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**Study 323: Groundwater Monitoring at a Flood-MAR Pilot Study Site
near Helm, California**

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June 2023

SUMMARY

A flood-managed aquifer recharge (Flood-MAR) experiment was performed by the University of California at Davis with funding from the California Department of Pesticide Regulation (DPR) at the TerraNova Ranch, a large farming operation near Helm, California, during February of 2021. A major experimental objective was to evaluate impacts of on-farm recharge using excess surface applied water on the leaching behavior of agricultural pesticides in the soil root and deep vadose zones underlying the field where the recharge was applied. Prior to the experiment, the Groundwater Protection Program (GWPP) staff sampled wells on the ranch property for analysis of pesticide active ingredients (AIs) listed in regulation on the Groundwater Protection List (Title 3 of the California Code of Regulations, § 6800) and other AIs used in agricultural pesticide products. For this study, 16 irrigation wells were sampled during the summer of 2019 for 68 pesticide AIs and 11 degradation products. All groundwater samples were analyzed by the California Department of Food and Agriculture's Center for Analytical Chemistry. All 16 wells contained at least one detection of an AI or a degradation product at a trace concentration or higher. The detected AIs were azoxystrobin, diuron, hexazinone, and simazine and the detected degradation products were 2,3,5,6-tetrachloroterephthalic acid (TPA), ACET (deethyl-simazine or deisopropyl atrazine), and diaminochlorotriazine (DACT). The concentrations of all detected AIs and degradation products were below their respective health-protective drinking water standards (CDPR, 2022a). Ten of the 16 wells had detections of ACET or DACT at concentrations greater than the GWPP reporting limit of 0.05 parts per billion (ppb). Based on these detections, it is recommended that DPR establish sections M15S17E26, M15S17E27, M15S17E35, M15S17E36, and M16S17E01 as Groundwater Protection Areas (GWPA). A relatively high concentration of linuron (12.1 ppb in the primary sample) was detected in a single well. A careful post-analysis examination of the wellhead discharge system revealed that the original sampling port from which the sample with the high concentration was collected was located on the wrong side of the backflow prevention device. To correct the situation, the farming operation installed a clean port at the proper location between the

backflow prevention device and the well. The well was resampled, and no pesticide AIs or degradation products were detected in the laboratory analysis of the sample. The linuron detection in the original sample was subsequently determined to be due to contamination of the sample at the incorrectly located sampling port rather than the presence of linuron in the underlying groundwater.

Migration of any pesticide residues present in the soil root and deep vadose zones underlying the Flood-MAR experimental site due to on-farm recharge and future irrigation applications to crops on that field will require multiple years to reach the aquifer water table. The GWPP plans to conduct post-experiment resampling of the wells on the ranch in the future to assess the impacts of current and future on-farm recharge and irrigation practices on pesticide concentrations in the underlying groundwater.

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 GWPL is further divided into two parts: § 6800(a) and § 6800(b). 3CCR § 6800(a) includes seven AIs that have been detected in groundwater and subsequently have restricted use. 3CCR § 6800(b) is a list of 98 AIs identified as having the potential to leach to groundwater but have not yet been determined to pollute groundwater. The GWPP conducts routine monitoring in California groundwater basins to determine if these pesticides have migrated to groundwater due to their agricultural use patterns.

DPR provided funding to the University of California at Davis (UCD) to perform a flood-managed aquifer recharge (Flood-MAR) experimental study at the TerraNova Ranch near Helm, California in western Fresno County (Figure 1). The TerraNova Ranch is situated in the western part of the Kings Subbasin of the San Joaquin Valley Groundwater Basin (CDWR, 2006). A major experimental objective was to evaluate the impacts of on-farm recharge using excess surface applied water on the leaching behavior of agricultural pesticides in the soil root and deep vadose zones underlying the field where the recharge was applied. During the summer of 2019 and prior to UCD conducting the actual Flood-MAR experiment, GWPP staff sampled agricultural wells on the ranch property in and around the proposed recharge field site for analysis of numerous pesticide active ingredients (AIs) listed in regulation on the GWPL and other AIs registered in California for use in agricultural pesticide products.

