Department of Pesticide Regulation
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STUDY 228: PROTOCOL FOR MONITORING THE CONCENTRATION OF DETECTED PESTICIDES IN WELLS LOCATED IN HIGHLY SENSITIVE AREAS (WELL NETWORK STUDY)

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I. INTRODUCTION

In 1999, the Department of Pesticide Regulation (DPR) initiated the Well Network Study to monitor for potential changes in groundwater concentrations of pesticides resulting from new regulatory management practices designed to minimize pesticide movement to groundwater (Garretson, 1999). A network of 75 domestic groundwater wells in Fresno and Tulare counties were established through volunteer resident participation by selecting previously sampled wells that had detectable residues of simazine, bromacil, or diuron. The number of wells in the Well Network can fluctuate from year-to-year due to changes in property ownership or wells going dry. All wells in the Well Network were sampled for triazine pesticides at least annually through 2020 (Davalos, 2021). A statistical analysis of data collected from 2000–2012 is reported in Troiano et al. (2013), along with a complete description of this study and characterization of the conditions of the vulnerable areas, pesticide use, and the required mitigation measures.

The Well Network is located in areas susceptible to pesticide movement to groundwater within Fresno and Tulare counties. Wells within this network are located in Ground Water Protection Areas (GWPAs), which are areas vulnerable to groundwater contamination from the agricultural use of pesticides (Troiano et al., 2013). There are two types of GWPAs: leaching and runoff. Leaching GWPAs are areas where pesticides are more likely to leach from the soil surface to groundwater, generally areas with coarse soils and relatively rapid infiltration rates. Runoff GWPAs are areas where pesticides are more likely to be carried in runoff water into direct routes to groundwater (e.g., dry wells, soil cracks, coarse soils). Runoff GWPAs are usually located in areas where the soils are comprised of hardpan layers and/or have low infiltration rates.

Due to the vulnerability of the study area, the Well Network has also served as a resource to sample for additional pesticides that have the potential to contaminate groundwater. In 2018, samples were analyzed for Dacthal (DCPA) and its degradates in addition to the routine Well Network analysis (Triazine and/or Multi-Analyte Screens) (Garretson, 2019). This practice has been incorporated into the current 2021 study year, which will result in

samples from all 59 wells being analyzed with the Triazine Screen (Table 1) and Glyphosate Screen (Table 2). In addition, samples from 10 wells will be analyzed with the Multi-Analyte Screen (Table 3) based on prior positive well samples from this analysis.

In future study years, DPR plans to increase the Well Network from the current 59 wells to approximately 70 total wells. Samples from these wells may be analyzed for additional analytes or screens depending on DPR's Groundwater Protection Program (GWPP) objectives.

II. OBJECTIVES

The objectives of this study are to monitor for potential changes in groundwater concentrations of pesticides in areas vulnerable to groundwater contamination and to evaluate the success of regulatory management practices. This study will also allow for the exploration of additional pesticides that could potentially contaminate groundwater.

III. PERSONNEL

Well sampling for this study will be conducted by staff from DPR's Environmental Monitoring Branch, Groundwater Protection Program under the direction of the Groundwater Protection Program's Supervisor, Carissa Ganapathy.

Project personnel will include:

Project Leaders:	Jennifer Davalos, Alfredo DaSilva
QA/QC Officer:	Vaneet Aggarwal, Ph.D.
Senior Scientist:	Tiffany Kocis
Analytical Chemistry:	Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

Please direct questions regarding this study to Jennifer Davalos at (916) 324-4111 or by email at jennifer.davalos@cdpr.ca.gov.

IV. STUDY PLAN

For the 2021 study, approximately 59 wells located in Tulare and Fresno counties will be analyzed with the Triazine Screen and Glyphosate Screen. Approximately 10 wells will be analyzed with the Multi-Analyte Screen based on previous detections from this screen within the past five years of sampling. Well sampling will be conducted from May through June of 2021, following the procedures of SOP FSWA001.03 (Kocis, 2020).

DPR will sample the Well Network annually on an on-going basis. In future study years, DPR plans to increase the Well Network from the current 59 wells to approximately 70 total wells. Samples from these wells may include additional analytes or screens depending on DPR's Groundwater Protection Program (GWPP) objectives.

May - June 2021:	Conduct sampling of wells in the Well Network.
August 2021:	Obtain and review analytical results from CDFA's Center for Analytical Chemistry, and provide results to participating residents.
September 2021:	Complete study report and potentially revise monitoring plans for the next study based on incoming analytical results.
Following Years:	Repeat monitoring annually, including revisions to the monitoring plan as needed. An annual report will be published for each year that the Well Network is sampled. Approximately every 10 years, a comprehensive report will be produced to evaluate long-term trends and monitor pesticide use.

V. ANALYTICAL METHODS

CDFA's Center for Analytical Chemistry will analyze well samples using the Triazine Screen analytical method EM 62.9 (CDFA, 2020a), the Multi-Analyte Screen analytical method EMON-SM-05-032 (CDFA, 2021), and the Glyphosate Screen analytical method EMON-SM-05-045 (CDFA, 2020b). The reporting limit for each of the analytes is listed below (Tables 1–4). The Triazine Screen includes 14 analytes by Liquid Chromatography Mass Spectrometry (LCMS) (Table 1), the Glyphosate Screen includes 3 analytes by Ion Chromatography-Mass Spectroscopy (IC-MS/MS) (Table 2), and the Multi-Analyte Screen includes 38 analytes by LCMS (Table 3) and 14 analytes by Gas Chromatography Mass Spectrometry (GCMS) (Table 4).

Table 1. 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 2. Glyphosate Screen method detection limits (MDL) and reporting limits (RL) in ppb.

Analyte	MDL	RL
Glyphosate	0.00820	0.05
Glufosinate	0.00940	0.05
Aminomethylphosphonic Acid (AMPA)	0.01437	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

Results obtained from CDFA's Center for Analytical Chemistry will be entered into DPR's Well Inventory Database and used to monitor temporal changes in pesticide concentrations within the study area, assist in evaluating the success of regulatory pesticide management practices, and determine if pesticides are migrating to groundwater. DPR will publish an annual summary report listing the sample analysis results from the Well Network. Approximately every ten years, DPR will publish an additional report that includes statistical trend analyses of detections and pesticide use.

VII. REFERENCES

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

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