Department of Pesticide Regulation
Environmental Monitoring Branch
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STUDY GW17A: PROTOCOL FOR ADDITIONAL GROUNDWATER PROTECTION LIST MONITORING FOR IMIDACLOPRID

I. INTRODUCTION

Imidacloprid was recently detected in domestic wells in areas of Fresno, Santa Barbara, and Tulare Counties with depth to groundwater less than 60 feet (Aggarwal, 2017). Imidacloprid is a systemic, neonicotinoid insecticide used in urban and agricultural environments worldwide to control insects on a wide variety of vegetable, field, and fruit crops. This expanded study will investigate areas throughout California where over 2,000 pounds of imidacloprid have been used from 1995 to 2015 and will prioritize areas that have groundwater depths of less than 130 feet and potential wells available for sampling.

II. OBJECTIVE

- Investigate areas of imidacloprid use throughout California where over 2,000 pounds of imidacloprid have been applied from 1995 to 2015 to determine if it has migrated to groundwater as a result of legal agricultural use.

- Samples will also be analyzed for additional pesticides known to, or with the potential to, migrate to groundwater.

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 Joy Dias. Project personnel will include:

Project Leader:	Vaneet Aggarwal
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 Vaneet Aggarwal at (916) 445-3870 or by e-mail at Vaneet.Aggarwal@cdpr.ca.gov.

IV. STUDY PLAN

Monitoring will be focused in sections with over 2,000 pounds of imidacloprid reported applied from 1995 to 2015. There are 109 sections in the state with such high use (CDPR, 2017). Study sections will additionally be prioritized for sampling based on historical depths to groundwater of 130 feet or less and potential availability of wells within or adjacent to the section. The availability of wells will be determined by:

a. Wells listed in DPRs well inventory database.
b. Recent surveys of the section by DPR indicating the presence or absence of wells available for sampling.
c. Examination of recent Google Earth® maps for potential sites, such as homes or other structures, where a well and well owner could be located.

Up to three wells may be sampled per target section. Wells may be sampled in the neighboring sections if there are no available wells in the target section. Sections where DPR has recently tested a well for imidacloprid (2015 or later) will be considered already sampled for this study. Potential target sections are located in Imperial, Kern, Monterey, Riverside, San Benito, San Luis Obispo, Santa Barbara, Tulare, and Ventura Counties (Table 1):

- Imperial County:
    - Five sections, maximum use of 2,344 pounds from 1995 to 2015.
    - There is no record of any of the sections having wells sampled in or near them. Google Earth® imagery also does not show any likely wells.
    - Crews will not conduct surveys in these areas until potential wells can be located.

- Kern County:
    - Nineteen sections, maximum use of 3,201 pounds from 1995 to 2015.
    - Two sections with historical groundwater depths of 130 feet or less will be targeted.

- Monterey County:
    - Twenty sections, maximum use of 3,882 pounds from 1995 to 2015.
    - Seven sections meet the groundwater depth and potential well availability criteria.

- Riverside County:
    - Six sections, maximum use of 3,288 pounds from 1995 to 2015.
    - Three of the sections were recently surveyed by DPR and no wells were found.
    - None of the sections has any record of wells (well logs or sampling results) since 1985.
    - None of the sections meet the well availability criteria.

- San Benito County:
    - One section, with use of 3,353 pounds from 1995 to 2015, will be targeted.

- San Luis Obispo County:
    - Fourteen sections, maximum use of 4,449 pounds from 1995 to 2015.
    - One of the sections contains a well recently tested for imidacloprid with no residues detected.
    - Three of the sections meet the well availability criteria.

- Santa Barbara County:
    - Thirty-nine sections, maximum use of 5,148 pounds from 1995 to 2015.
    - DPR previously detected imidacloprid in a well in one of these sections. All available wells in the section with the detection have been recently sampled. This section will not be resampled. Priority will be given to sampling wells in sections surrounding this detection regardless of imidacloprid use levels. This will add two potential sections that do not meet the 2,000 pound use requirement.
    - Six potential sections were recently sampled for imidacloprid by DPR with no detections. These sections will not be resampled.
    - Twelve sections meet the well availability and water depth criteria. Two additional sections will be surveyed that are adjacent to the reported imidacloprid detection for a total of fourteen sections.

- Tulare County:
    - Two sections, maximum use of 2,481 pounds from 1995 to 2015.
    - Both sections have historical groundwater depths greater than 130 feet. Neither sections meets the well availability criteria.