The Flood-MAR experiment was performed by UCD on a 10-acre portion of a 40-acre field during February of 2021. The experimental findings will be documented in a separate report to be issued by UCD at a later date. Study 323 organized and documented the groundwater sampling conducted by GWPP staff during 2019 prior to the Flood-MAR experiment and the results of the subsequent laboratory pesticide analysis. This report summarizes the monitoring results of Study 323 (Ruud, 2019). It includes a brief description of the groundwater sampling

methods; the analytical laboratory methods and associated quality assurance/quality control (QA/QC) standards used to measure the suite of pesticide AIs and degradation products in groundwater samples; and the results of the laboratory analysis of the collected groundwater samples.

METHODS

Sampling Methods

The GWPP and UCD staff conducted sampling at the TerraNova Ranch in two separate sampling events during 2019. Table 1 lists geographic location information, well identification, well type, and sampling dates for the wells sampled in the study. The first event consisted of sampling 16 water wells on the ranch over the two-day period of July 1-2 (Table 1). The selection of the 16 wells was facilitated by TerraNova staff. As described later in more detail, the second event consisted of resampling a single well (location code 10-06) on October 1 that yielded a high detection of linuron when initially sampled on July 2. GWPP staff collected water samples from the wells using methods described in the standard operating procedure (SOP) by Nordmark and Herrig (2011).

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

County	Groundwater Basin, Subbasin	Public Lands Survey System (Meridian/Township/Range/Section)	Location Code ¹	Well Type	Sampling Date(s)
Fresno	San Joaquin Valley, Kings	M15S17E26	10-01	agricultural irrigation	7/1/2019
Fresno	San Joaquin Valley, Kings	M15S17E26	10-02	agricultural irrigation	7/1/2019
Fresno	San Joaquin Valley, Kings	M15S17E36	10-03	agricultural irrigation	7/1/2019
Fresno	San Joaquin Valley, Kings	M15S17E36	10-04	agricultural irrigation	7/1/2019
Fresno	San Joaquin Valley, Kings	M16S17E01	10-05	agricultural irrigation	7/1/2019
Fresno	San Joaquin Valley, Kings	M16S17E01	10-06	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S17E35	10-07	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S17E35	10-08	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S17E35	10-09	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S17E26	10-10	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S17E26	10-11	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S17E27	10-12	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S18E29	10-13	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S18E29	10-14	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S18E29	10-15	agricultural irrigation	7/2/2019
Fresno	San Joaquin Valley, Kings	M15S17E36	10-16	agricultural irrigation	7/2/2019, 10/1/2019

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.

Analytical Methods

The California Department of Food and Agriculture's (CDFA) Center for Analytical Chemistry (CAC) performed chemical analysis of the groundwater samples. CDFA's CAC analyzed samples collected from the wells listed in Table 1 using four analytical methods: 1) GWPP Multi-Analyte Screen (EMON SM 05 032; CDFA, 2013), 2) Triazine Screen (EMON-SM-62.9; CDFA, 2009), 3) DCPA Screen (EMON-SM-05-040; CDFA, 2016), and 4) Surface Water Protection Program (SWPP) Multi-Analyte Screen (EMON-SM-05-037; CDFA, 2017). The chemicals analyzed by the GWPP Multi-Analyte Screen, Triazine Screen, and DCPA Screen are listed in Table 2a, and the chemicals analyzed by the SWPP Multi-Analyte Screen are listed in Table 2b.

The reporting limit for all chemicals tested by the GWPP Multi-Analyte Screen, the Triazine Screen, and the DCPA Screen was 0.05 parts per billion (ppb). The reporting limits of the chemicals tested 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 each 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]). The SOP by Peoples (2019) updated the previous SOP (Segawa, 1995) to reflect this verification requirement and Aggarwal (2012) details DPR's process for evaluating analytical methods to determine if they provide unequivocal identification of a chemical. Although the previous SOP (Segawa, 1995) had not yet been updated at the time Study 323 was conducted, the verification requirement documented in the updated SOP (Peoples, 2019) was nevertheless followed in this study with the unequivocal determinations of the four methods used documented in Aggarwal (2016; 2017; 2019) and Fattah (2008).

