Hexazinone	
Dimethenamide	Prometon**	Methyl parathion	Norflurazon**	
Dimethoate	Simazine**	Phorate	Prometon**	
Diuron**	Tebuthiuron**	Piperonyl butoxide	Simazine**	
Ethofumesate	Thiamethoxam	Prometryn	Tebuthiuron**	
Fenamiphos	Thiobencarb	Propanil		
Fludioxonil	Uniconazole	Triallate		
Imidacloprid				

*Only used for samples collected in groundwater basins in Ventura and Riverside counties.
**Analytes are included in both screens.
[1]Mefenoxam and metalaxyl are stereoisomers. The analytical method cannot differentiate the two analytes.
[2]ACET: deisopropyl atrazine; degradate of atrazine and simazine.
[3]DACT: diaminochlortriazine; degradate of simazine.
[4]DEA: deethyl atrazine; degradate of atrazine.
[5]DSMN: desmethyl norflurazon; degradate of norflurazon.

All well water samples collected in this study from the six groundwater basins noted in Table 1 were analyzed for DCPA, MTP, and TPA using method EMON-SM-05-040. Groundwater samples collected from two basins located in Riverside and Ventura counties were additionally analyzed using methods EMON-SM-62.9 (Triazine Screen) (CDFA, 2009; Fattah, 2008) and EMON-SM-05-032 (Multi-Analyte Screen) (CDFA, 2013; Aggarwal, 2016). A complete list of the AIs and degradation products in the DCPA, Triazine, and Multi-Analyte screens is presented in Table 2. The Triazine Screen analyzes for six of the seven restricted-use AIs on the Groundwater Protection List (Title 3 of the California Code of Regulations [CCR], section 6800[a]); the major degradation products of atrazine, simazine, and norflurazon (i.e., ACET, DACT, DEA, and DSMN); and the AIs hexazinone and tebuthiuron (i.e., two AIs in section 6800[b] of the Groundwater

Protection List: AIs with the potential to leach to groundwater). The Multi-Analyte Screen analyzes for 44 AIs, including six AIs from the 6800(a) list and 29 AIs from the 6800(b) list (Table 2).

Quality Assurance and Quality Control

CDFA's CAC analyzed continuing quality control samples with every set of samples to assess lab precision. The procedures for continuing quality control (QC) measures are specified in SOP QAQC001.01 (Peoples, 2019) and were implemented in Study 300 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 lab matrix-blank and a continuing QC matrix-spike. The lab 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 Program, and the Environmental Monitoring Branch (EM) Quality Assurance (QA) Officer to ensure analytical integrity. The evaluation includes comparing the continuing 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 continuing QC were used to assess and monitor ongoing sample analysis and minor variation was expected. Additionally, the EM QA Officer submitted blind spikes to the lab disguised as field samples per SOP QAQC008.00 (Ganapathy, 2005), where the blind spike consists of the analyte-free groundwater (matrix-blank sample) fortified with the chosen analytes.

RESULTS

Sample Analysis

Laboratory-measured concentrations of DCPA, MTP, and TPA in groundwater samples from each of the 45 sampled wells are listed in Table 3 and summarized by county in Table 4. Detections in each groundwater basin are briefly described in the following sections.

Table 3. DCPA Screen sample analysis results.

Sample Number	Sample Code[1]	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code	Analysis Date	DCPA (ppb)	MTP (ppb)	TPA (ppb)
533	P	M15S04E22	27-01	1/20/2017	ND	ND	**0.916**
534	BU	M15S04E22	27-01	2/7/2017	ND	ND	**1.07**
535	FB	M15S04E22	27-01	2/7/2017	ND	ND	ND
539	P	M19S07E05	27-02	1/26/2017	ND	**0.13**	**22.7**

