

Department of Pesticide Regulation
Environmental Monitoring Branch
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January 2020

**STUDY 328: PROTOCOL FOR FOLLOW-UP GROUNDWATER MONITORING OF
FLUDIOXONIL**

I. INTRODUCTION

The Pesticide Contamination Prevention Act (PCPA) of 1985 (amended 1996, 2014) requires the Department of Pesticide Regulation (DPR) to identify pesticides or degradates with the potential to pollute groundwater and monitor for those pesticides to determine if they have migrated to groundwater. The PCPA outlines procedures for gathering physical and chemical data on pesticides to identify pesticides or degradates that have the potential to contaminate groundwater and placing those on the Groundwater Protection List (GWPL) (Title 3 California Code of Regulations § 6800[b]). The PCPA requires the Department of Pesticide Regulation (DPR) to monitor for GWPL pesticides to determine if they have migrated to groundwater.

Fludioxonil, a 6800(b) GWPL pesticide with the potential to pollute groundwater (**Table 1**), was detected in a domestic well in Fresno County (section 10M15S22E05) near the city of Del Rey (about 0.2 miles directly south of the city limits), as part of the Groundwater Protection Program's Well Network long-term groundwater monitoring study (1999 - present) in Fresno and Tulare counties (Garretson, 2019). In this well, fludioxonil has been detected at increasing concentrations for the past three consecutive years. The well was installed in 2014 as a replacement for a well on the same property, and the previous well on the property tested negative for fludioxonil in 2014 (the only year it had been sampled for fludioxonil). Fludioxonil has not been detected in any other well tested in the state. Groundwater flow in the area is generally northeast to southwest.

Fludioxonil is a non-systemic fungicide used during crop production (can be applied directly to the soil or with aerial/ground based equipment) and used for postharvest disease control. There has been no reported use of fludioxonil to the Pesticide Use Reporting system (PUR) in the section containing the detection, and 63 lbs. total use (2014-2019, no use before 2014) in the surrounding eight sections. In a surrounding two-row section radius (25 total sections), there has been 109 total lbs. of fludioxonil used (2013-2019, no use before 2013) (CDPR, 2019).

There are fruit processing and packing facilities within the city of Del Rey and Fresno County that have recorded use of fludioxonil (County of Fresno, 2018). The well with the detection of fludioxonil is located approximately 0.5 miles southwest from the packing facilities. Postharvest uses of fludioxonil are not reported to the PUR on a section basis; postharvest uses are reported to the PUR as a monthly, countywide, non-section-based total with no identifying information. From 2000 to 2009, yearly use in Fresno County (a sum of the countywide, non-section based total) ranged from 225 - 772 lbs. of fludioxonil (average of 225 lbs. /year). From 2010 to 2019, yearly use in Fresno County ranged from 791 – 2,435 lbs. of fludioxonil (average of 1,244 lbs. /year). Postharvest use reports acquired from Fresno County indicate that fludioxonil is being applied by licensed pest control applicators that report use by company not location, and thus location-based determination of fludioxonil use from these reports is limited.

Detections in the well of interest are listed in **Table 2**. A time series plot of the detections at the well of interest are shown in **Figure 1**.

Table 1. Specific numerical values (SNVs) for mobility and persistence compared to values for fludioxonil.

	Mobility Properties			Persistence Properties			
	Water Solubility [mg/L]	Soil Adsorption Coefficient, K_{oc} [cm ³ /g]		Hydrolysis Half-life [days]	Soil Metabolism Half-life [days]		
		K_{foc} (1/n)	K_{doc}		Aerobic	Anaerobic	
SNVs¹	> 3	Not Included in SNVs		< 1,900	> 14	> 610	> 9
Fludioxonil	1.83	8.64 (0.77) – 29.8 (0.79)		N/A	> 30	102	> 365

Table 2. Detections of fludioxonil in a single well in section 10M15S22E05.

