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

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STUDY GW09: PROTOCOL FOR GROUND WATER PROTECTION LIST MONITORING FOR METOLACHLOR, S-METOLACHLOR, AND IMIDACLOPRID

I. INTRODUCTION

The Pesticide Contamination Prevention Act (PCPA) (Statutes of 1985, Chapter 1298, Section 1) added sections 13141–13152 to the Food and Agricultural Code to prevent pesticide pollution of California's ground water aquifers. The PCPA outlines procedures for (1) gathering physical and chemical data on pesticides, (2) establishing specific numerical values (SNVs [threshold values]) for specified types of those data that the PCPA associates with the potential of a pesticide to leach through soil to ground water, (3) identifying pesticides that "exceed" those SNVs, and (4) placing pesticides that "exceed" SNVs and are applied in specified ways on the Groundwater Protection List (GWPL) (Title 3, California Code of Regulations, 3 CCR section 6800[b]). The PCPA then requires the Department of Pesticide Regulation (DPR) to monitor for GWPL pesticides to determine if they have migrated to ground water.

II. OBJECTIVE

The purpose of this study is to determine whether metolachlor, s-metolachlor or imidacloprid have migrated to ground water in areas of California with high reported agricultural use or in areas identified with the properties to move pesticide residues off-site.

III. PERSONNEL

GWPL well sampling will be conducted by Environmental Monitoring Branch. Project personnel include:

- Project Leader: Craig Nordmark
- Field Coordinator: Rick Bergin
- Project Supervisor: Lisa Quagliaroli
- Senior Scientist: Murray Clayton
- Lab Liaison: To be determined
- Chemists: California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry, Staff Chemists

All questions concerning this protocol should be directed to Mark Pepple at (916) 324-4086, e-mail: <mpepple@cdpr.ca.gov>.

IV. STUDY PLAN

a) Active Ingredient Selection

The pesticides on the GWPL were ranked according to their use patterns and physical-chemical properties. Those compounds with heavy, increasing use and the ability to leach past the crop root zone, based on the LEACHM model (Hutson 1992), are ranked higher. Using this system, pesticides can be prioritized based on their potential risk to contaminate ground water. For fiscal year 2008/2009, DPR chose to monitor for metolachlor (2-chloro-*N*- (2-ethyl-6-methylphenyl)-*N*- (2-methoxy-1-methylethyl) acetamide), s-metolachlor (2-chloro-*N*- (2-ethyl-6-methylphenyl)-*N*- [(1*S*)-2-methoxy-1-methylethyl] acetamide) and imidacloprid ((2*E*)-1-[(6-chloro-3-pyridinyl) methyl]-*N*-nitro-2-imidazolidinimine). For the results of our previous monitoring studies of these active ingredients, please see the study memos for metolachlor and imidacloprid.

In addition to monitoring for the parent compounds, DPR will also monitor for several main degradates:

1. Metolachlor/S-metolachlor Degradates
   - Metolachlor oxanilic acid (OA)
   - Metolachlor ethanesulfonic acid (ESA)
2. Imidacloprid Degradates
   - Imidacloprid urea
   - Imidacloprid guanidine
   - Imidacloprid olefin
   - Imidacloprid olefinic guanidine

The wells will also be sampled for the presence of hexazinone, tebuthiuron, and the known ground water contaminants (3 CCR section 6800(a)) and some of their degradates. We periodically monitor for known ground water contaminants to help assess the adequacy of our mitigation measures and to determine if the Ground Water Protection Areas (GWPAs) need to be expanded. Samples are also analyzed for hexazinone and tebuthiuron because those pesticides may be migrating to ground water (please see previous monitoring studies for hexazinone and tebuthiuron) and additional data is needed to formulate a regulatory decision, if necessary.

b) Study Area Selection

Potential study sections were chosen based on the amounts of pesticide applied and/or soil vulnerability. Data obtained from DPR's Pesticide Use Reports (PURs) indicate that s-metolachlor and imidacloprid use throughout California has steadily increased from 1996 to 2006 (Figure 1) (CDPR, 2008). Much of the metolachlor in the state is used in the Central Valley, mainly in Fresno, Stanislaus, Kings, Merced, and San Joaquin counties (Figure 2). Imidacloprid is chiefly used in Fresno, Santa Barbara, Imperial, Kern, and Monterey counties, with the largest applications occurring in the Salinas Valley (Figure 3). Then, we identified which sections in these counties are vulnerable to pesticide leaching or run-off. Vulnerable areas generally have either coarse soils indicating a potential for residue leaching or an impermeable layer indicating a potential for residue run-off, and a shallow ground water table. We will target 80-120 wells located in the highest use areas, giving those sections that also have vulnerable soils priority. Up to three wells may be sampled in a selected section, depending on the priority of the section and the availability of wells both in the section and the surrounding sections. Wells

may be sampled from the sections surrounding a target section if they are within 0.2 miles of the target section. If we find a positive detection, we will return to the area for further sampling in an effort to characterize the extent of ground water contamination.