Sample Number	Sample Code[1]	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code	Analysis Date	DCPA (ppb)	MTP (ppb)	TPA (ppb)
540	BU	M19S07E05	27-02	2/7/2017	ND	ND	**21.1**
541	FB	M19S07E05	27-02	2/7/2017	ND	ND	ND
518	P	M16S05E18	27-03	1/20/2017	ND	ND	ND
515	P	M18S06E09	27-04	1/20/2017	ND	ND	ND
536	P	M17S06E32	27-05	1/20/2017	ND	ND	ND
542	P	M19S06E01	27-06	1/26/2017	ND	**0.073**	**101**
543	BU	M19S06E01	27-06	2/7/2017	ND	**0.069**	**94.4**
544	FB	M19S06E01	27-06	2/7/2017	ND	ND	**Trace**
503	P	M18S06E23	27-07	1/20/2017	ND	ND	ND
530	P	M14S03E35	27-08	6/1/2017	ND	ND	ND
524	P	M18S06E36	27-09	6/1/2017	**Trace**	ND	ND
526	FB	M18S06E36	27-09	8/30/2017	ND	ND	ND
506	P	M18S07E31	27-10	6/1/2017	ND	ND	ND
557	P	M19S07E05	27-11	6/1/2017	ND	**Trace**	**12.7**
559	FB	M19S07E05	27-11	8/30/2017	ND	ND	ND
500	P	M19S06E01	27-12	6/1/2017	ND	**0.056**	**38.2**
501	BU	M19S06E01	27-12	9/1/2017	ND	ND	**57.2**
502	FB	M19S06E01	27-12	10/26/2017	ND	ND	ND
527	P	M15S04E16	27-13	6/1/2017	ND	ND	ND
512	P	M15S04E17	27-14	6/1/2017	ND	ND	
514	FB	M15S04E17	27-14	8/30/2017	ND	ND	ND
554	P	M15S03E02	27-15	6/19/2017	ND	**Trace**	**10.9**
556	FB	M15S03E02	27-15	8/30/2017	ND	ND	ND
584	P	M32S13E01	40-01	10/26/2017	ND	ND	ND
590	P	M32S14E18	40-02	10/26/2017	ND	ND	ND
578	P	S06N32W06	42-01	10/26/2017	ND	ND	ND
575	P	S07N33W27	42-02	10/26/2017	ND	ND	ND
569	P	S07N34W35	42-03	10/26/2017	ND	ND	ND
593	P	S10N34W18	42-04	10/26/2017	ND	ND	**1.87**
595	FB	S10N34W18	42-04	1/3/2018	ND	ND	ND
587	P	S10N34W17	42-05	10/26/2017	ND	ND	**0.521**
589	FB	S10N34W17	42-05	1/3/2018	ND	ND	ND
572	P	S10N35W09	42-06	10/26/2017	ND	ND	ND
566	P	S10N35W09	42-07	10/26/2017	ND	ND	**10.1**
568	FB	S10N35W09	42-07	1/3/2018	ND	ND	ND
611	P	M32S13E12	40-51	12/8/2017	ND	ND	**Trace**
613	FB	M32S13E12	40-51	1/3/2018	ND	ND	ND
614	P	M32S13E13	40-52	12/8/2017	ND	ND	ND

Sample Number	Sample Code[1]	Public Lands Survey System (Meridian/Township/ Range/Section)	Location Code	Analysis Date	DCPA (ppb)	MTP (ppb)	TPA (ppb)
602	P	M32S13E28	40-53	12/8/2017	ND	ND	**0.383**
604	FB	M32S13E28	40-53	1/3/2018	ND	ND	ND
644	P	M32S13E32	40-54	12/8/2017	ND	ND	**0.121**
646	FB	M32S13E32	40-54	1/3/2018	ND	ND	ND
629	P	S11N35W26	40-55	12/8/2017	ND	ND	**0.147**
631	FB	S11N35W26	40-55	1/3/2018	ND	ND	ND
608	P	S10N35W09	42-61	12/13/2017	ND	**0.063**	**159**
610	FB	S10N35W09	42-61	1/3/2018	ND	ND	ND
635	P	S10N35W23	42-62	12/13/2017	ND	ND	**13.1**
637	FB	S10N35W23	42-62	1/3/2018	ND	ND	ND
617	P	S09N33W02	42-63	12/8/2017	ND	ND	ND
653	P	S07N35W25	42-64	12/8/2017	ND	ND	**0.867**
655	FB	S07N35W25	42-64	1/3/2018	ND	ND	ND
632	P	S07N35W24	42-65	12/8/2017	ND	ND	**0.435**
634	FB	S07N35W24	42-65	1/3/2018	ND	ND	ND
656	P	S09N34W08	42-71	12/8/2017	ND	ND	ND
650	P	S10N35W08	42-72	12/13/2017	ND	**0.065**	**66.5**
652	FB	S10N35W08	42-72	1/3/2018	ND	ND	ND
581	P	S10N35W10	42-73	12/13/2017	ND	**0.101**	**133**
583	FB	S10N35W10	42-73	1/3/2018	ND	ND	ND
647	P	S10N34W17	42-74	12/13/2017	ND	ND	**15.3**
649	FB	S10N34W17	42-74	1/3/2018	ND	ND	ND
834	P	S07S07E01	33-01	4/10/2018	ND	ND	ND
820	P	S07S08E04	33-02	4/10/2018	ND	ND	ND
876	P	S07S08E02	33-03	4/10/2018	ND	ND	ND
764	P	S08S08E13	33-14	4/10/2018	ND	ND	ND
855	P	S08S08E02	33-15	4/10/2018	ND	ND	ND
848	P	S07S09E26	33-16	4/10/2018	ND	ND	ND
778	P	S07S08E01	33-17	4/10/2018	ND	ND	ND
736	P	S01N21W21	56-01	4/13/2018	ND	ND	ND
862	P	S01N21W02	56-02	4/13/2018	ND	ND	**0.158**
867	FB	S01N21W02	56-02	5/23/2018	ND	ND	ND

[1]P = primary sample, BU = backup 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

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

County	Number of Unique Wells Sampled	Number of Unique Wells with Detections	Pesticides or Degradates Detected
Monterey	13	5	MTP, TPA
Riverside	7	0	None
San Luis Obispo	7	3	TPA
Santa Barbara	16	10	MTP, TPA
Ventura	2	1	TPA

