Department of Pesticide Regulation
Environmental Monitoring Branch
Groundwater Protection Program
1001 I Street, P.O. Box 4015
Sacramento, California 95812

Study GW13a: Updated Protocol for Additional Groundwater Protection List Monitoring for Penoxsulam

Rick Bergin
Senior Environmental Scientist
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I. INTRODUCTION

The Department of Pesticide Regulation (DPR) previously monitored groundwater for rice herbicides in the Sacramento Valley resulting in detections of penoxsulam residues in domestic wells (Bergin, 2013). These detections, 12 out of 165 wells sampled, occurred in rice fields adjacent to nut orchards (reporting limit of 0.05 ppb). Penoxsulam is mainly applied to rice; however, it does have uses on other crops such as almonds, pistachios, and walnuts. Because of multiple crop use patterns, the source of penoxsulam detected in groundwater was obscured and additional monitoring is required. Follow-up sampling was delayed due to limitations in laboratory staffing, contract funding, method development, and the COVID-19 pandemic. This study will re-establish monitoring of penoxsulam, evaluate the source of penoxsulam in groundwater, and determine the potential circumstances of penoxsulam's migration to groundwater. This study will investigate penoxsulam use outside of the rice-growing regions of the Sacramento Valley to determine if penoxsulam has migrated to groundwater due to legal agricultural use in those areas.

II. STUDY OBJECTIVES

- Investigate areas of penoxsulam use that are outside of rice-growing regions in the Sacramento Valley to determine if penoxsulam has migrated to groundwater as a result of legal agricultural use.

- Resample wells with penoxsulam detections, or adjacent wells, to determine if previous detections are transitory and/or a product of well location.

- Analyze samples for pesticides previously found in California's groundwater and for pesticides that have the potential to migrate to groundwater but have not been detected.

III. PERSONNEL

Staff from DPR's Environmental Monitoring Branch, Groundwater Protection Program (GWPP) will conduct the well sampling for this study under the general direction of Environmental Program Manager, Joy Dias. Project Personnel will include:

Project Leader:	Rick Bergin
Field Coordinator:	Craig Nordmark
Lab Liaison:	Vaneet Aggarwal
Staff Chemists:	California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry

Please direct questions regarding this study to Rick Bergin at 916-883-0940 or by e-mail at Rick.Bergin@cdpr.ca.gov.

IV. STUDY PLAN

Groundwater monitoring will primarily focus on areas outside of the rice-growing region of the Sacramento Valley. Penoxsulam in the targeted areas is mainly applied to almonds, pistachios, walnuts, and rice growing outside the Sacramento Valley. The GWPP will prioritize sections with high penoxsulam use, shallow groundwater depths, and Ground Water Protection Area designations. In addition, follow-up sampling of previous penoxsulam detections in Sutter County will also be conducted. The following is a non-exhaustive list of the selected areas; reported use is cumulative from 2005 to 2019 (CDPR, 2021):

1. Arbuckle: This area is west of Highway 5, between Hahn Road and the Colusa/Yolo County line. There is no adjacent rice use. Penoxsulam is predominately used on almonds; several sections have penoxsulam use ranging from 10 to 20 pounds (lbs).

2. Escalon: This area consists of fifteen sections of penoxsulam use on rice at 20 to 40 lbs per section. These sections comprise one of the few rice-growing areas outside of the Sacramento Valley or Sacramento-San Joaquin River Delta. The targeted sections are located between Mariposa Road and Valley Home Road.

3. Orland/Hamilton City: This area consists of a dozen sections with use on almonds and walnuts at 20-50 lbs per section. Rice use begins several miles to the southeast towards the Sacramento River.

4. Stockton/Linden: In this area, the dominate use of penoxsulam is on walnuts. Penoxsulam use in these sections total around 3-12 lbs per section.

5. Madera County: There are two main areas with penoxsulam use on almonds and pistachios varying between 20 and 45 lbs per section—2 miles north of Mendota and 3 miles east of Madera City.

6. Sutter County: This area is around the towns of Rio Oso, East Nicolaus, and Pleasant Grove. GWPP will resample wells with penoxsulam detections or adjacent wells if the original wells are not available.

7. Merced City/Chowchilla: This area consists of over a dozen sections with penoxsulam use on almonds that is greater than 25 lbs. These sections are located directly east of Highway 99 between Merced City and Chowchilla.

V. SAMPLING AND ANALYTICAL METHODS

Wells will be selected in the designated areas following procedures described in SOP FSWA001.03 (Kocis, 2020). Domestic wells will be prioritized for sampling because they are typically accessible year round and tend to be shallower than irrigation or municipal wells. During collection of groundwater samples, all efforts will be taken to bypass pressure tanks, hoses, and filters to sample water directly from the aquifer as outlined in FSWA001.03 (Kocis, 2020).

Chemical analysis will be performed by CDFA's Center for Analytical Chemistry. CDFA will analyze well samples using the Rice Herbicide Screen analytical method EMON-SM-05-044 (CDFA, 2020b), the Triazine Screen analytical method EMON-SM-62.9 (CDFA, 2020a), and the Multi-Analyte Screen analytical method EMON-SM-05-032 (CDFA, 2021). The reporting limits for each of the analytes are listed below (Tables 1-4). SOP QAQC001.01 (Peoples, 2019) guidelines will be followed for analytical laboratory quality control and for collecting quality assurance samples in the field. DPR has determined that the analytical methods used for this study provide unequivocal identification of the chemicals (Aggarwal, 2020a; Aggarwal, 2020b; Aggarwal, 2021).

Table 1. Rice Herbicide Screen method detection limits (MDL) and reporting limits (RL) in ppb.

