**Department of Pesticide Regulation**
**Environmental Monitoring Branch**
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# STUDY GW11: PROTOCOL FOR GROUND WATER PROTECTION LIST MONITORING FOR LINURON, MEFENOXAM, METALAXYL, METHOMYL, AND PROPYZAMIDE

## I. INTRODUCTION

In 1985, California passed the Pesticide Contamination Prevention Act (PCPA) to prevent further contamination of California drinking water aquifers by agricultural pesticides (Food and Agricultural Code 13141-13152). The act outlines procedures for the Department of Pesticide Regulation (DPR) to gather physical and chemical data on pesticides to establish specific numerical values (SNVs) for water solubility, soil adsorption coefficient ($K_{oc}$), hydrolysis, aerobic and anaerobic soil metabolism, and field dissipation. This information is used to identify pesticides that may be mobile and persistent in the environment. Pesticides that exceed the SNVs and are intended to be applied to or injected into the soil by ground-based application equipment or by chemigation, or that have a label recommendation or requirement for an irrigation within 72 hours after an application are placed on the Ground Water Protection List (GWPL) (Title 3, California Code of Regulations [3 CCR] section 6800[b]). DPR is required to monitor for pesticides on the GWPL to determine if they have migrated to ground water.

## II. OBJECTIVE

The purpose of this study is to monitor for linuron, mefenoxam, methomyl, and propyzamide in high use areas to determine if they have migrated to ground water as a result of their agricultural use. DPR will also monitor for atrazine, bromacil, diuron, norflurazon, prometon, simazine, and selected degradation products – agricultural pesticides identified as ground water contaminants in 3 CCR section 6800(a) - in areas where their use is not regulated to determine the adequacy of the current ground water protection areas (GWPAs). DPR will also monitor for hexazinone and tebuthiuron – agricultural pesticides that have been detected in ground water – to gather additional data on their fate and movement in the environment and to determine whether further regulatory action is warranted.

## III. PERSONNEL

The well sampling for this study will be conducted by the Environmental Monitoring Branch of DPR. Project Personnel will include:

Project Supervisor: Lisa Quagliaroli

Project Leader: Cindy Garretson
Field Coordinator: Michelle Wong
Senior Scientist: Craig Nordmark
Lab Liaison: Sue Peoples
Chemists: California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry, Staff Chemists

Please direct questions regarding this study to Lisa Quagliaroli at 916-445-3677, e-mail: <lquagliaroli@cdpr.ca.gov>.

## IV. STUDY PLAN

### a) GWPL Active Ingredient Selection

As of April 2011, there were 101 pesticides on the GWPL. DPR developed a system to prioritize these pesticides for analytical method development and monitoring based on their potential threat to ground water (Clayton, 2011). Each pesticide was assigned a rank based on its reported use and the results of a computer modeling simulation that considered mobility, persistence, maximum application rate, soil and weather conditions, and irrigation practices. Pesticides that are used intensively and have greater simulated movement to ground water receive the highest priority for method development and monitoring. About half of the pesticides on the GWPL were assigned the lowest ranking because:

- Adequate monitoring had been conducted by DPR; or
- The registration had been cancelled; or
- The physical-chemical properties (e.g. high volatility) made it highly unlikely that the pesticide would migrate to ground water in measurable concentrations.

Linuron, mefenoxam, methomyl, and propyzamide were selected for this monitoring study from among other highly ranked pesticides on the GWPL because:

- There was no history of monitoring by DPR or, if monitoring had been conducted, it occurred prior to 1995 and/or was not comprehensive in the number of wells sampled or areas studied;
- The major crops treated require supplemental irrigation throughout the growing season which increases the potential for some pesticides to migrate to groundwater;
- With the exception of methomyl, the pesticides are typically applied directly to soil which increases the potential for some pesticides to migrate to ground water; and
- Annual use was increasing, staying the same, or decreasing only slightly.

An additional consideration in the selection of these pesticides was monitoring results reported by organizations other than DPR. An overview of these results follows:

1) Linuron (3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea) has been detected in ground water nationally at levels of 0.001 to 5 parts per billion (ppb) (USGS, 2011, Effland et al., 1995). No linuron has been detected in California ground water though 225 wells were sampled by

pesticide registrants, universities, and government agencies from 1985 through 1990 (Williams et al., 1988, Hoheisel et al., 1992) and 32 wells were sampled by DPR between 1989 and 1991. However, most of the 32 wells sampled by DPR were located in sections with minimal linuron use.

2) Mefenoxam ((R)-2-[(2,6-dimethylphenyl)-methoxyacetylamino]-propionic acid methyl ester) has no reports of ground water monitoring nationally and DPR has never included it in a ground water sampling study.