Salinas Valley Groundwater Basin

The Salinas Valley Groundwater Basin is located in Monterey County and is divided into four sub-basins, including the Eastside Aquifer Sub-basin (CDWR, 2004a) and the Forebay Aquifer Sub-basin (CDWR, 2004b) (Figure 1). GWPP collected samples at thirteen unique wells in the Salinas Valley during 2017 over the three sampling periods of January 9-12, May 22-25, and June 15 (Table 1). Six of the sampled wells (one municipal well, four agricultural wells, and one domestic well) were located in the Eastside Aquifer Sub-basin and the other seven wells (two municipal wells and five domestic wells) were located in the Forebay Aquifer Sub-basin (Figure 1). Eleven of the 13 wells were sampled once and two of the 13 wells were sampled twice for a total of 15 groundwater samples from the 13 wells. (The location codes 27-06 and 27-12 in Tables 1 and 3 and on Figure 1, refer to the same well in M19S06E01 that was sampled on two separate occasions. Similarly, location codes 27-02 and 27-11 refer to the same well in M19S07E05 that was also sampled twice. Both sampling events included replicate analysis since both the primary and back-up samples were analyzed.) No wells in the Pressure Sub-basin and Upper Valley Sub-basin were sampled in Study 300 due to an inability to acquire well-owner authorization.

Five of the 13 wells contained detections of TPA ranging in concentration from 0.916 to 101 ppb (Table 3). When GWPP collected samples on January 12, the well in M19S06E01 with location code 27-06 was found to contain a TPA concentration of 101 ppb. When that same well was resampled over four months later on May 24, the measured TPA concentration decreased to 57.2 ppb. Similarly, the well in M19S07E05 with location code 27-02 when sampled on January 10, 2017 was found to contain a TPA concentration of 22.7 ppb. When that same well was resampled on May 24, the measured TPA concentration had decreased to 12.7 ppb. The decrease in measured TPA concentration in both resampled wells between January and May is likely due to dilution of TPA levels in the groundwater by aquifer recharge from the significant amount of rainfall that occurred in the region during that sampling interval. The only wells sampled in the Salinas Valley that contained measured concentrations of MTP (0.073 and 0.13 ppb) above the reporting limit of 0.05 ppb were the two wells with the highest concentrations of TPA (101 and 22.7 ppb) (Table 3). These two wells are located just southwest and south of the city of Greenfield, respectively (Figure 1). A trace detection of DCPA was also found in a municipal well in M18S06E36 just east of the city of Greenfield (Table 3).

Santa Maria River Valley Groundwater Basin

The Santa Maria River Valley Groundwater Basin (CDWR, 2004c) spans in the north-south direction across the east-west boundary of San Luis Obispo and Santa Barbara counties (Figure 2). GWPP staff collected samples at eighteen unique wells in the basin during 2017 over the two sampling periods of October 10-12 and November 28-30 (Table 1). Six domestic wells were located in the Arroyo Grande area (San Luis Obispo County) of the basin and the other 12 wells (two municipal wells, two agricultural wells, and eight domestic wells) were located in and around the cities of Guadalupe and Santa Maria in the Santa Barbara County portion of the basin.

Two wells located near Arroyo Grande contained detections of TPA at concentrations of 0.383 ppb (location code 40-53) and 0.121 ppb (location code 40-54) (Figure 2). Three wells west of Santa Maria contained detections of TPA in the range of 0.521 to 15.3 ppb (location codes 42-05, 42-62, and 42-74). Two of the three wells were located just east of Guadalupe and contained detections of TPA with concentrations of 133 and 159 ppb (location codes 42-73 and 42-61). The third well on the western edge of Guadalupe had a TPA concentration of 66.5 ppb (location code 42-72). These three wells contained the highest measured concentrations of TPA (133, 159, and 66.5 ppb) in the basin and were located individually in three consecutively adjacent sections spanning Guadalupe in the east to west direction (Figure 2). These three wells were also the only wells sampled in the basin that contained concentrations of MTP (0.101, 0.063, and 0.065 ppb) above the reporting limit of 0.05 ppb (Table 3).

Santa Ynez River Valley Groundwater Basin

The Santa Ynez River Valley Groundwater Basin (CDWR, 2004d) is located in Santa Barbara County (Figure 3). GWPP staff collected samples at five domestic wells located in and around the city of Lompoc in the basin either on October 9 or November 29, 2017 (Table 1). Two of five wells contained detections of TPA at concentrations of 0.867 ppb (location code 42-64) and 0.435 ppb (location code 42-65) (Figure 3). DCPA or MTP were not detected in any of the five sampled wells (Table 3).

Santa Clara River Valley Groundwater Basin

The Santa Clara River Valley Groundwater Basin (CDWR, 2004e) is located in Ventura County and is divided into several sub-basins including the Oxnard Aquifer Sub-basin (Figure 4). GWPP staff collected a sample at a single domestic/agricultural well in the Oxnard Sub-basin on April 3, 2018 (Table 1). The sample collected from the well was analyzed for the AIs and degradation products in the DCPA, Triazine, and Multi-Analyte screens (Table 2). There were no detections of any analyte found in the groundwater sample.

