

**Department of Pesticide Regulation
Environmental Monitoring Branch
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May 2018

**STUDY GW18: PROTOCOL FOR GROUNDWATER PROTECTION LIST
MONITORING FOR 2,4-DICHLOROPHENOXYACETIC ACID HERBICIDE**

I. INTRODUCTION

In the United States, 2,4-Dichlorophenoxyacetic acid (2,4-D) is registered as a selective herbicide for control of broadleaf weeds and also as a plant growth-regulator. There are many forms or derivatives of 2,4-D including esters, amines, and salts. 2,4-D is used in agricultural crops, in pasture and rangelands, forest management practices, home and garden applications, and for aquatic vegetation control (Pohanish, 2015). The herbicide acts as plant growth hormone (auxin), which results in uncontrolled cell growth and eventually leads to death in susceptible plants (University of Georgia Center, 2001).

2,4-D has been marketed since the early 1940s and it is one of the most widely available herbicides in the world. It is now produced by many chemical companies since the patent on it has long expired. The active ingredient (ai) can be found in numerous commercial agriculture products. As of January 2017, there were 1,500 actively registered 2,4-D products in California labelled under a variety of trade names (CDPR, 2017a). From 1996 to 2016 over 8.6 million pounds of 2,4-D ai were used in the state (CDPR, 2017a).

Section 13148 of the California Food and Agricultural Code directs the Department of Pesticide Regulation (DPR) to conduct groundwater monitoring for pesticides that have been designated as having the potential to pollute groundwater. These pesticides are identified on DPR's Groundwater Protection List (GWPL) in section 6800(b) of Title 3, California Code of Regulations. DPR annually samples for several pesticides listed on the GWPL in areas of high use to determine if they have migrated to groundwater as a result of their legal agricultural use. Because of its low binding affinity in soil containing low organic matter, 2,4-D is expected to be moderately to highly mobile in sediment and mineral soils. As it may have the capability to leach down the soil profile if not degraded, it can potentially contaminate groundwater (Jarvais et al., 2008) and is identified as having the potential to pollute groundwater.

DPR maintains a Well Inventory Database (WIDB) that also includes data from multiple agencies that test well water for pesticide residues in California. The WIDB contains over 28,000 samples from 8,953 wells that were tested for 2,4-D in the last 30 years. Out of those 8,953 wells, 19 wells had reported detections. These reported detections were either not confirmed by subsequent testing by the reporting agencies or were not confirmed by additional sampling conducted by DPR. Since 1987, DPR has conducted eleven field studies for 2,4-D in response to

reported detections from other agencies and was unable to confirm the detections in any of the original wells or to detect 2,4-D in surrounding wells (Weaver, 1989; Weaver 1990a; Weaver 1990b; Weaver 1990c; Weaver 1992; Weaver 1993a; Weaver 1993b, Weaver 1993c; Weaver 1993d; Weaver 1995; Weaver 1999). DPR has only verified the detection of 2,4-D in one well but none of the four wells surrounding this detection had any 2,4-D residues. This detection was determined to be an isolated detection from an unknown source (CDPR 2016).

II. OBJECTIVE

The purpose of this study is to determine whether 2,4-D has migrated to groundwater in areas of California with moderate to high reported agricultural use or in areas identified to be vulnerable to groundwater contamination. Collected samples will also be analyzed for additional pesticides known to, or with the potential to, contaminate groundwater.

III. PERSONNEL

Well sampling will be conducted by the Environmental Monitoring Branch of DPR under the general supervision of Senior Environmental Scientist Joy Dias. Project personnel will include:

Project Leader: Alfredo DaSilva
Field Coordinator: Craig Nordmark
Laboratory Liaison: Sue Peoples
Analytical Chemistry: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Please direct questions regarding this study to Alfredo DaSilva at (559) 297-5404 or adasilva@cdpr.ca.gov.

IV. STUDY PLAN

This study will be conducted statewide (Figure 1) but targeting counties with high use areas to determine if current legal agricultural uses are resulting in contamination of groundwater. Eight counties have been chosen as the highest use: Butte, Fresno, Imperial, Kings, Merced, San Joaquin, Solano, and Stanislaus. Approximately 56% of statewide applications of 2,4-D occur in those eight counties. Within these counties, sections will be compared and prioritized based on the following factors:

- 1) 2,4-D use levels within the section
- 2) 2,4-D use levels within the surrounding sections
- 3) Average depth-to-water within the section based on historical levels
- 4) Previous reported detections of any pesticides in wells within or surrounding the section
- 5) Availability of wells to sample based on existing records in the Well Inventory Database

ACTIVE INGREDIENT SELECTION

2,4-D will be the primary focus of this study. In order to help assess the effectiveness of our mitigation measures and to determine if regions regulated as Ground Water Protection Areas need to be expanded, DPR routinely analyzes samples for known groundwater contaminants such as atrazine, simazine, and some of their degradates (3CCR section 6800[a]) using the Triazine screen (Table 1). All wells sampled in this study will be screened for these known contaminants.