Conc. [ppb]	Reporting Limit	Sampling Date	County	Chemical	Sampling Agency	Analytical Lab
0	0.05	2015-05-11	Fresno	fludioxonil	CDPR	CDFFA Sacramento Lab
Trace	0.05	2016-04-27	Fresno	fludioxonil	CDPR	CDFFA Sacramento Lab
0.066	0.05	2017-05-02	Fresno	fludioxonil	CDPR	CDFFA Sacramento Lab
0.165	0.05	2018-05-14	Fresno	fludioxonil	CDPR	CDFFA Sacramento Lab
0.38	0.05	2019-04-23	Fresno	fludioxonil	CDPR	CDFFA Sacramento Lab

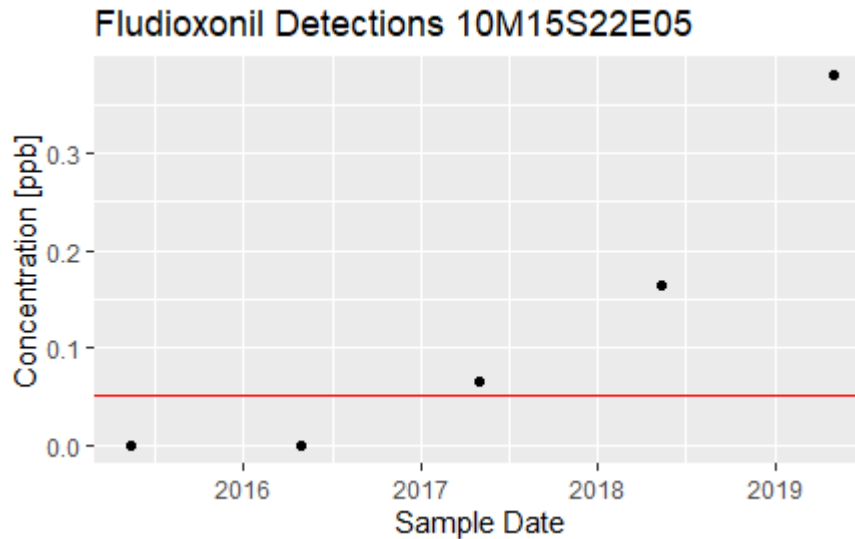


Figure 1. Fludioxonil detections in well of interest in section 10M15S22E05.

II. OBJECTIVES

Investigate groundwater wells surrounding the well in section 10M15S22E05 with the positive fludioxonil detection in order to characterize the extent and potential source of fludioxonil contamination in the nearby area. Samples will also be analyzed for additional pesticides with the potential to contaminate groundwater in California.

III. PERSONNEL

Well sampling for this study will be conducted by the Environmental Monitoring Branch of the Department of Pesticide Regulation (DPR) under the general supervision of Carissa Ganapathy. Project personnel will include:

Project Leader:	Tiffany Kocis
Field Coordinator:	Kevin Richardson
Laboratory Liaison:	Sue Peoples
Analytical Chemistry:	Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Please direct questions regarding this study to Tiffany Kocis at (916) 324-4273 or by e-mail at tiffany.kocis@cdpr.ca.gov.

IV. STUDY PLAN

Monitoring will be focused on sampling approximately 10 wells based on availability within a two-mile radius of section 10M15S22E05. The area of interest may be expanded to a three-mile or more radius if there are not a sufficient number of wells within the two-mile radius, with preference given to include wells that lie to the southwest or northeast of the well of interest (general direction of groundwater flow in the area). Trace detections (values between method detection limit and reporting limit of 0.05 parts per billion [ppb]) will be reported with an estimated concentration.

A map of wells previously sampled for fludioxonil around the area of Del Rey, CA, including each of the year(s) sampled, is shown in **APPENDIX 1** (available upon request at GWPP@cdpr.ca.gov).

V. SAMPLING AND ANALYTICAL METHODS

Wells will be chosen in the designated areas following procedures described in Standard Operating Procedure (SOP) FSWA001.02 (Nordmark and Herrig, 2011). Domestic wells will be prioritized for sample collection because they are usually shallower than municipal and irrigation wells and they are usually accessible year round. However, due to the limited area of interest, deeper wells, municipal wells, and agricultural wells may be sampled. During sample collection, all efforts will be taken to bypass pressure tanks, hoses, and filters to sample water directly from the aquifer as outlined in the SOP (Nordmark and Herrig, 2011).