The four analytical methods in the laboratory analysis for this study each include agricultural pesticide AIs that have been historically used in the western Fresno County region where Study 323 was conducted. Chlorthal-dimethyl (DCPA) is a pre-emergent herbicide that was entered into the Pesticide Detection Response Process in 2018 due to detections of its degradation product TPA in groundwater throughout California since the late 1980s (Ruud, 2017). It was then formally reviewed by the Pesticide Registration Evaluation Committee (PREC) subcommittee per the mandates of the PCPA. The PREC subcommittee determined that DCPA had not polluted the groundwaters of the state and allowed for its continued use without further regulation (Sanders, 2018). During the formal review, the Office of Environmental Health Hazard Assessment (OEHHA) set a health-protective drinking water level of 2,500 ppb for DCPA, MTP, and TPA (OEHHA, 2018). DPR is required by FAC § 13152(a)(1) to continue groundwater monitoring for DCPA, MTP, and TPA in areas of the state where DCPA is used (Sanders, 2018). The DCPA Screen was therefore included in this study given historical use of DCPA in townships M15S17E and M16S17E where portions of the TerraNova Ranch are situated (Ruud, 2017).

The GWPP Multi-Analyte Screen analyzes for 44 pesticide AIs, including six of the seven restricted-use AIs listed in regulation in § 6800(b) of the GWPL and 29 AIs in § 6800(b) of the GWPL: AIs with the potential to leach to groundwater (Table 2a). The Triazine Screen also analyzes for six of the seven restricted-use AIs in § 6800(a) of the GWPL; 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 § 6800[b] of the GWPL) (Table 2a). The SWPP Multi-Analyte Screen analyzes for 29 AIs, including eight AIs in § 6800(b) of the GWPL (Table 2b).

Table 2a. Pesticide AIs and degradation products analyzed by the GWPP Multi-Analyte Screen, the Triazine Screen, and the DCPA Screen. 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)	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***	
Dimethenamid	Prometon*	Methyl parathion	Norflurazon*	
Dimethoate	Simazine*	Phorate	Prometon*	
Diuron*	Tebuthiuron*	Piperonyl butoxide	Simazine*	
Ethofumesate	Thiamethoxam	Prometryn	Tebuthiuron*	
Fenamiphos	Thiobencarb	Propanil		
Fludioxonil	Uniconazole	Triallate		
Imidacloprid				

*Analytes in both the GWPP Multi-Analyte and Triazine screens.

**Ethoprophos and metolachlor are in both the GWPP Multi-Analyte and SWPP Multi-Analyte screens.

***Hexazinone is in both the Triazine and SWPP Multi-Analyte screens.

¹Mefenoxam and metalaxyl are stereoisomers. The analytical method cannot differentiate the two analytes.

²ACET: deethyl-simazine or deisopropyl-atrazine; degradate of atrazine and simazine.

³DACT: diaminochlorotriazine; degradate of simazine.

⁴DEA: deethyl-atrazine; degradate of atrazine.

⁵DSMN: desmethyl-norflurazon; degradate of norflurazon.

Table 2b. Pesticide AIs and degradation products analyzed by the SWPP Multi-Analyte Screen.

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 ^{1,3}	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
Quinoxifen	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

¹AIs in § 6800(b) of the Groundwater Protection List: AIs with the potential to leach to groundwater.

²Ethoprophos and metolachlor are in both the GWPP Multi-Analyte and SWPP Multi-Analyte screens.

³Hexazinone is in both the Triazine and SWPP Multi-Analyte screens.

Quality Assurance and Quality Control

CDFA’s CAC analyzed quality control 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 Nevada 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. Additionally, the EM QA Officer 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 and were analyzed to confirm the validity of detections when deemed necessary (Richardson, 2011).

RESULTS AND DISCUSSION

Sample Analysis

Laboratory-measured concentrations of the analytes analyzed by the GWPP Multi-Analyte, Triazine, SWPP Multi-Analyte, and DCPA screens are presented in Tables 3 through 6, respectively. Analytes which were not detected (i.e., non-detections) in any of the samples were not included in Tables 3 through 6.

Detections of GWPL § 6800(a) AIs and Degradation Products

Diuron and simazine were the only restricted-use AIs from § 6800(a) of the GWPL detected in the sampled wells. Trace concentrations of diuron were detected in three wells (location codes 10-06, 10-08, and 10-09) by the GWPP Multi-Analyte Screen (Table 3) and the Triazine Screen (Table 4). Both methods also detected a trace concentration of simazine in a single well with location code 10-09 (Tables 3 and 4). ACET and DACT were the only degradation products of AIs from § 6800(a) of the GWPL detected in the sampled wells. ACET concentrations ranged from a trace to 0.33 ppb in 10 of the 16 wells sampled on July 1 or 2, and DACT concentrations ranged from a trace to 0.347 ppb in 13 of the 16 wells (Table 4).