3) Methomyl (S-methyl N-((methylcarbamoyl)oxy) thioacetimidate) has been detected in ground water nationally at levels of 0.04 to 20 ppb (USGS, 2011, Eiden, 1988). In California, 1,296 wells were sampled for methomyl by pesticide registrants, universities, and government agencies between 1984 and 1989 with no methomyl detections (Williams et al., 1988, Hoheisel et al., 1992). Between 1993 and 2006, DPR sampled six wells for methomyl in response to reported detections of this pesticide. Methomyl was not detected in these samples; however use reporting shows little to no use in the vicinity of the sampled wells.

4) Propyzamide (3,5-dichloro-N-(1,1-dimethyl-2-propynyl) benzamide) has been detected in ground water nationally at levels of 0.001 to 1.3ppb (USGS, 2011). No propyzamide has been detected in California ground water though 254 wells were sampled by pesticide registrants, universities, and government agencies from 1984 through 1987 (Williams et al., 1988, Hoheisel et al., 1992). DPR sampled 25 wells in 1995 as part of a GWPL study and also did not detect this pesticide. The wells sampled by DPR were located in or adjacent to sections with total propyzamide use of 28 to 4274 pounds from 1989 through 1995. None of the 25 wells were located in areas that became GWPAs in 2004.

**b) GWPL Active Ingredient Use Patterns**

1) Linuron

- Linuron is a selective preemergence and postemergence herbicide that is used for control of a large spectrum of annual weeds. Application methods include ground spray, and since 1997, chemigation in carrots. When Linuron is used as a preemergence ground spray it is applied directly to soil with a label recommendation for water in the form of rainfall or irrigation to be applied within 2 weeks of treatment to carry the chemical into the root zone of germinating weed seeds. When Linuron is used as a postemergence it is applied as a nondirected foliar spray when crops are established and weeds are generally less than 6" tall. No post treatment irrigation is required. For application by chemigation linuron may be applied using center pivot, lateral move, solid set, or hand move irrigation systems. The label recommendation is to add enough water either during or after injection to activate the herbicide. The proportion of Linuron that is soil applied compared to foliar applied is estimated to be greater than 50% (Clayton, 2011).
- Examples of names of commonly used products are: Lorox DF, Lorox, and Linex 50DF.
- More than 80% of linuron use was in carrots, 10% was used in asparagus, and 5% in celery (CDPR, 2011).
- The amount of linuron used annually from 1990 to 2010 has remained steady at 100,000 lbs or less except for 1992, when reported use was over 100,000 lbs, and 1993 when use was over 200,000 lbs (Figure 1.) (CDPR, 2011).

2) Mefenoxam

- Mefenoxam is a fungicide used to control certain fungi in plants and soil including *Pythium* spp., *Phytophthora* spp., and downy mildews. Application methods include foliar by ground spray, aerial application, or chemigation, in-furrow, at planting (soil), postplant (soil), soil drench, and seed treatment. For application by chemigation mefenoxam may be applied using center pivot, lateral move, solid set, or hand move irrigation systems. The proportion of mefenoxam that is soil applied is estimated to be 90% (Clayton, 2011).
- Examples of names of commonly used products are: Ridomil Gold, Apron XL, Ultra Flourish, and Subdue Maxx.
- It is used in a wide variety of crops with more than 50% its use in carrots, spinach, onions and tomatoes for processing (CDPR, 2011).
- Mefenoxam's first reported use in California was in 1996. Its use has remained at less than 100,000 lbs. per year (Figure 1.).

3) Methomyl

- Methomyl is a broad-spectrum insecticide that kills insects on contact and also through systemic action by killing target insects when they ingest treated plants. It is a carbamate that works by inhibiting cholinesterase, an enzyme important in nervous system functioning. Application methods include ground spray and aerial application. The proportion of mefenoxam that is soil applied is estimated to be <1% (Clayton, 2011).
- Examples of names of commonly used products are: Lannate, Lannate Methomyl, Lannate SP, and Lannate LV.
- It is used in a wide variety of crops with more than 50% of its use in lettuce (head and leaf), alfalfa, corn, grapes and tomatoes (fresh and processing) (CDPR, 2011).
- From 1990-2000, reported use ranged from 500,000 lbs. to almost 900,000 lbs. per year. After 2000, methomyl use declined and now ranges from 200,000 lbs. to 400,000 lbs. annually (Figure 1.) (CDPR 2011).