Pleasant Valley Groundwater Basin

The Pleasant Valley Groundwater Basin (CDWR, 2004f) is adjacent to and east of the Oxnard Aquifer Sub-basin in Ventura County (Figure 4). GWPP staff collected a sample at one domestic well in the Pleasant Valley Groundwater Basin on April 4, 2018 (Table 1). The sample collected from the well was analyzed for the AIs and degradation products in the DCPA, Triazine, and Multi-Analyte screens (Table 2). Laboratory analysis of the sample yielded a detection of TPA with a measured concentration of 0.158 ppb (location code 56-02) (Table 3). There were no detections of any analyte on the Triazine or Multi-Analyte screens found in this groundwater sample.

Coachella Valley Groundwater Basin

The Coachella Valley Groundwater Basin (CDWR, 2004g) is located in Riverside County (Figure 5). GWPP staff collected samples at seven wells (one small public water system well and six domestic wells) in the basin between March 20-22, 2018 (Table 1). Samples collected from each well were analyzed for the AIs and degradation products in the DCPA, Triazine, and Multi-Analyte screens (Table 2). There were no detections of any analyte found in the seven sampled wells.

Quality Assurance and Quality Control

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

DCPA Screen QC Samples

The continuing QC data for the DCPA Screen is summarized in Table 5. Fifteen matrix spikes with DCPA, MTP, and TPA and two matrix spikes with TPA alone were analyzed along with 47 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 75.4, 91.3, and 81.4%, respectively. The associated standard deviation of the recovery of DCPA, MTP, and TPA was 15.1, 12.1, and 15.7%, respectively. All recoveries of TPA were within its control limits. Three of 15 recoveries of DCPA were just above its upper control limit and one recovery of DCPA was below its lower control limit. One of 15 recoveries of MTP was below its lower control limit.

Table 5. Continuing quality control data for the DCPA Screen.

Analysis Date	Analyte	Spike Level (ppb)	% Recovery	Control Limited Exceeded?
1/20/2017	DCPA	0.200	85.0	Yes
	MTP	0.200	103	No
	TPA	0.200	103	No
1/26/2017	TPA	0.200	103	No
2/7/2017	DCPA	0.200	74.0	No
	MTP	0.200	101	No
	TPA	0.200	99.0	No
2/14/2017	DCPA	0.200	80.5	No
	MTP	0.200	106	No
	TPA	0.200	93.5	No
6/1/2017	DCPA	0.200	80.0	No
	MTP	0.200	90.5	No
	TPA	0.200	81.5	No
6/16/2017	DCPA	0.200	85.5	Yes
	MTP	0.200	94.5	No
	TPA	0.200	87.5	No
6/19/2017	DCPA	0.200	84.5	No
	MTP	0.200	89.5	No
	TPA	0.200	73.5	No
8/30/2017	DCPA	0.200	96.5	Yes
	MTP	0.200	90.5	No
	TPA	0.200	92.0	No
9/1/2017	DCPA	0.200	82.0	No
	MTP	0.200	61.0	Yes
	TPA	0.200	67.0	No
10/23/2017	DCPA	0.200	35.8	Yes
	MTP	0.200	89.5	No
	TPA	0.200	70.0	No
10/26/2017	DCPA	0.200	73.0	No
	MTP	0.200	90.0	No
	TPA	0.200	58.0	No
12/8/2017	DCPA	0.200	81.5	No
	MTP	0.200	94.0	No
	TPA	0.200	57.5	No
12/13/2017	TPA	0.200	92.0	No
1/3/2018	DCPA	0.200	90.0	No
	MTP	0.200	106	No
	TPA	0.200	77.0	No

4/10/2018	DCPA	0.200	60.5	No
	MTP	0.200	75.5	No
	TPA	0.200	63.5	No
4/13/2018	DCPA	0.200	66.0	No
	MTP	0.200	99.0	No
	TPA	0.200	97.5	No
6/1/2018	DCPA	0.200	65.5	No
	MTP	0.200	80.0	No
	TPA	0.200	69.0	No
Mean (SD*)	DCPA		75.4% (15.1%)	
	MTP		91.3% (12.1%)	
	TPA		81.4% (15.7%)	
Control Limits	DCPA		57.3 – 84.5%	
	MTP		73.3 – 115%	
	TPA		48.5 – 104%	

*SD: Standard deviation (values in parenthesis).

Multi-Analyte Screen QC Samples

For the Multi-Analyte Screen, continuing 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. Two matrix spikes were analyzed along with two sets of samples using LCMS for the Multi-Analyte Screen. All 29 analytes in the LCMS portion were spiked at 0.2 ppb in the QC matrix-spikes and found to be within the control limits. The recoveries ranged from 59 to 113%. One recovery of phorate (59%) was below its lower control limit. Two QC matrix-spikes were also analyzed along with two sets of samples using GCMS for the Multi-Analyte Screen. All 14 analytes were spiked at 0.1 ppb in one matrix-spike and at 0.4 ppb in the other. The recoveries ranged from 76 to 111% with all analyte recoveries within the control limits.