V. SAMPLING AND ANALYTICAL METHODS

Where domestic wells are available, they will be selected according to procedures in SOP FSWA006.01 (Nordmark, 2008b). Where domestic wells are unavailable, other types of wells, such as irrigation, municipal, stock, community, and small water system wells, will be sampled. Samples will be collected using the methods described in SOP FSWA001.01 (Nordmark, 2008a). CDFA's Center for Analytical Chemistry will analyze primary samples for metolachlor/s-metolachlor, imidacloprid, and triazines (CDFA, 2001; CDFA, 2008a; CDFA, 2008b). Metolachlor and s-metolachlor are racemic mixtures of the same two isomers, S and R, in the proportions of 50:50 and 88:12, respectively. There is no analytical distinction between the two racemic mixtures and CDFA will report all detections, regardless of source, as simply metolachlor. Samples containing known amounts of metolachlor or imidacloprid and disguised as actual samples (blind spikes) will be prepared and analyzed in accordance with SOP QAQC001.00 (Segawa, 1995). Samples containing deionized water (field blanks) will be collected at the same time as field samples and analyzed to confirm the validity of positive results. The reporting limit for all analytes is 0.05 parts per billion, except for imidacloprid olefin; that analyte has a reporting limit of 0.1 parts per billion. The reporting limit is the smallest amount that can be reliably detected and is set by the testing laboratory for each compound.

VI. DATA ANALYSIS

Data obtained from the CDFA laboratory will be used to determine if pesticides are migrating to ground water. 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

- February 2009-May 2010: Conduct sampling for metolachlor, imidacloprid, and triazines.
- April 2009-July 2010: Obtain analysis results from CDFA laboratory.
- When sampling is concluded: Mail results to property owners.
- October 2010: Write study memorandum.

VIII. BUDGET

Budget Component	Units	Expense per Unit	Total Component Expense
Pesticide sample analysis	≤ 200	$720	$144,000
Travel	1	$15,000	$15,000
PY	1	$100,000	$100,000
Total			$259,000

IX. REFERENCES

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Weaver, D and C. Nordmark. 2004. Memorandum to B. Rollins: Summary of Results for FY 2003/04 Ground Water Protection List Monitoring. Available at: http://www.cdpr.ca.gov/docs/emon/grndwtr/rpts/gwpl_0304.pdf. California Department of Pesticide Regulation, Sacramento, California.

X. TABLES AND FIGURES

Figure 1. Total S-metolachlor and Imidacloprid Use in California for Reporting Years 1996-2006 (CDPR, 2008).

