Department of Pesticide Regulation
Environmental Monitoring Branch
Groundwater Protection Program
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Study 330: Development of Passive Sampling Methods and Non-target Screening of Agricultural Pesticides in Groundwater

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1 Introduction

Under the Food and Agricultural Code section 13148 of the Pesticide Contamination Prevention Act (PCPA), the Department of Pesticide Regulation (DPR) is required to monitor groundwater for pesticides that comprise the Groundwater Protection List (GWPL, Title 3 California Code of Regulations (3CCR) section 6800 [a and b]). Currently, more than 100 pesticides are on the GWPL; however, DPR currently monitors for fewer than 50 as it is infeasible and prohibitively expensive to monitor for and develop targeted quantitative analytical methods for all individual compounds on the list. Thus, non-target and suspect screening of pesticides may be a suitable option for long-term monitoring of the ever-evolving GWPL. The analytical methods developed for this study utilize high-resolution mass spectrometry, which allows simultaneous screening for the presence of a wide range of pesticides, degradates, or other contaminants in a single sample. These methods, referred to as suspect and non-target screening (SNTS), can be used to prioritize DPR's conventional targeted analysis method development requests to contracted laboratories. While SNTS is effective for groundwater sampling via grab samples (sections 2.1, 4.3), limits of detection and quantification may be higher than conventional analytical methods (standard LC/GC-MS). In contrast to grab sampling, integrated passive sampling of groundwater over long periods (one month to one year) amplifies the signal of the pesticide concentrations as it represents an integrated concentration over time. Coupled with SNTS, integrative passive sampling can be a powerful tool for early detection of pesticides in groundwater.

2 Study Objectives

There are two primary objectives for this study:

- Develop new passive sampling methods for groundwater monitoring, and
- Analyze groundwater's grab samples and passive samples using the SNTS methods.

2.1 Develop passive sampling methods for groundwater

Passive sampling technologies for monitoring pesticides and other contaminants in groundwater are utilized worldwide. A passive sampler consists of a collection media in a protective housing that is then deployed for a predefined time interval either inside the well or in a sampling chamber outside the well. The resulting sample represents an integrated concentration over time; this concentration is an amplified signal of the concentration in a grab sample. A grab sample refers to a water sample taken at one location at a single point in time. GWPP traditionally collects grab samples when sampling groundwater for pesticides.

Generally, passive samplers for groundwater are deployed in monitoring wells. This study aims to develop passive sampling equipment and methods for use on active, shallow domestic wells using a custom passive sampler that is developed and fabricated by DPR's Groundwater Protection Program (GWPP). Passive samples will be analyzed with the SNTS methods and conventional, targeted methods currently utilized by GWPP. The analytical results will be compared to the results from grab samples collected at the same well.

2.2 Screen groundwater grab samples and passive samples using SNTS methods

This objective will rely on concurrent method development at the California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA) laboratory and Thomas Young laboratory at University of California, Davis (described in section 3). These two laboratories will develop SNTS methods to scan for the presence of pesticides and degradates listed on the GWPL and other compounds that may be associated with formulated products used in agriculture. The SNTS methods developed at both laboratories will include targeted analysis of a defined list of pesticides and degradates determined jointly by GWPP and laboratory staff. Results from the SNTS methods from both laboratories will be compared to each other and to results from the conventional methods currently utilized by GWPP.

3 Personnel

Well sampling and development, deployment, and collection of passive sampling devices will be conducted by staff from DPR's Environmental Monitoring Branch, Groundwater Protection Program under the general supervision of Joy Dias and Carissa Ganapathy. Project personnel will include:

Project Lead:	Tiffany Kocis
Project Staff:	Rick Bergin
	Annette Narzynski
Analytical Chemistry:	Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)
	Thomas Young Laboratory, University of California, Davis
Laboratory Liaison:	Vaneet Aggarwal for analyses conducted by CDFA

Please direct questions regarding this study to Tiffany Kocis at (916) 883-0920 or by email at tiffany.kocis@cdpr.ca.gov.

4 Study Plan

4.1 Tasks and Timetable

Timetable is subject to change due to unforeseen circumstances.

July 2020 – December 2021:	GWPP – Passive sampler design development; pilot site testing of equipment and sampling methods CDFA Laboratory and Thomas Young Laboratory – Method development for extraction of passive samples and SNTS of passive samples and grab samples
December 2021 – April 2022:	GWPP – Collect passive samples and grab samples from study sites CDFA Laboratory and Thomas Young Laboratory – Analyze passive samples and grab samples with conventional analysis and SNTS methods
May 2022 – July 2022:	GWPP – Prepare report of findings

4.2 Sampling Sites

The first pilot site for this project is a domestic well in Fresno County with known contamination from triazine pesticides. GWPP will use this site, and others, to develop equipment and sampling methods. The project will be expanded to approximately ten additional sites. Grab samples will be taken at all potential sites to determine if pesticide contamination is present. Sites for passive sampler deployment should ideally have known contamination in a grab sample for comparison to passive samples (see section 4.5). Ideal sites should additionally allow access up to four times for the duration of the study and have a protected area for equipment deployed near the well (regular well use is acceptable).