Samples also collected in this study will be analyzed using the new DPR / CDFA multi-analyte screen which consists of 34 analytes on the GWPL (3CCR section 6800[a] and [b]). Of these 34 active ingredients, 7 overlap with the Triazine screen (Table 1). DPR will use this overlap as quality control if there are positive detections of these pesticides.

V. SAMPLING AND ANALYTICAL METHODS

A total of 61 samples will be collected in accordance with 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. All efforts will be taken to collect sample water directly from the aquifer as outlined in the SOP.

Chemical analysis will be performed by the CDFA Center for Analytical Chemistry. CDFA will analyze samples for 2,4-D (EMON-SM-05-012) (CDFA, 2008). They will also analyze for the triazine group of pesticides using method EMON-SM-62.9 (CDFA, 2009) and the multi-analyte group using method EMON-SM-05-032 (CDFA, 2016).

SOP QAQC001.00 (Segawa, 1995) guidelines will be followed for analytical laboratory quality control and for collecting quality assurance samples in the field. The reporting limit for all analytes is 0.05 parts per billion (ppb).

VI. DATA ANALYSIS

The analytical results obtained from CDFA will be used to determine if 2,4-D is migrating to groundwater under current use patterns. Detections of GWPL pesticides may trigger additional focused sampling in the study regions or may lead to expansion of Ground Water Protection Areas. These data will also be used to generate a study memorandum detailing the analysis findings. Analytical results will be provided to participating property owners for their respective wells within 12 to 16 weeks of sampling.

VII. TIMETABLE

- June 2018 – November 2018: Well sampling
- October 2018 – December 2018: Reception and review of laboratory results

- July 2019 – 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.
 - Provide results to state and local agencies when sampling is concluded and results have been reviewed and approved by the project team.

VIII. REFERENCES

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IX. TABLES

Table 1. Pesticide Active Ingredient Screen CDFA Lab Methods (Shading indicates overlapping analytes)

MULTI-RESIDUE EMON-SM-05-032	TRIAZINE SCREEN EMON-SM-62.9
Atrazine	ACET
Azoxystrobin	Atrazine
Bensulide	Bromacil
Bromacil	Cyanazine
Carbaryl	DACT
Clomazone	DEA
Diazinon	Diuron
Dichloran	Hexazinone
Dichlorbenil	Metribuzin
Dimethenamide	Norflurazon
Dimethoate	Prometon
Diuron	Prometryn
Ethofumesate	Simazine
Ethoprophos	Tebuthiuron
Fludioxonil	
Imidacloprid	
Linuron	
Malathion	
Mefenoxam/Metalaxyl	
Methiocarb	
Metolachlor	
Metribuzin	
Napropamide	
Norflurazon	
Oryzalin	
Phorate	
Prometon	
Prometryn	
Propanil	
Simazine	
Tebuthiuron	
Thiamethoxam	
Thiobencarb	
Triallate	

X. FIGURES

Figure 1. Statewide Use of 2,4-D per Year (CDPR, 2017)