At present, none of the sections containing the sampled wells with detections of diuron, simazine, ACET, or DACT are designated as Groundwater Protection Areas (GWPAs) (3CCR § 6487.3-6487.5). Under the Pesticide Detection Response Process, to establish new GWPAs in sections not adjacent to current GWPAs, two or more wells within a four-section area (within a single section, two diagonally touching sections, or two adjacent sections) must have 6800(a) or degradate detections above DPR's reporting limit of 0.05 ppb (Ross et al., 2011). It is recommended that DPR establish sections M15S17E26, M15S17E27, M15S17E35, M15S17E36, and M16S17E01 as GWPAs based on detections of ACET or DACT above the 0.05 ppb reporting limit in wells located in those sections (Table 4).

Table 3. GWPP Multi-Analyte Screen sample analysis results.

Sample Number	Sample Code ¹	Public Lands Survey System (Meridian/Township/Range/Section)	Location Code	Sample Date	Azoxystrobin (ppb)	Diuron (ppb)	Linuron (ppb)	Simazine (ppb)
407	P3	M15S17E26	10-01	7/1/2019	ND	ND	ND	ND
428	P3	M15S17E26	10-02	7/1/2019	ND	ND	ND	ND
358	P3	M15S17E36	10-03	7/1/2019	ND	ND	ND	ND
414	P3	M15S17E36	10-04	7/1/2019	ND	ND	ND	ND
337	P3	M16S17E01	10-05	7/1/2019	ND	ND	ND	ND
421	P3	M16S17E01	10-06	7/2/2019	Trace	Trace	12.1	ND
423	BU	M16S17E01	10-06	7/2/2019	0.528	Trace	11.0	ND
424	FB3	M16S17E01	10-06	7/2/2019	ND	ND	ND	ND
309	P3	M15S17E35	10-07	7/2/2019	ND	ND	ND	ND
379	P3	M15S17E35	10-08	7/2/2019	ND	Trace	ND	ND
382	FB3	M15S17E35	10-08	7/2/2019	ND	ND	ND	ND
344	P3	M15S17E35	10-09	7/2/2019	ND	Trace	ND	Trace
347	FB3	M15S17E35	10-09	7/2/2019	ND	ND	ND	ND
351	P3	M15S17E26	10-10	7/2/2019	ND	ND	ND	ND
365	P3	M15S17E26	10-11	7/2/2019	ND	ND	ND	ND
316	P3	M15S17E27	10-12	7/2/2019	ND	ND	ND	ND
302	P3	M15S18E29	10-13	7/2/2019	ND	ND	ND	ND
330	P3	M15S18E29	10-14	7/2/2019	ND	ND	ND	ND
393	P3	M15S18E29	10-15	7/2/2019	ND	ND	ND	ND
400	P3	M15S17E36	10-16	7/2/2019	ND	ND	ND	ND
501	P2	M16S17E01	10-06	10/1/2019	ND	ND	ND	ND

¹P = 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

Detections of GWPL § 6800(b) AIs

Azoxystrobin, hexazinone, and linuron were the only AIs from § 6800(b) of the GWPL detected in the sampled wells. Linuron was detected in a single well (location code 10-06) with concentrations of 12.1 ppb (primary sample) and 11.0 ppb (backup sample) from sampling performed on July 2 (Table 3). Given this relatively high concentration, the wellhead discharge system (e.g., locations of sampling ports, backflow prevention devices, chemical injection lines, etc.) of the sampled well was carefully reexamined to determine whether the detection was due to contamination of the sample at the wellhead or due to the actual presence of linuron in the underlying groundwater. After assessment of the discharge system and follow-up discussions with the ranch manager, it was determined that the port used for collecting the groundwater sample was located on the wrong side of the backflow prevention device. To correct the situation, the farming operation installed a clean port at the proper location between the backflow prevention device and the well. The well was then resampled by GWPP staff on October 1 and no detections of linuron, other AIs, or degradation products were

measured from the laboratory analysis of the sample. The detection of linuron in the original sample collected on July 2 was subsequently determined to be due to contamination from the incorrectly located sampling port rather than from the presence of linuron in the underlying groundwater.