4) Propyzamide

- Propyzamide is a systemic preemergence and early postemergence herbicide used primarily for controlling certain winter annual and perennial grasses and broadleaf weeds. Application methods include ground spray, aerial spray, and chemigation in some areas and some crops (including lettuce). When propyzamide is used as a preemergence ground spray it is applied directly to soil with a label recommendation for water in the form of rainfall or irrigation to be applied after treatment to carry the chemical into the root zone of germinating weed seeds. In warm weather conditions, a shallow mechanical incorporation is recommended to slow degradation of the product. For application by chemigation, propyzamide may be applied using center pivot, lateral move, solid set, or hand move irrigation systems. The label recommendation is to add enough water either during or after injection to activate the herbicide. The proportion of propyzamide that is soil applied compared to foliar applied is estimated to be 75% (Clayton, 2011).
- Examples of names of commonly used products are: Kerb and Pronamide.
- In California 90% of propyzamide use was in lettuce (head and leaf) (CDPR, 2011).

- The amount of propyzamide used annually between 1990 to 2010 has remained steady at slightly over 100,000 lbs except for 1990, when almost 200,000 lbs were reported used(Figure 1.) (CDPR, 2011).

**c) Study Area Selection**

It will be a priority to sample sections that have the highest reported use of each pesticide as well as sections that have been identified as leaching or runoff GWPAs. GWPAs, areas vulnerable to ground water contamination by certain pesticides, generally have shallow depths to ground water (< 70 feet) and either coarse textured soils, where pesticides can potentially leach to ground water, or hardpan layers above which pesticides may move laterally with percolating irrigation water until they reach more permeable soils, abandoned wells, or other manmade or naturally occurring pathways. The counties with the highest total use of each of the pesticides from 1990-2010 in GWPAs and nonGWPAs were determined from DPR's Pesticide Use Reports (PUR) and presented in Figures 2 through 5 (CDPR, 2011). Although use in the highest nonGWPA counties was much greater than use in the GWPA counties (Figures 2 – 5), sampling will target high use sections within the top five counties in each category to determine if the pesticides have migrated to groundwater.

The following counties will be targeted for well sampling: Fresno, Kern, Monterey, San Joaquin, San Luis Obispo, and Tulare. These counties either have the highest use of the selected pesticides or have the most areas of vulnerable soils in which these pesticides have been used. Imperial County has significant use of linuron and methomyl and will be included as a potential study area, but because there are very few irrigation and domestic wells available for sampling it is not clear how many samples will be obtained. Imperial Valley ground water is highly saline and generally not suitable for drinking or irrigating crops so nearly all the water used for those purposes is surface water supplied by the Imperial Irrigation District (IID) from the Colorado River (IID, 2012). The IID delivers almost 3 million acre feet of water per year to half a million acres of irrigated land. Additional counties may be sampled if enough wells are not found in the highest priority counties.

Approximately 40-60 wells per pesticide will be sampled for this study for a total of 160-240 wells. Up to three wells may be sampled in each target section depending on the availability of wells. If wells are not available in a target section, wells may be sampled from within 0.2 miles of the surrounding sections. If pesticides are detected, additional samples may be taken in the vicinity of the detection(s) to determine the extent of the area impacted.

**d) Triazine Sampling**

Depending on use patterns, wells may be sampled for pesticides included in 3 CCR section 6800(a) of the GWPL (atrazine, bromacil, diuron, norflurazon, prometon, and simazine) and the following degradation products: deethyl atrazine (DEA), deisopropyl atrazine (ACET), and diamino chlorotriazine (DACT). Pesticides listed in 3 CCR section 6800 (a) have been previously detected in ground water and are already regulated in GWPAs therefore, samples will only be taken for these pesticides in areas where their use is not yet regulated. This data will be used to determine if more areas need to be added to the GWPA list. Sampling for hexazinone and tebuthiuron, pesticides detected in ground water but not yet regulated, will provide additional information on which to base future regulatory actions.

## V. SAMPLING AND ANALYTICAL METHODS

Wells will be chosen in the designated areas following procedures described in SOP FSWA001.01 (Nordmark and Pinera-Pasquino, 2008). Domestic wells are preferable because they usually are accessible year round and are shallower than irrigation or municipal wells. During collection of ground water samples from the wells all efforts will be taken to bypass pressure tanks, hoses, filters, etc., and to sample water directly from the aquifer as outlined in SOP FSWA006.01 (Nordmark and Herrig, 2011).

Chemical analysis will be performed by the CDFA Center for Analytical Chemistry using method EMON-SM-05-025 (CDFA, 2011) and method EMON-SM-62.9 (CDFA, Revised 2009). Both methods have been determined to provide unequivocal identification of a chemical by a single analytical method conducted by a single analytical laboratory (Aggarwal, 2012) and (Fattah, 2008). Although method detection limits vary, DPR set the reporting limit for all analytes included in this study at 0.05 ppb (Tables 1 and 2). SOP QAQC001.00 (Segawa, 1995) guidelines will be followed for analytical laboratory quality control and for collecting quality assurance samples in the field.