Analyte	MDL	RL
Bensulfuron-methyl	0.02215	0.05
Bispyribac sodium	0.02330	0.05
Clomazone	0.02161	0.05
Halosulfuron methyl	0.02506	0.05
MCPA	0.02325	0.05
Molinate	0.02540	0.05
Orthosulfamuron	0.01805	0.05
Penoxsulam	0.02081	0.05
Propanil	0.02327	0.05
Propiconazole	0.02403	0.05
Thiobencarb	0.03308	0.05
Triclopyr	0.02639	0.05

Table 2. Triazine Screen method detection limits (MDL) and reporting limits (RL) in ppb.

Analyte	MDL	RL
Deisopropyl-atrazine or Deethyl-simazine (ACET)	0.00580	0.03
Atrazine	0.00316	0.02
Bromacil	0.00241	0.02
Diaminochlorotriazine (DACT)	0.00235	0.05
Deethyl-atrazine (DEA)	0.00226	0.02
Diuron	0.00241	0.02
Desmethyl-norflurazon (DSMN)	0.00181	0.01
Hexazinone	0.00197	0.01
Metribuzin	0.00238	0.05
Norflurazon	0.00252	0.02
Prometon	0.00240	0.02
Prometryn	0.00265	0.05
Simazine	0.00286	0.02
Tebuthiuron	0.00236	0.05

Table 3. Multi-Analyte Screen (LCMS) method detection limits (MDL) and reporting limits (RL) in ppb.

Analyte	MDL	RL
Alachlor	0.00920	0.03
Atrazine	0.00286	0.02
Azinphos-methyl	0.01440	0.05
Azoxystrobin	0.00584	0.02
Bensulide	0.00571	0.02
Bromacil	0.00393	0.02
Carbaryl	0.00323	0.02
Carbofuran	0.00393	0.02
Chlorantraniliprole	0.00345	0.02
Cyprodinil	0.00427	0.02
Diazinon	0.01050	0.03
Dimethenamide	0.00490	0.02
Dimethoate	0.00330	0.02
Diuron	0.00484	0.02
Ethofumesate	0.00845	0.03
Fenamiphos	0.01070	0.03
Fludioxonil	0.00892	0.03
Flutriafol	0.00298	0.02
Imidacloprid	0.00323	0.02
Isoxaben	0.00493	0.02
Linuron	0.00697	0.02
Mefenoxam/metalaxyl	0.00295	0.02
Methiocarb	0.00710	0.02
Metolachlor	0.01660	0.02
Methomyl	0.00301	0.02
Methoxyfenozide	0.00628	0.03
Metribuzin	0.00414	0.02
Napropamide	0.00462	0.02
Norflurazon	0.00550	0.02
Oryzalin	0.01140	0.05
Prometon	0.00245	0.02
Propiconazole	0.00424	0.02
Pyraclostrobin	0.00210	0.02
Simazine	0.00279	0.02
Tebuthiuron	0.00524	0.02
Thiamethoxam	0.00386	0.02
Thiobencarb	0.00245	0.02
Uniconazole	0.01370	0.05

Table 4. Multi-Analyte Screen (GCMS) method detection limits (MDL) and reporting limits (RL) in ppb.

Analyte	MDL	RL
Clomazone	0.00799	0.05
Dichloran	0.01103	0.05
Dichlobenil	0.00678	0.03
Disulfoton	0.01040	0.05
Ethoprophos	0.00506	0.03
Fonofos	0.00616	0.03
Malathion	0.00691	0.03
Parathion ethyl	0.00646	0.03
Parathion methyl	0.00655	0.03
Phorate	0.00521	0.03
Piperonyl butoxide	0.00785	0.03
Prometryn	0.00738	0.03
Propanil	0.00836	0.05
Triallate	0.00638	0.03

VI. DATA ANALYSIS

Data obtained from samples analyzed by CDFA will be used by GWPP to determine if pesticides are migrating to groundwater. These data will also be used to generate a study report detailing the results. Detections in the targeted and surrounding areas will be used to assess regional vulnerability to groundwater contamination. These results may trigger additional sampling, lead to expansion of Ground Water Protection Areas, or formal review of a detected pesticide as outlined in Food and Agricultural Code sections 13149-13151. Results from this study will be published to the Well Inventory Database during the annual update

VII. TIMETABLE

October 2021 – January 2022:	Conduct sampling
January 2022 – May 2022:	Obtain and review analytical results from CDFA laboratory
December 2022:	Complete study report

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 from the laboratory.
- Provide a summary of results to state and local agencies when sampling is concluded and results have been reviewed and approved by DPR.

IX. REFERENCES

Contact GWPP@cdpr.ca.gov for references not currently available on the web.

Aggarwal, V. 2020a. The Qualification of Method EM 62.9 as Unequivocal According to Criteria in the Pesticide Contamination Prevention Act. Available at: https://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/method_em_62.9_unequivical_memo.pdf (verified September 3, 2021). California Department of Pesticide Regulation, Sacramento, California.

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CDPR. 2021. Pesticide Use Reports. Available at: http://www.cdpr.ca.gov/docs/pur/purmain.htm (verified September 3, 2021). California Department of Pesticide Regulation, Sacramento, California.

Kocis, T. 2020. SOP FSWA001.03. Obtaining and Preserving Well Water Samples. Available at: https://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa00103.pdf (verified September 3, 2021). California Department of Pesticide Regulation, Sacramento, California.

Peoples, C. 2019. SOP QAQC001.01. Chemistry Laboratory Quality Control. Available at: https://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc00101.pdf (verified September 3, 2021). California Department of Pesticide Regulation, Sacramento, California.