A trace concentration (primary sample) and a concentration of 0.528 ppb (backup sample) of azoxystrobin were also detected in the well with location code 10-06 that was sampled on July 2 (Table 3). No azoxystrobin was detected when the well was resampled on October 1. Given the relatively low concentrations of azoxystrobin detected in the primary and backup samples collected on July 2, it is not possible to determine whether these detections were also due to contamination of the sample at the sampling port (as with linuron) or whether azoxystrobin was actually present in the underlying groundwater but not detected in the resampled well on October 1 by the GWPP Multi-Analyte Screen (i.e., below the method detection limit). It is worth noting that azoxystrobin was not detected in any of the other 15 wells sampled in this study (Table 1).

Hexazinone in the samples was analyzed by both the Triazine Screen and the SWPP Multi-Analyte Screen and the combined results from the two screens are presented in Table 5. Overall, hexazinone was detected in six wells by the Triazine Screen and in nine wells by the SWPP Multi-Analyte Screen. The highest quantified concentration of hexazinone from either method was 0.078 ppb. From the Triazine Screen analysis, five of the six hexazinone detections were trace concentrations. From the SWPP Multi-Analyte Screen analysis, five of the nine hexazinone detections were trace concentrations. Since the SWPP Multi-Analyte Screen had a reporting limit of 0.02 ppb for hexazinone in comparison to the reporting limit of 0.05 ppb for the Triazine Screen, it is reasonable to expect more detections of hexazinone from the analysis of the samples by the SWPP Multi-Analyte Screen. In general, the ranges of measured hexazinone concentrations between the two screens were similar (Table 5). In 2011, groundwater detections from agricultural use of hexazinone were entered into the Pesticide Detection Response Process and formally reviewed by the PREC subcommittee per the mandates of the PCPA. The PREC subcommittee determined that hexazinone had not polluted the groundwaters of the state and OEHHA set a health-protective drinking water level of 170 ppb for hexazinone (Reardon, 2011). The concentrations detected in this study were below the health-protective drinking water level.

Table 4. Triazine Screen sample analysis results.

Sample Number	Sample Code ¹	Public Lands Survey System (Meridian/Township/Range/Section)	Location Code	Sample Date	ACET (ppb)	DACT (ppb)	Diuron (ppb)	Hexazinone (ppb)	Simazine (ppb)
406	P2	M15S17E26	10-01	7/1/2019	Trace	0.050	ND	ND	ND
427	P2	M15S17E26	10-02	7/1/2019	0.106	0.077	ND	Trace	ND
432	FB1,2,4	M15S17E26	10-02	7/1/2019	ND	ND	ND	ND	ND
357	P2	M15S17E36	10-03	7/1/2019	Trace	Trace	ND	ND	ND
362	FB1,2,4	M15S17E36	10-03	7/1/2019	ND	ND	ND	ND	ND
413	P2	M15S17E36	10-04	7/1/2019	Trace	Trace	ND	0.074	ND
418	FB1,2,4	M15S17E36	10-04	7/1/2019	ND	ND	ND	ND	ND
336	P2	M16S17E01	10-05	7/1/2019	ND	0.055	ND	ND	ND
341	FB1,2,4	M16S17E01	10-05	7/1/2019	ND	ND	ND	ND	ND
420	P2	M16S17E01	10-06	7/2/2019	ND	ND	Trace	ND	ND
425	FB1,2,4	M16S17E01	10-06	7/2/2019	ND	ND	ND	ND	ND
308	P2	M15S17E35	10-07	7/2/2019	0.196	0.114	ND	ND	ND
313	FB1,2,4	M15S17E35	10-07	7/2/2019	ND	ND	ND	ND	ND
378	P2	M15S17E35	10-08	7/2/2019	0.080	0.083	Trace	Trace	ND
383	FB1,2,4	M15S17E35	10-08	7/2/2019	ND	ND	ND	ND	ND
343	P2	M15S17E35	10-09	7/2/2019	0.127	0.115	Trace	Trace	Trace
348	FB1,2,4	M15S17E35	10-09	7/2/2019	ND	ND	ND	ND	ND
350	P2	M15S17E26	10-10	7/2/2019	0.071	0.071	ND	ND	ND
355	FB1,2,4	M15S17E26	10-10	7/2/2019	ND	ND	ND	ND	ND
364	P2	M15S17E26	10-11	7/2/2019	ND	ND	ND	ND	ND
315	P2	M15S17E27	10-12	7/2/2019	0.330	0.347	ND	ND	ND
320	FB1,2,4	M15S17E27	10-12	7/2/2019	ND	ND	ND	ND	ND
301	P2	M15S18E29	10-13	7/2/2019	ND	ND	ND	Trace	ND
306	FB1,2,4	M15S18E29	10-13	7/2/2019	ND	ND	ND	ND	ND
329	P2	M15S18E29	10-14	7/2/2019	ND	0.054	ND	ND	ND
334	FB1,2,4	M15S18E29	10-14	7/2/2019	ND	ND	ND	ND	ND
392	P2	M15S18E29	10-15	7/2/2019	ND	Trace	ND	ND	ND
397	FB1,2,4	M15S18E29	10-15	7/2/2019	ND	ND	ND	ND	ND
399	P2	M15S17E36	10-16	7/2/2019	0.196	0.090	ND	Trace	ND
404	FB1,2,4	M15S17E36	10-16	7/2/2019	ND	ND	ND	ND	ND
500	P1	M16S17E01	10-06	10/1/2019	ND	ND	ND	ND	ND