Chemical analysis will be performed by the CDFA Center for Analytical Chemistry. CDFA will analyze samples for fludioxonil as part of the multi-analyte groundwater method EMON-SM-05-032 (CDFA, 2013) (**Table 3**). This multi-analyte method also includes 37 other analytes with the potential to contaminate groundwater. CDFA will also analyze for the triazine group of pesticides using method EMON-SM-62.9 (CDFA, 2009) (**Table 4**). The reporting limit for all analytes is 0.05 ppb. DPR has described the criteria for determining whether an analytical method is unequivocal (Aggarwal, 2012) and has determined that the two analytical methods used for this study provide unequivocal identification of the chemicals (Fattah, 2008; Aggarwal, 2016). SOP QAQC001.01 (Peoples, 2019) guidelines will be followed for analytical laboratory quality control and for collecting quality assurance samples in the field.

Table 3. Pesticide active ingredients in the multi-analyte groundwater screen CDFA Lab method.

MULTI-ANALYTE EMON-SM-05-032	
Atrazine	Malathion
Azoxystrobin	Mefenoxam/Metalaxyl
Bensulide	Methiocarb
Bromacil	Metolachlor
Carbaryl	Metribuzin
Carbofuran	Napropamide
Clomazone	Norflurazon
Diazinon	Oryzalin
Dichloran	Phorate
Dichlorbenil	Piperonyl Butoxide
Dimethenamide	Prometon
Dimethoate	Prometryn
Diuron	Propanil
Ethofumesate	Simazine
Ethoprophos	Tebuthiuron
Fenamiphos	Thiamethoxam
Fludioxonil	Thiobencarb
Imidacloprid	Triallate
Linuron	Uniconizole

Table 4. Pesticide active ingredients and degradates in the triazine groundwater screen CDFA Lab method.

TRIAZINE SCREEN EMON-SM-62.9
ACET
Atrazine
Bromacil
DACT
DEA
Diuron
DMN
Hexazinone
Norflurazon
Prometon
Simazine
Tebuthiuron

VI. DATA ANALYSIS

Data obtained from the CDFA laboratory will be used to determine if pesticides are migrating to groundwater. These data will also be used to generate a study report detailing the analysis findings. Detections of pesticides may trigger additional well sampling (domestic, agricultural

and/or monitoring wells), expansion of Ground Water Protection Areas, or formal review of a detected pesticide as outlined in Food and Agricultural Code sections 13149-13151. Analytical results will be provided to participating property owners for their respective wells within 16 to 20 weeks of sampling.

VII. TIMETABLE

February 2020: Conduct sampling.
April - July 2020: Obtain and review analytical results from CDFA laboratory.
August 2020: Complete study report or expand the study as needed based on analytical results and provide analytical results to property owners.

Communication

- Provide notice to the County Agricultural Commissioner, DPR Enforcement Branch Regional Office, and the local Farm Bureau two weeks prior to initiating monitoring in a county. Additional notice will be provided if there is a six-month lapse in monitoring within a county.
- Provide results to property owners within 30 days of receipt.
- Provide results to state and local agencies when sampling is concluded and results have been reviewed and approved by the project team.

IX. REFERENCES

- Aggarwal, V. 2012. Memorandum to Lisa Ross dated July 10, 2012. "Evaluating analytical methods for compliance with the Pesticide Contamination Prevention Act requirements." California Department of Pesticide Regulation, Sacramento, California.
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Fattah, W. 2008. Memorandum to Randy Segawa dated August 21, 2008. "Determination if the California Department of Food and Agriculture, Center for Analytical Chemistry's liquid chromatography-atmospheric pressure chemical ionization mass spectrometry method for atrazine, bromacil, cyanazine, diuron, hexazinone, metribuzin, norflurazon, prometon, prometryn, simazine, deethyl atrazine, deisopropyl atrazine, diamino chlorotriazine, des-methyl norflurazon in well water and river water (method EM-62.9), meets the 'unequivocal detection' criteria." California Department of Pesticide Regulation, Sacramento, California.

Garretson, C. 2019. "Monitoring the Concentrations of Detected Pesticides in Wells Located in Highly Sensitive Areas (Well Network Sampling). Annual Update 2018." California Department of Pesticide Regulation, Sacramento, California.

Nordmark, C. and J. Herrig. 2011. SOP FSWA001.02. "Obtaining and Preserving Well Water Samples." California Department of Pesticide Regulation, Sacramento, California.

Peoples, C. 2019. SOP QAQC001.01. "Chemistry Laboratory Quality Control." California Department of Pesticide Regulation, Sacramento, California.