- Ventura County:
    - Three sections, maximum use of 2,875 pounds from 1995 to 2015.
    - No sections meet the well availability criteria.

A total of twenty-seven sections are targeted in this study for well selection. Maps of the targeted counties showing sections that meet the well availablility criteria are included in Appendix I.

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. 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 imidacloprid using method EMON-SM-05-032 (CDFA, 2013). This multi-analyte method also includes 37 other analytes with the potential to reach groundwater. In the first part of this study, a separate analysis, EMON-SM-13.0 (CDFA, 2008), was used for imidacloprid and four degradates along with the multi-analyte screen. The results showed virtually no difference in the levels of imidacloprid detected by each method and no imidacloprid degradates were detected. Therefore, the separate imidacloprid method was deemed redundant. CDFA will also analyze for the triazine group of pesticides using method EMON-SM-62.9 (CDFA, 2009) (Table 2). The reporting limit for all analytes, is 0.05 parts per billion. 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.

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 sampling, 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 12 to 16 weeks of sampling.

VII. TIMETABLE

- November 2019 - January 2020: Conduct sampling.
- March - May 2020: Obtain and review analytical results from CDFA laboratory.
- August 2020: 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.
    - 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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Aggarwal, V. 2017. Protocol for ground water protection list monitoring for imidacloprid. California Department of Pesticide Regulation, Sacramento, California.

CDFA. 2008. Determination of Imidacloprid and the Olefinic Imidacloprid, Guanidine, Olefinic Guanidine, Urea Metabolites in Well Water by High Performance Liquid Chromatography Tandem Mass Spectrometry. California Department of Pesticide Regulation, Sacramento, California.

CDFA. 2009. Determination of Atrazine, Bromacil, Cyanazine, Diuron, Hexazinone, Metribuzin, Norflurazon, Prometon, Prometryn, Simazine, Deethyl Atrazine (DEA), Deisopropyl Atrazine (ACET), Diamino Chlorotraizine (DACT), Tebuthiuron and the metabolites Tebuthiuron-104, Tebuthiuron-106, Tebuthiuron-107 and Tebuthiuron-108 in Well Water and River Water By Liquid Chromatography- Atmospheric Pressure Chemical Ionization Mass Spectrometry. California Department of Pesticide Regulation, Sacramento, California.

CDFA. 2013. Determination of 44 Pesticides on Well Water by Liquid Chromatography Coupled to Linear Ion Trap Quadrupole and Gas Chromatography Coupled to Triple Quadrupole Mass Spectrometer. California Department of Pesticide Regulation, Sacramento, California.

CDPR. 2017. Pesticide Use Reports. Available at: http://www.cdpr.ca.gov/docs/pur/purmain.htm (verified September 23, 2019). California Department of Pesticide Regulation, Sacramento, California.

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, deisoproryl 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.

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.

X. TABLES

Table 1: Target Sections for Well Sampling

Imidacloprid Use 1995-2015 (LBSAI)			
COUNTY	**COMTRS**	**In-section**	**In 9-Section Area**
Kern	15M25S26E16	2542	14645
Kern	15M25S26E21	2228	11503
Monterey	27M14S02E27	3063	10359
Monterey	27M15S02E12	2332	8850
Monterey	27M15S03E15	2596	10480
Monterey	27M15S03E17	3457	8513
Monterey	27M15S03E25	2542	11221
Monterey	27M19S07E10	2520	7671
Monterey	27M19S07E22	2362	7789
San Benito	35M12S05E08	3353	5582
San Luis Obispo	40M32S13E33	3335	8571
San Luis Obispo	40S11N35W28	2566	23309
San Luis Obispo	40S12N35W30	2093	8981
Santa Barbara	42S08N32W21	2256	2639
Santa Barbara	42S08N33W24	3179	7145
Santa Barbara	42S08N34W23	2036	7017
Santa Barbara	42S08N34W24	3293	6584
Santa Barbara	42S09N32W23	2297	2846
Santa Barbara	42S10N33W19	2260	14225
Santa Barbara	42S10N33W20	4639	13143
Santa Barbara	42S10N33W21	2068	11590
Santa Barbara	42S10N33W32	2672	7712
Santa Barbara	42S10N33W34	3534	12685
Santa Barbara	42S10N34W13	2077	11265
Santa Barbara	42S10N35W16	2522	36169
Santa Barbara	42S10N35W21	431	8027
Santa Barbara	42S10N35W20	385	12378

Table 2: Pesticide Active Ingredient Screen CDFA Lab Method
(Shading indicates overlapping analytes)

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