Triazine Screen QC Samples

Four continuing QC matrix-spikes, two in duplicate, were analyzed along with three sets of samples for the Triazine Screen. All analytes were spiked at 0.2 ppb, resulting in an average recovery for the 12 analytes ranging from 60 to 108%. Each of the continuing QC matrix-spikes had one or more analyte recoveries below the lower control limit; however, the lab was consulted and there were no detections between the minimum detection limit and the reporting limit. To save on resources, the sets were not reanalyzed. The propazine surrogate recovery was within the control limits in the continuing QC matrix-spikes, as well as in every sample analyzed for this screen.

Blind Spikes

A blind spike is a matrix-blank sample spiked by a chemist other than the chemist extracting and analyzing that screen. Six blind spikes containing DCPA, MTP, and TPA were submitted throughout the study period (Table 6). The average recovery of DCPA, MTP, and TPA was 78.9, 98.5, and 101.2%, respectively. The associated standard deviation of the recovery of DCPA, MTP, and TPA was 14.9, 28.2, and 24.5%, respectively. One recovery of TPA and one recovery of DCPA were both above their respective upper control limits. Two recoveries of MTP were above its upper control limit and one recovery of MTP was below its lower control limit.

Table 6. Blind spike levels and recoveries.

Sample Number	Analysis Date	Analysis Screen	Analyte	Spike Level (ppb)	Result (ppb)	Recovery (%)	Control Limit Exceeded?
521	1/20/2017	DCPA	DCPA	0.200	0.166	83.0	No
			MTP	0.200	0.205	103	Yes
			TPA	0.200	0.255	128	No
509	6/1/2017	DCPA	DCPA	0.150	0.088	58.7	No
			MTP	0.100	0.074	74.0	No
			TPA	0.250	0.171	68.4	No
563	6/19/2017	DCPA	DCPA	0.150	0.115	76.7	No
			MTP	0.100	0.132	132	Yes
			TPA	0.100	0.094	94.0	No
596	10/26/2017	DCPA	DCPA	0.200	0.144	72.0	No
			MTP	0.300	0.250	83.3	No
			TPA	0.250	0.256	102	No
597	12/8/2017	DCPA	DCPA	0.100	0.104	104	Yes
			MTP	0.150	0.163	109	No
			TPA	0.300	0.287	95.7	No
890	4/10/2018	DCPA	DCPA	0.250	0.197	78.8	No
			MTP	0.250	0.164	65.6	Yes
			TPA	0.250	0.353	144	Yes

CONCLUSIONS

This report summarized the findings of Study 300: groundwater monitoring for DCPA and its degradation products MTP and TPA. The motivation and preliminary field sampling plan for Study 300 were documented in the protocol: "Study #300: Protocol for Groundwater Monitoring of DCPA and its Degradates MTP and TPA" (Ruud, 2017). The findings of Study 300 were used to evaluate detections of MTP and TPA in groundwater as occurrences of non-point source contamination due to the legal agricultural use of DCPA in a subsequent report (Ruud, 2018). For Study 300, 45 unique water wells located in six different groundwater basins/sub-basins spanning five counties were sampled from January 2017 through April 2018. Forty-three of the 45 wells were sampled once and two of the 45 wells were sampled twice for a total of 47 groundwater samples from the 45 wells. None of the sampled wells contained detections of DCPA above the reporting limit of 0.05 ppb. Five wells contained detections of MTP with concentrations ranging from 0.056 to 0.13 ppb. Nineteen wells contained detections of TPA with concentrations ranging from 0.121 to 159 ppb. In particular, one well near the city of Greenfield in the Salinas Valley contained a TPA detection of 101 ppb and three wells around the city of Guadalupe in the Santa Maria River Valley Groundwater Basin contained TPA detections of 66.5, 133, and 159 ppb. All detections of TPA were well below the health-protective drinking water level of 2,500 ppb set for DCPA, MTP, and TPA by the Office of Environmental Health Hazard Assessment (OEHHA, 2018). As required by the PCPA, GWPP will continue monitoring for MTP and TPA in high-use areas of DCPA to assess concentrations of those constituents in groundwater relative to their health-protective drinking water levels.

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Figure 1. Total DCPA use (pounds per section) from 2000 to 2010 and locations of sampled water wells in the Eastside and Forebay sub-basins of the Salinas Valley Groundwater Basin in Monterey County (CDPR, 2019a; 2019b).