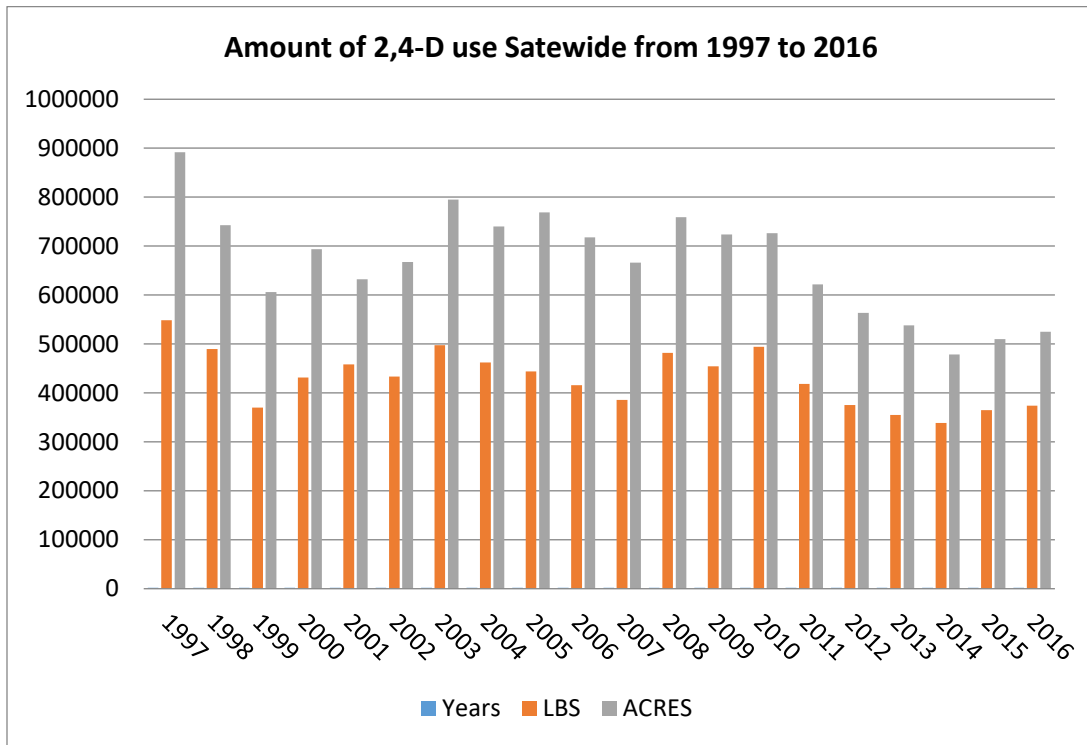


Figure 2. 2,4-D Use Statewide (CDPR, 2017)

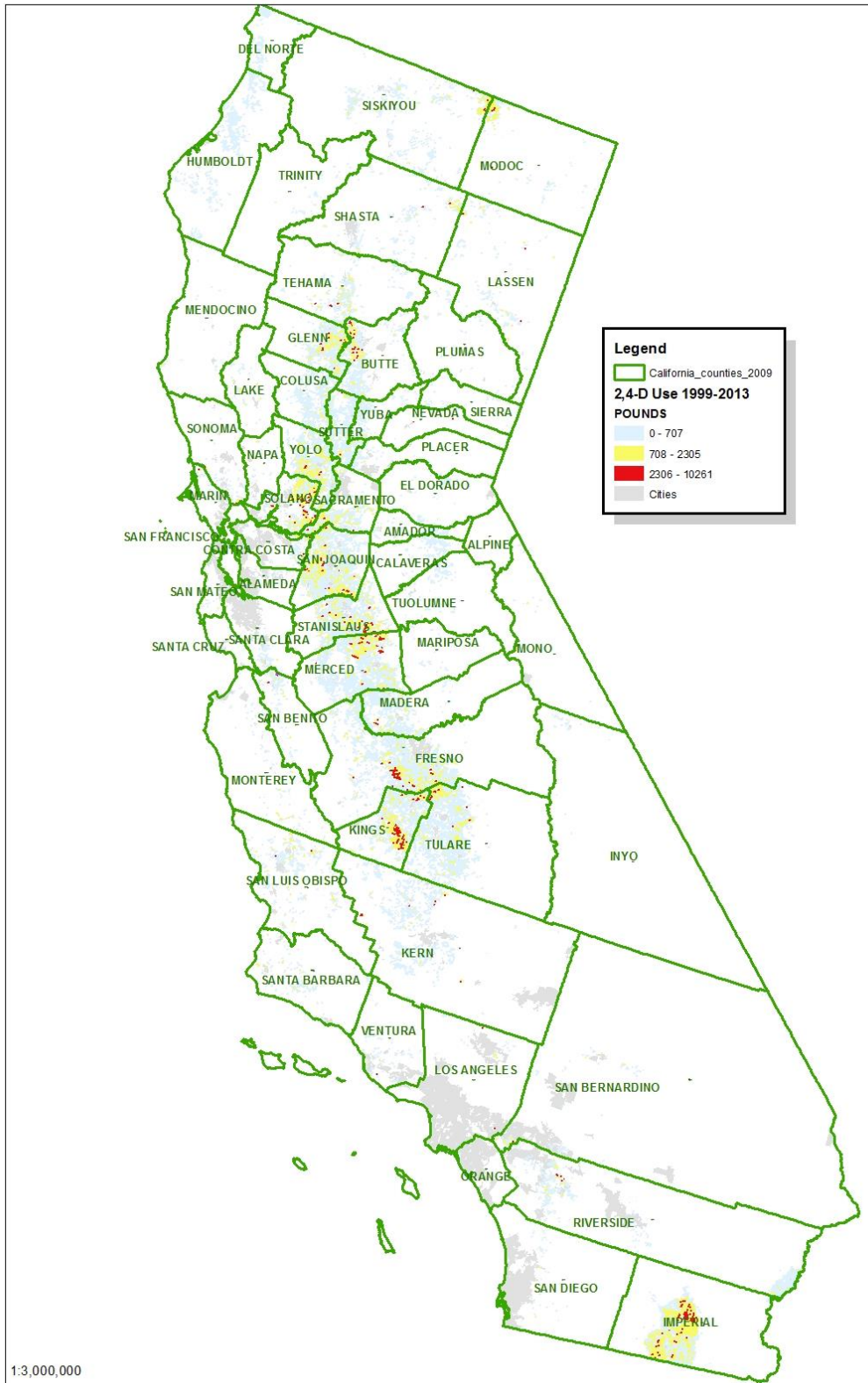


Figure 3. Amount of 2,4-D Applied in 8 Major Counties (CDPR, 2017)