¹P = 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

Table 5. Measured hexazinone concentrations in samples by the SWPP Multi-Analyte Screen and the Triazine Screen.

Sample Number	Sample Code ¹	Public Lands Survey System (Meridian/Township/Range/Section)	Location Code	Sample Date	SWPP Multi-Analyte Screen Hexazinone ² (ppb)	Triazine Screen Hexazinone ³ (ppb)
408	P4	M15S17E26	10-01	7/1/2019	ND	ND
429	P4	M15S17E26	10-02	7/1/2019	Trace	Trace
359	P4	M15S17E36	10-03	7/1/2019	Trace	ND
415	P4	M15S17E36	10-04	7/1/2019	0.078	0.074
338	P4	M16S17E01	10-05	7/1/2019	ND	ND
422	P4	M16S17E01	10-06	7/2/2019	ND	ND
310	P4	M15S17E35	10-07	7/2/2019	0.038	ND
380	P4	M15S17E35	10-08	7/2/2019	Trace	Trace
345	P4	M15S17E35	10-09	7/2/2019	0.021	Trace
352	P4	M15S17E26	10-10	7/2/2019	Trace	ND
366	P4	M15S17E26	10-11	7/2/2019	ND	ND
317	P4	M15S17E27	10-12	7/2/2019	Trace	ND
303	P4	M15S18E29	10-13	7/2/2019	ND	Trace
331	P4	M15S18E29	10-14	7/2/2019	ND	ND
394	P4	M15S18E29	10-15	7/2/2019	ND	ND
401	P4	M15S17E36	10-16	7/2/2019	0.072	Trace

¹P = primary sample, FB = field blank sample

²SWPP Multi-Analyte Screen reporting limit for hexazinone is 0.02 ppb

³Triazine Screen reporting limit for hexazinone is 0.05 ppb

ND = not detected below the method detection limit

Trace = positive result between the method detection limit and the reporting limit

Detections of Non-GWPL AIs and Degradation Products

No non-GWPL AIs or degradation products on the SWPP Multi-Analyte Screen were detected in any of the sampled wells. From the DCPA screen, TPA was detected in two wells (location codes 10-10 and 10-11) at concentrations of 1.07 and 0.434 ppb (Table 6). One other well (location code 10-01) contained a trace concentration of TPA (Table 6). As noted earlier, agricultural use of DCPA was formally reviewed in 2018 and a health-protective drinking water level of 2,500 ppb was set by OEHHA for MTP and TPA (OEHHA, 2018). The detected concentrations of TPA in this study were below the health-protective drinking water level.

Table 6. DCPA Screen sample analysis results.