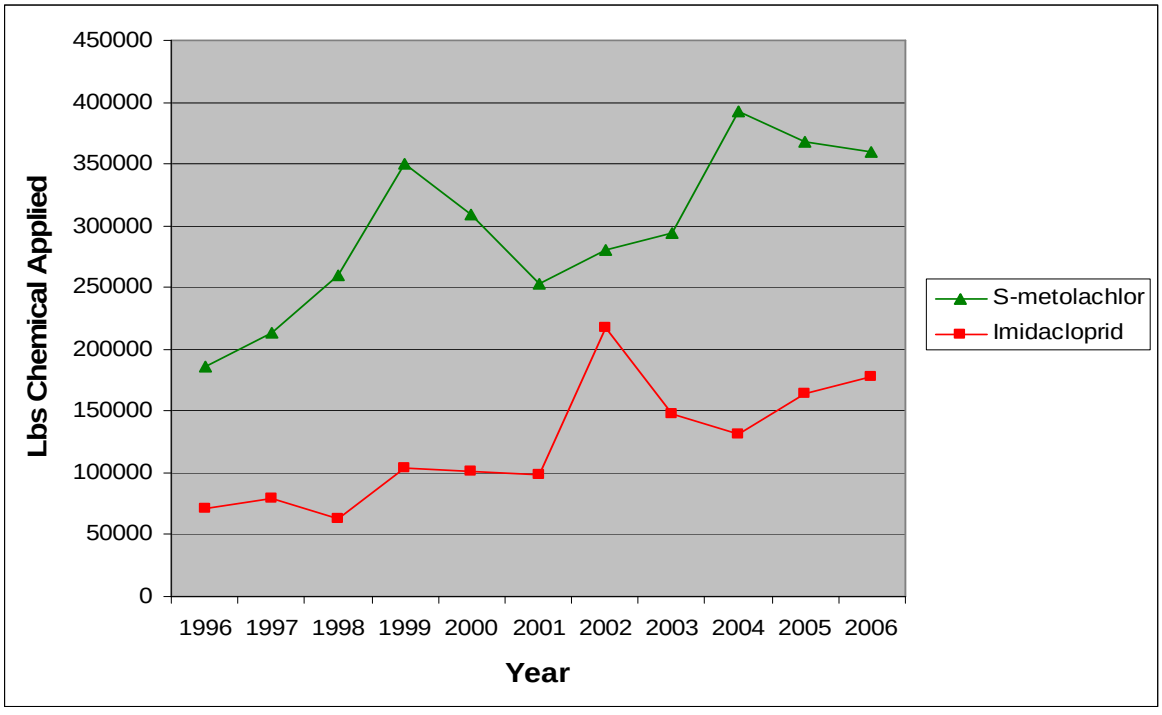

Figure 2. S-metolachlor Use in Five Counties for Reporting Years 1999-2006 (CDPR, 2008).

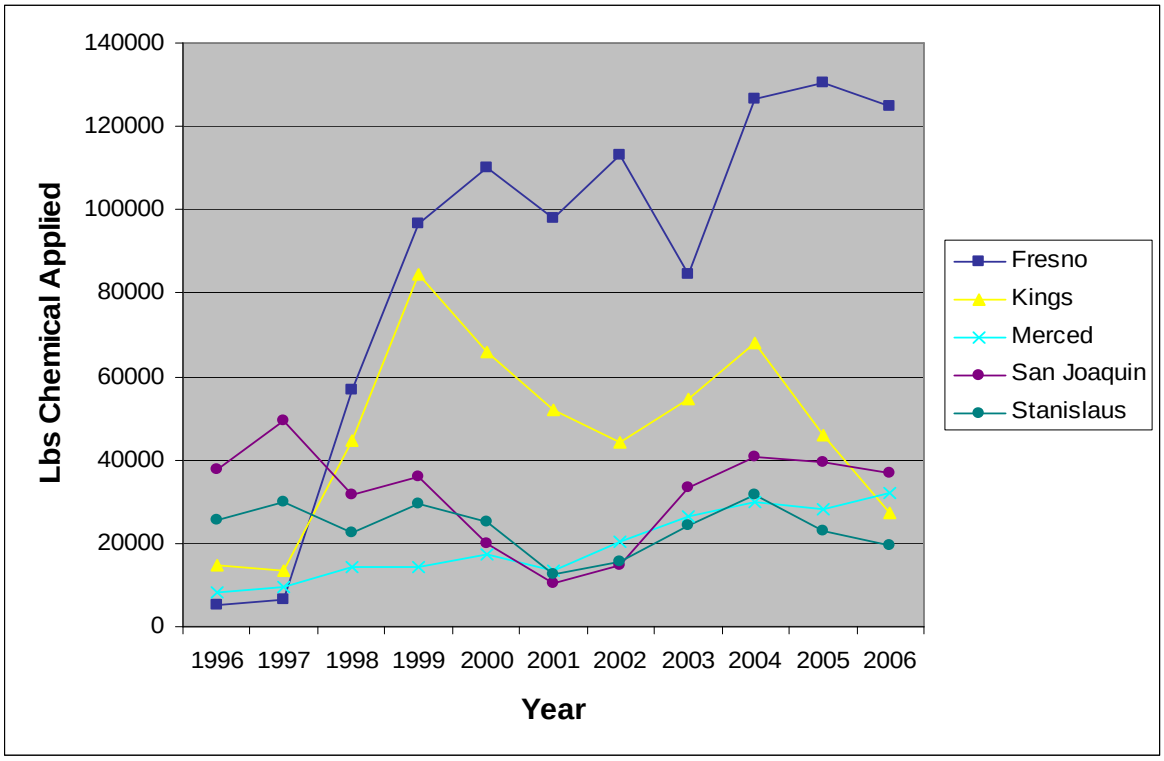

Figure 3. Imidacloprid Use in Five Counties for Reporting Years 1999-2006 (CDPR, 2008).