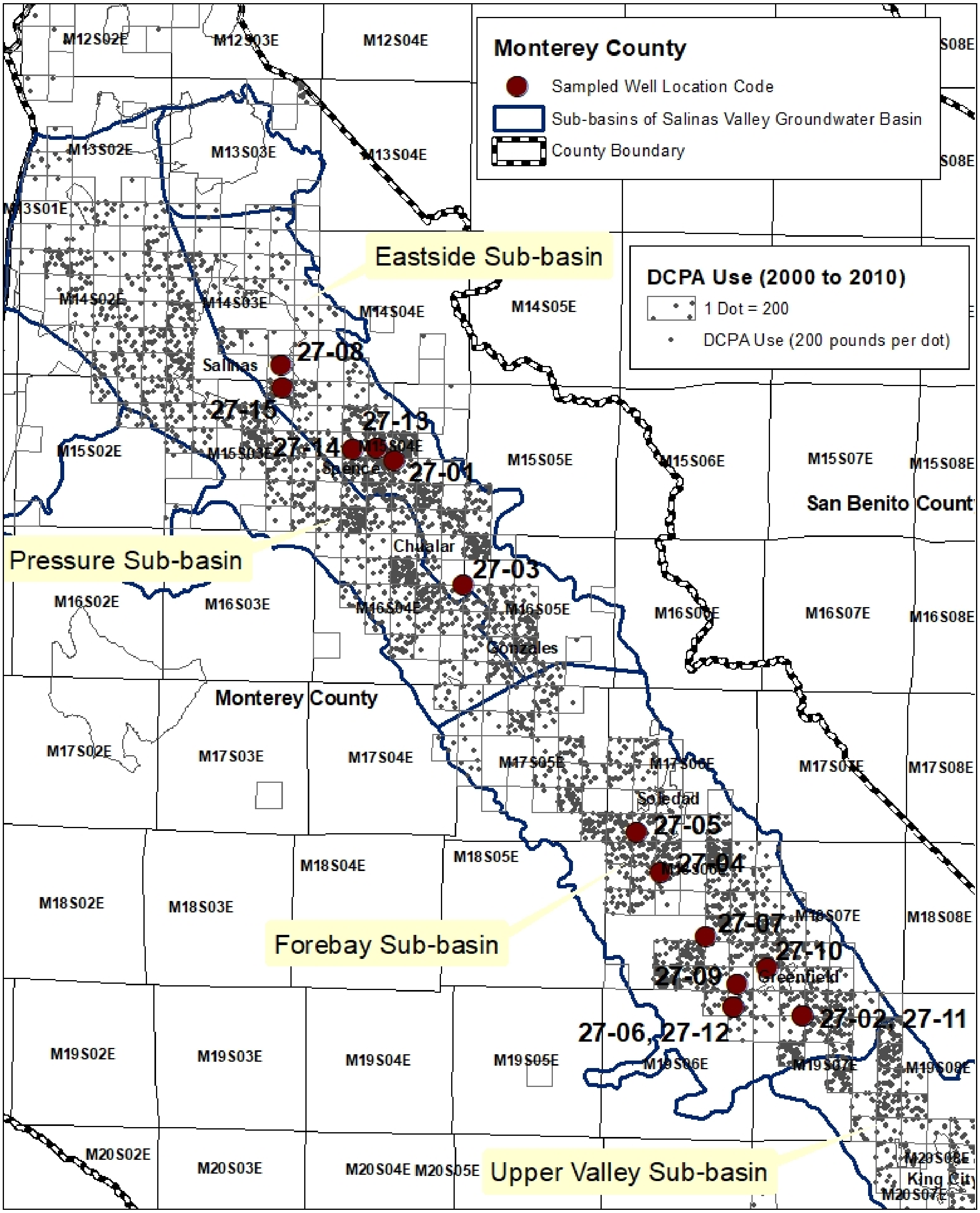

Figure 2. Total DCPA use (pounds per section) from 2000 to 2010 and locations of sampled water wells in the Santa Maria River Valley Groundwater Basin in San Luis Obispo and Santa Barbara counties (CDPR, 2019a; 2019b).