Sample Number	Sample Code ¹	Public Lands Survey System (Meridian/Township/Range/Section)	Location Code	Sample Date	TPA (ppb)
405	P1	M15S17E26	10-01	7/1/2019	Trace
411	FB1,2,4	M15S17E26	10-01	7/1/2019	ND
426	P1	M15S17E26	10-02	7/1/2019	ND
356	P1	M15S17E36	10-03	7/1/2019	ND
412	P1	M15S17E36	10-04	7/1/2019	ND
335	P1	M16S17E01	10-05	7/1/2019	ND
419	P1	M16S17E01	10-06	7/2/2019	ND
307	P1	M15S17E35	10-07	7/2/2019	ND
377	P1	M15S17E35	10-08	7/2/2019	ND
342	P1	M15S17E35	10-09	7/2/2019	ND
349	P1	M15S17E26	10-10	7/2/2019	1.07
355	FB1,2,4	M15S17E26	10-10	7/2/2019	ND
363	P1	M15S17E26	10-11	7/2/2019	0.434
369	FB1,2,4	M15S17E26	10-11	7/2/2019	ND
314	P1	M15S17E27	10-12	7/2/2019	ND
300	P1	M15S18E29	10-13	7/2/2019	ND
328	P1	M15S18E29	10-14	7/2/2019	ND
391	P1	M15S18E29	10-15	7/2/2019	ND
398	P1	M15S17E36	10-16	7/2/2019	ND

¹P = 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

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 GWPP Multi-Analyte Screen, Triazine Screen, SWPP Multi-Analyte Screen, and DCPA 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). Two 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 67.5 to 108%. One recovery of azoxystrobin (67.5%) was slightly below its respective lower control limit. The other 28 analytes were within their respective control limits. Two 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 matrix spikes. The recoveries ranged from 69.8 to 129% with all analyte recoveries within their respective control limits.

Triazine Screen QC Samples

Ten QC matrix-spikes, five pairs of duplicates, were analyzed along with five sets of samples for the Triazine Screen. All analytes were spiked at 0.2 ppb and the recoveries for the 12 analytes ranged from 66.5 to 100.5%. One recovery of ACET (68%), one recovery of prometon (73.5%), and two recoveries of DEA (66.5 and 74%) were below their respective lower control limits. To save resources, the sets were not reanalyzed. The propazine surrogate recovery was within the control limits in the QC matrix-spikes, as well as in every sample analyzed for this screen.

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 using LCMS. One matrix spike was analyzed along with one set of samples using LCMS for the SWPP Multi-Analyte Screen. All 29 analytes were spiked at 0.2 ppb in the QC matrix-spikes. The recoveries ranged from 83.2 to 113%. One recovery of diflufenzuron (113%) and one recovery of ethoprophos (100%) were above their respective upper control limits. The other 27 analytes were within their respective control limits.

DCPA Screen QC Samples

Two matrix spikes with DCPA, MTP, and TPA were analyzed along with two sets of samples with the DCPA Screen. DCPA, MTP, and TPA were all spiked at 0.2 ppb and the recoveries of the three analytes ranged from 54.5 to 105%. One recovery of DCPA (54.5%) and one recovery of MTP (72.5%) were below their respective lower control limits while one recovery of DCPA (86.5%) was just above its upper control limit.

Blind Spikes

A blind spike is a matrix-blank sample spiked by a chemist different than the chemist extracting and analyzing that screen. One blind spike for the DCPA Screen was submitted for the July 1-2 sampling event. The recoveries of DCPA (64%), MTP (90%), and TPA (92%) were all within their respective control limits. One blind spike for linuron was also submitted when the well with location code 10-06 was resampled on October 1. The recovery of linuron (118%) from the blind spike analysis was just above the upper control limit.

CONCLUSIONS

For this study, 16 irrigation wells were sampled during the summer of 2019 for 68 pesticide AIs and 11 degradation products. All 16 wells contained at least one detection of an AI or a degradation product at a trace concentration or higher. The detected AIs were azoxystrobin, diuron, hexazinone, and simazine and the detected degradation products were TPA, ACET, and DACT. The concentrations of all detected AIs and degradation products were well below their respective health-protective drinking water standards (CDPR, 2022a). In particular, 10 of the 16 wells had detections of ACET or DACT at concentrations greater than the GWPP reporting limit

of 0.05 ppb. Based on these detections, it is recommended that DPR establish sections M15S17E26, M15S17E27, M15S17E35, M15S17E36, and M16S17E01 as GWPAs.