**Table 1.** Method detection and reporting limits for EMON-SM-05-025 **(**CDFA, 2011).

| Pesticide | Method Detection Limit (ug/L) | Reporting Limit (ug/L) |
|---|---|---|
| Linuron | 0.0129 | 0.05 |
| Mefenoxam | 0.0152 | 0.05 |
| Methomyl | 0.0157 | 0.05 |
| Propyzamide | 0.0147 | 0.05 |

**Table 2.** Method detection and reporting limits for EMON-SM-62.9(CDFA, Revised 2009).

| Compound | Method Detection Limit (ug/L) | Reporting Limit (ug/L) |
|---|---|---|
| DACT | 0.0063 | 0.05 |
| ACET | 0.0130 | 0.05 |
| DEA | 0.0110 | 0.05 |
| Hexazinone | 0.0250 | 0.05 |
| Simazine | 0.0135 | 0.05 |
| Bromacil | 0.0200 | 0.05 |
| Prometon | 0.0120 | 0.05 |
| Atrazine | 0.0150 | 0.05 |
| DSMN | 0.0150 | 0.05 |
| Norflurazon | 0.0063 | 0.05 |
| Diuron | 0.0430 | 0.05 |
| Tebuthiuron | 0.0140 | 0.05 |

## VI. DATA ANALYSIS

Data obtained from the CDFA Center for Analytical Chemistry will be used to determine if pesticides are migrating to ground water. These data will also be used to generate a study report detailing our findings.

## VII. TIMETABLE

- June 2012-July 2013: Conduct sampling.
- August 2012-September 2013: Obtain analysis results from CDFA laboratory.
- March 2013: 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.

## VIII. BUDGET

**Table 3**. Study Budget Estimate.

| Budget Component | Units | Expense per Unit | Total Component Expense |
|---|---|---|---|
| Pesticide sample analysis – initial samples | ≤ 240 samples | $720 | $172,800 |
| Pesticide sample analysis – QC samples[1] | ≤ 35 samples | $720 | $25,200 |
| Pesticide sample analysis – known CA contaminants | ≤ 60 samples | $720 | $43,200 |
| Pesticide sample analysis – New AI detection follow up | ≤ 40 samples | $720 | $28,800 |
| Travel[2] | ≤ 192 days | $130 | $24,960 |
| Person Years | ≤ 1 | $100,000 | $100,000 |
| Total | | | $394,960 |

[1] Approximately 10% of all samples analyzed

[2] Travel estimate is based on a two-person team sampling 10 wells per 4-day week with a total of 240 wells being sampled ( 240 wells/10 wells per week = 24 weeks x 2 people = 48 weeks = ≤ 1 Person Year) and (24 weeks x 4 days per week x 2 people = 192 Travel Days)

## IX. AMENDMENTS

Protocol amendment #1: Metalaxyl, an enantiomer of mefenoxam, was added to the analytical method in 2013 and the sampling plan was expanded to include additional wells in areas where there was high reported use of metalaxyl. The complete amendment is shown as an attachment to this protocol and available at <http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study_gw11_amendment1.pdf>.

## X. REFERENCES


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Figure 1. Agricultural Use of Linuron, Mefenoxam, Methomyl, and Propyzamide in California 1990-2010 (CDPR, 2011)