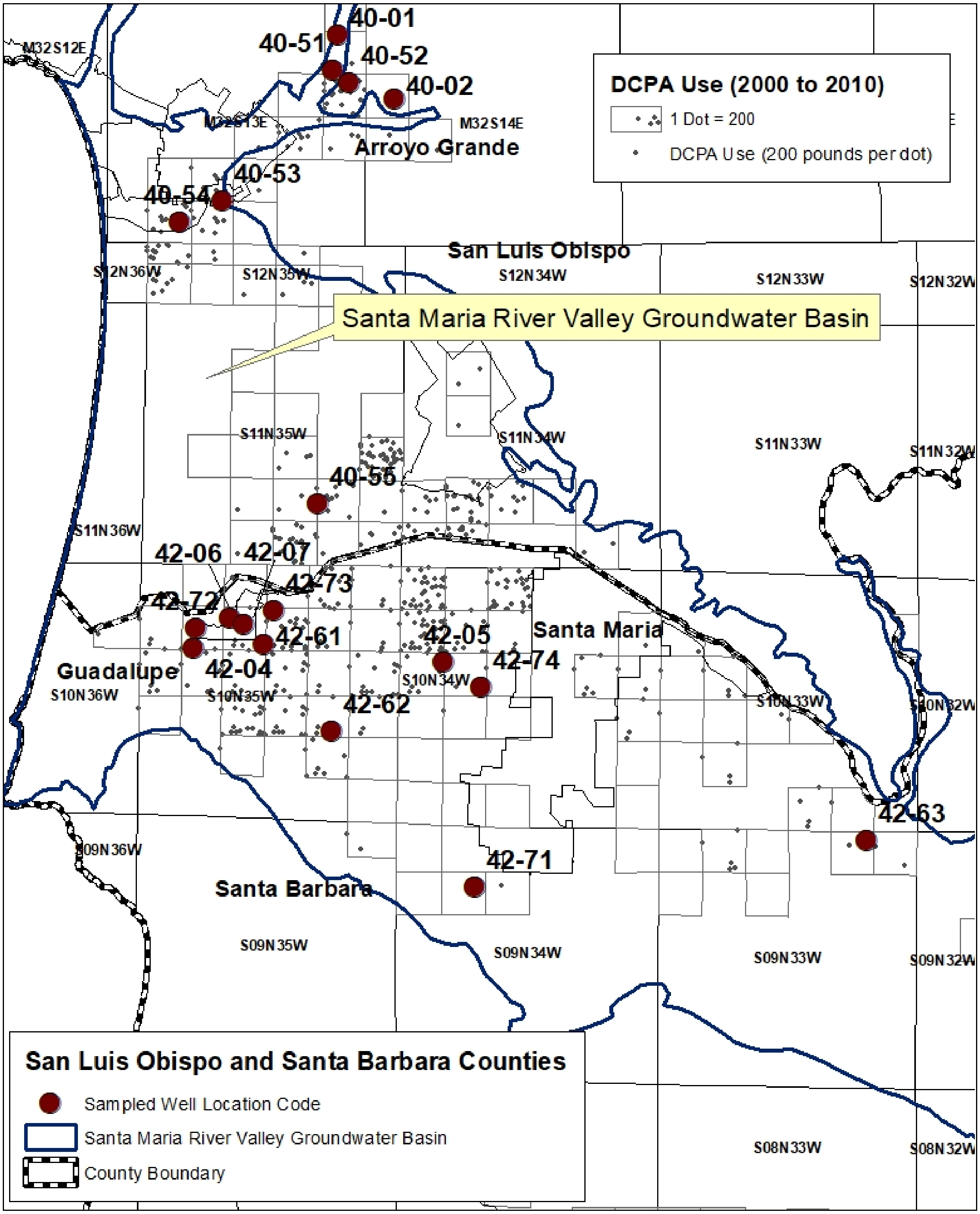

Figure 3. Total DCPA use (pounds per section) from 2000 to 2010 and locations of sampled water wells in the Santa Ynez River Valley Groundwater Basin in Santa Barbara County (CDPR, 2019a; 2019b).