4.3 Sampling Methods

Two types of sampling methods are expected for this study: passive sampling and grab sampling. Grab samples will be collected in accordance with FSWA001.03 (Kocis, 2020). The standard operating procedure for passive sampling methods is under development concurrently with the first phase of this study. Quality assurance samples will be collected in the field following the guidelines described in SOP QAQC001.01 (Peoples, 2019).

GWPP will collect up to four passive samples from each site; each passive sampler will be deployed for up to three months. Grab samples will be collected either immediately before deploying a passive sampler, immediately after collecting a passive sampler, or both.

4.4 Chemical Analysis and Quality Control

Passive samples and grab samples will be analyzed under a variety of analytical methods throughout the course of this project and are subject to change as methods are developed and improved. Analytical laboratory quality control will be conducted following the guidelines described in SOP QAQC001.01 (Peoples, 2019). Both passive samples and grab samples will likely be analyzed with a combination of the following analytical methods:

CDFA Laboratory:

- Conventional Methods
    - Multi-Analyte Groundwater Screen, EMON-SM-05-032 (CDFA, 2021)
    - Triazine Groundwater Screen, EMON-SM-62.9 (CDFA, 2020)
    - Multi-Analyte Surface Water Screen EMON-SM-05-037 (CDFA, 2017)
- SNTS methods (currently in development)

Thomas Young Laboratory at the University of California, Davis:

- SNTS methods on LC QTOF/MS in electrospray positive (ESI+) and negative (ESI-) modes
- SNTS methods on GC QTOF/MS in electron ionization (EI) and negative chemical ionization (NCI) modes
- Suspect screening against mass spectrometric databases (both in-house and public)
- Target analysis for a limited set of quantified compounds

4.5 Data Analysis

Results from groundwater grab samples will be compared to results from passive samples collected at the same sites. Results from the SNTS at both laboratories will be compared to each other and to conventional analytical methods at CDFA currently utilized by GWPP. This comparison will establish the performance of the SNTS methods, including the range of chemical characteristics suitable for passive sampling, effective detection limits, and the relative performance of grab and passive sampling techniques for the SNTS of groundwater.

Results obtained from the CDFA laboratory and Thomas Young laboratory will be used to inform future equipment design, additional method(s) development, and assess current levels of the analyzed pesticides in the sampled aquifers. Follow-up monitoring in areas around wells with pesticide detections will occur according to the Pesticide Detection Response Process.

5 Communication

Notice of upcoming sampling will be provided to the County Agricultural Commissioner prior to initiating monitoring in a county. Results will be provided to the participating well users within 30 days of receipt from the laboratory, and a summary of results will be provided to the County Agricultural Commissioners and the County Environmental Health Officers. Results will be published to the Well Inventory Database during the annual update. A final report will be prepared at the conclusion of the study.

6 References

CDFA. 2021. [Draft] EMON-SM-05-032, Revision 1. Determination of 53 pesticides in Groundwater by Gas Chromatography Tandem Mass Spectrometer (GC/MS/MS) and Liquid Chromatography Tandem Mass Spectrometer (LC/MS/MS). California Department of Food and Agriculture, Sacramento, California.

CDFA. 2020. EM 62.9, Revision 5. Determination of Atrazine, Bromacil, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotraizine (DACT), Desmethyl Norflurazon, Tebuthiuron and the metabolites Tebuthiuron-104, Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 in Well Water by MCX extraction and Liquid Chromatography-Triple Quadrupole Mass Spectrometry. California Department of Food and Agriculture, Sacramento, California.

CDFA. 2020. EMON-SM-05-049. Determination of 67 pesticides in Surface Water by Liquid Chromatography Coupled to Linear Ion Trap Quadrupole (LC-MS/MS). Analytical Method. California Department of Food and Agricultural Center for Analytical Chemistry, Sacramento, California. Available at: https://www.cdpr.ca.gov/docs/emon/pubs/anl_methds/emon_sm_05-49.pdf (verified August 19, 2021).

Kocis, T. 2020. FSWA001.03. Obtaining and Preserving Well Water Samples. Standard Operating Procedure. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, California. Available at: https://www.cdpr.ca.gov/docs/emon/pubs/sops/fswa00103.pdf (verified August 19, 2021).

Peoples, C. 2019. QAQC001.01 Chemistry Laboratory Quality Control. Standard Operating Procedure. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, California. Available at: https://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc00101.pdf (verified August 19, 2021).