A relatively high detection of linuron (12.1 ppb in the primary sample) was detected in a single well. Careful examination of the wellhead discharge system revealed that the original sampling port was located on the wrong side of the backflow prevention device. A clean port was then installed at the correct location between the backflow prevention device and the well by the farming operation. The well was resampled and no detections of linuron, other AIs, or degradation products were detected in the sample. Linuron in the original sample was subsequently determined to be due to contamination of the sample at the incorrectly located sampling port rather than the presence of linuron in the underlying groundwater.

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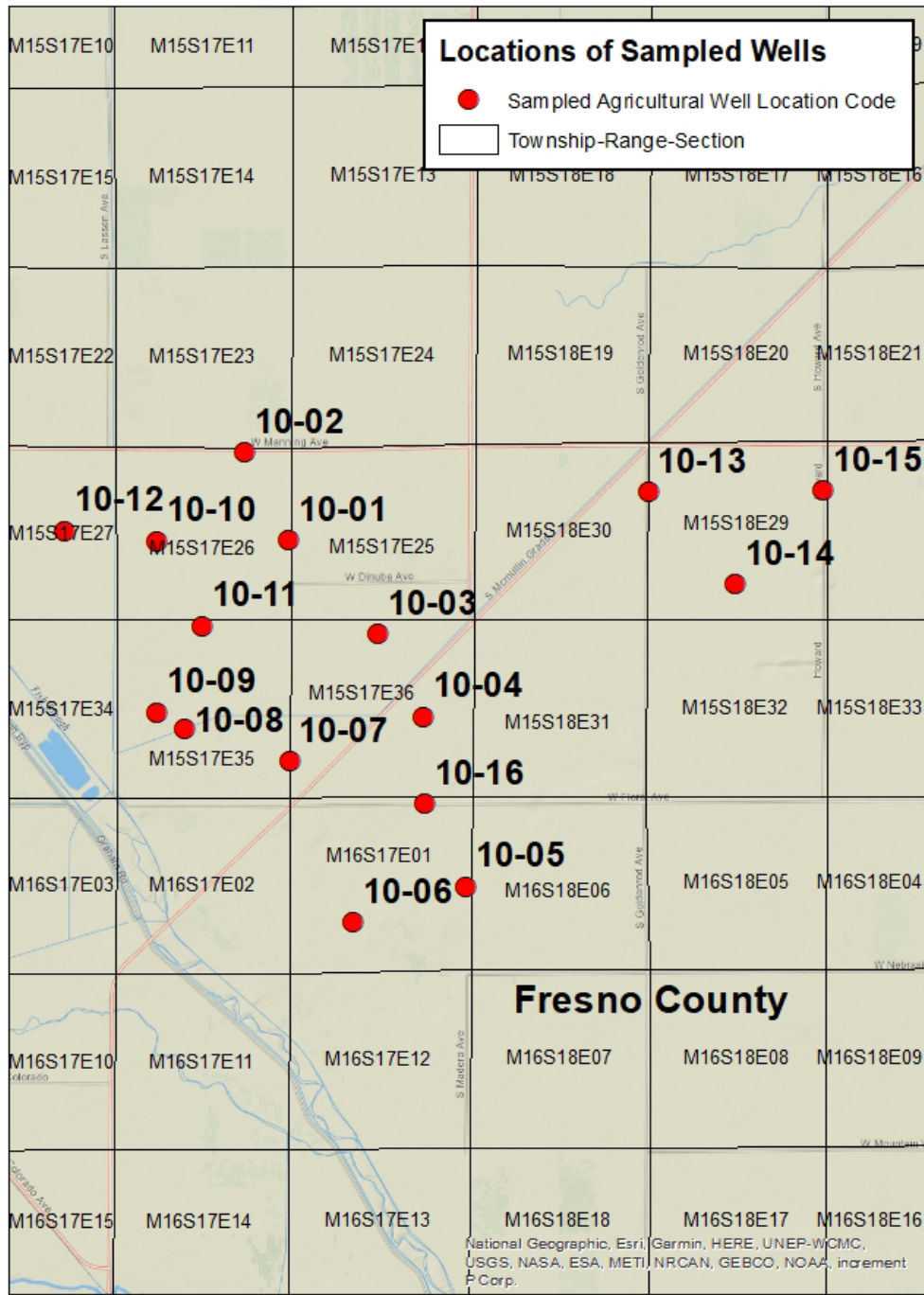


Figure 1. Locations of agricultural wells sampled on the TerraNova Ranch (CDPR, 2022b).