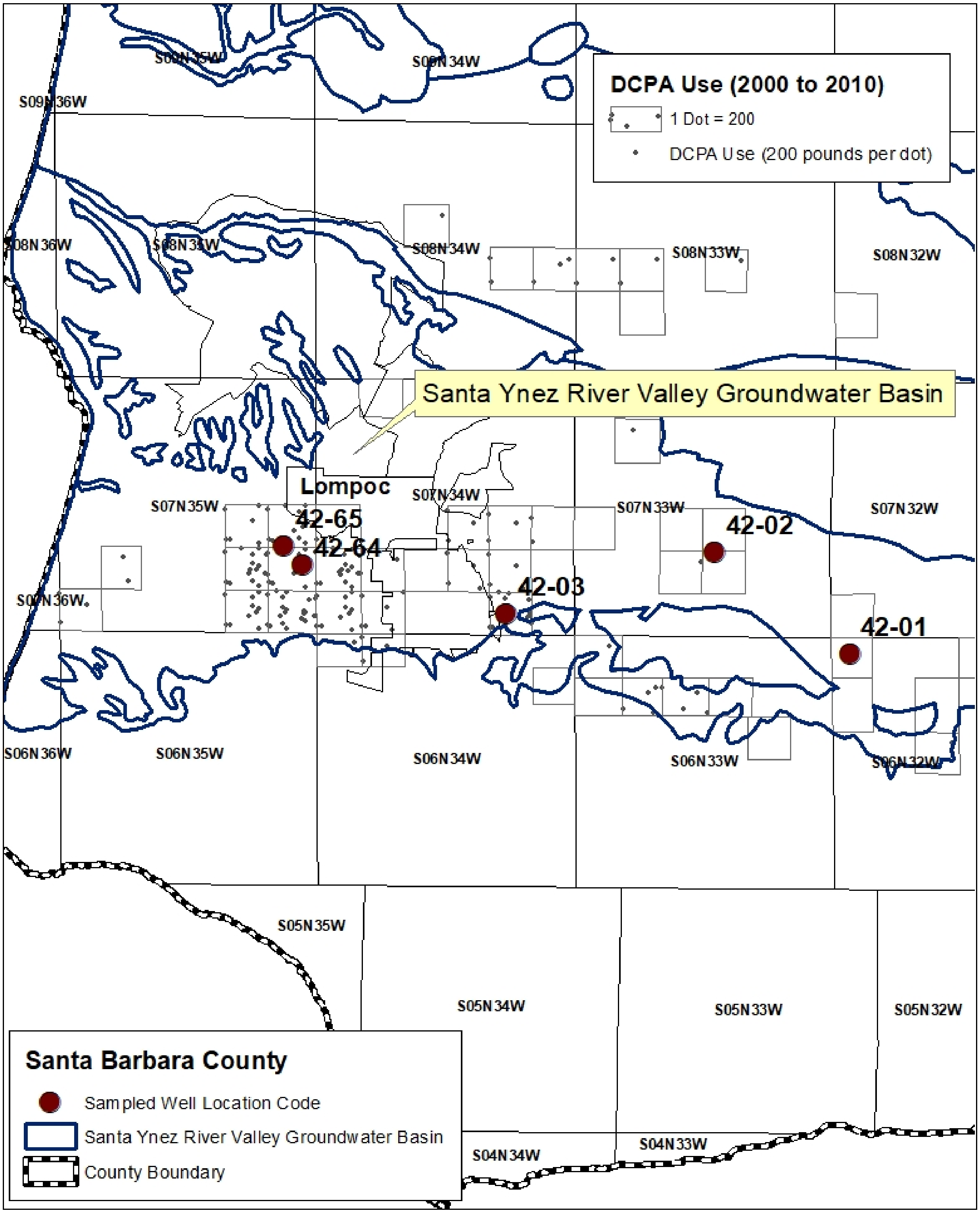

Figure 4. Total DCPA use (pounds per section) from 2000 to 2010 and locations of sampled water wells in the Pleasant Valley Groundwater Basin and Oxnard Aquifer Sub-basin in Ventura County (CDPR, 2019a; 2019b).

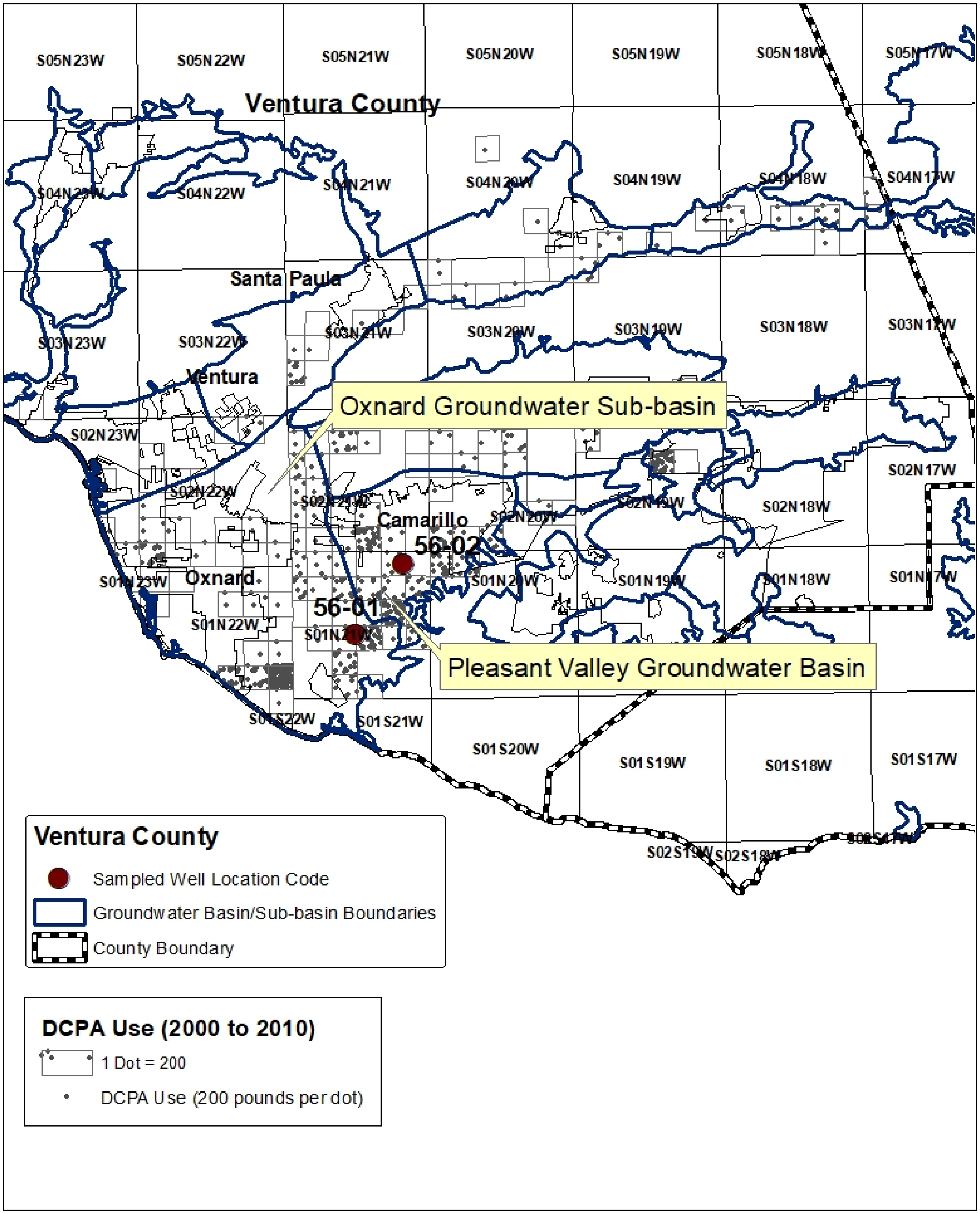

Figure 5. Total DCPA use (pounds per section) from 2000 to 2010 and locations of sampled water wells in the Coachella Valley Groundwater Basin in Riverside County (CDPR, 2019a; 2019b).