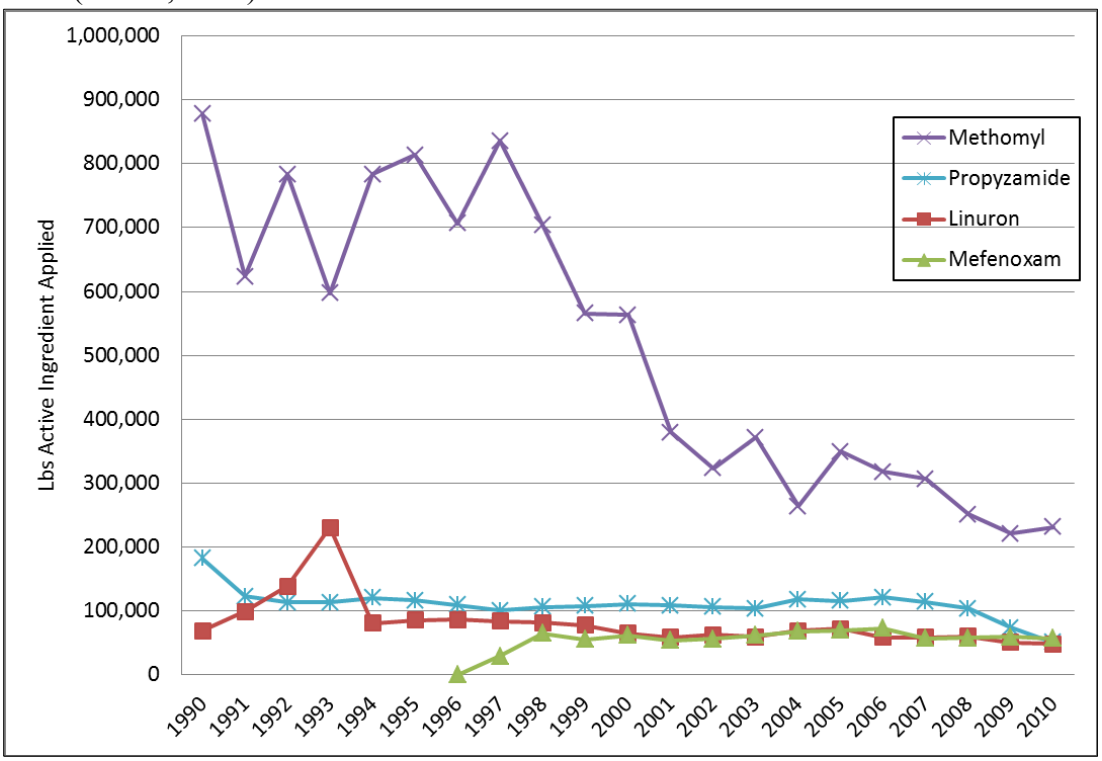


Figure 2. Total linuron use from 1990 through 2010 in non-GWPAs and GWPAs for the top 5 counties in each category. (CDPR, 2011).

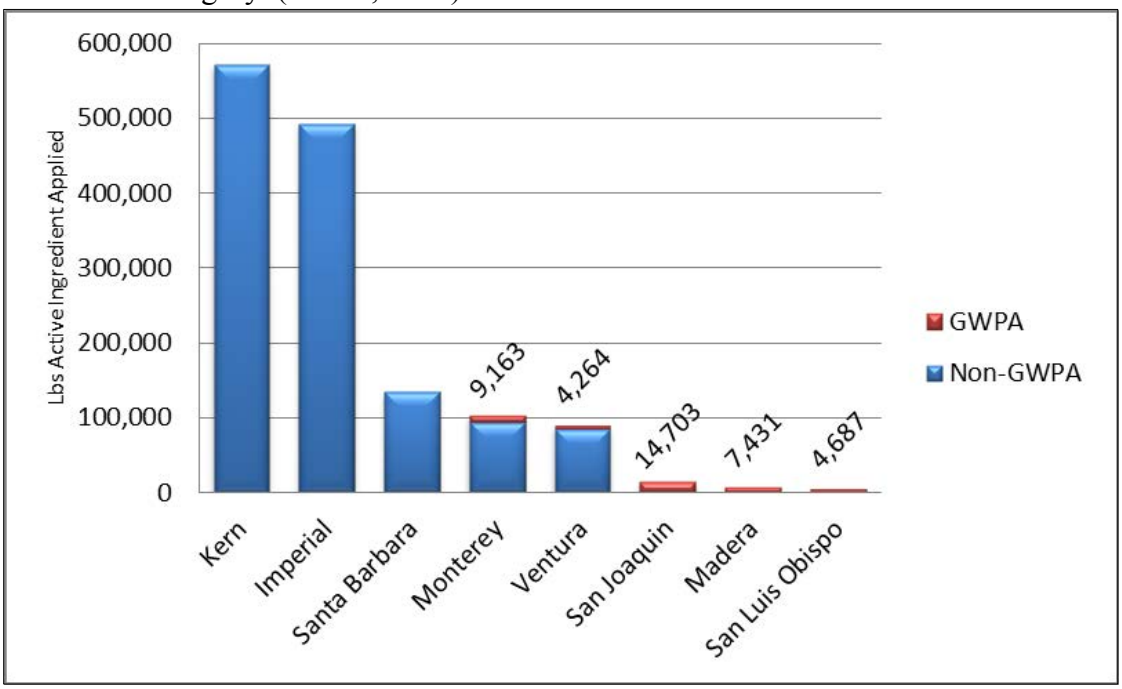

Figure 3. Total mefenoxam use from 1990 through 2010 in non-GWPAs and GWPAs for the top 5 counties in each category. (CDPR, 2011).

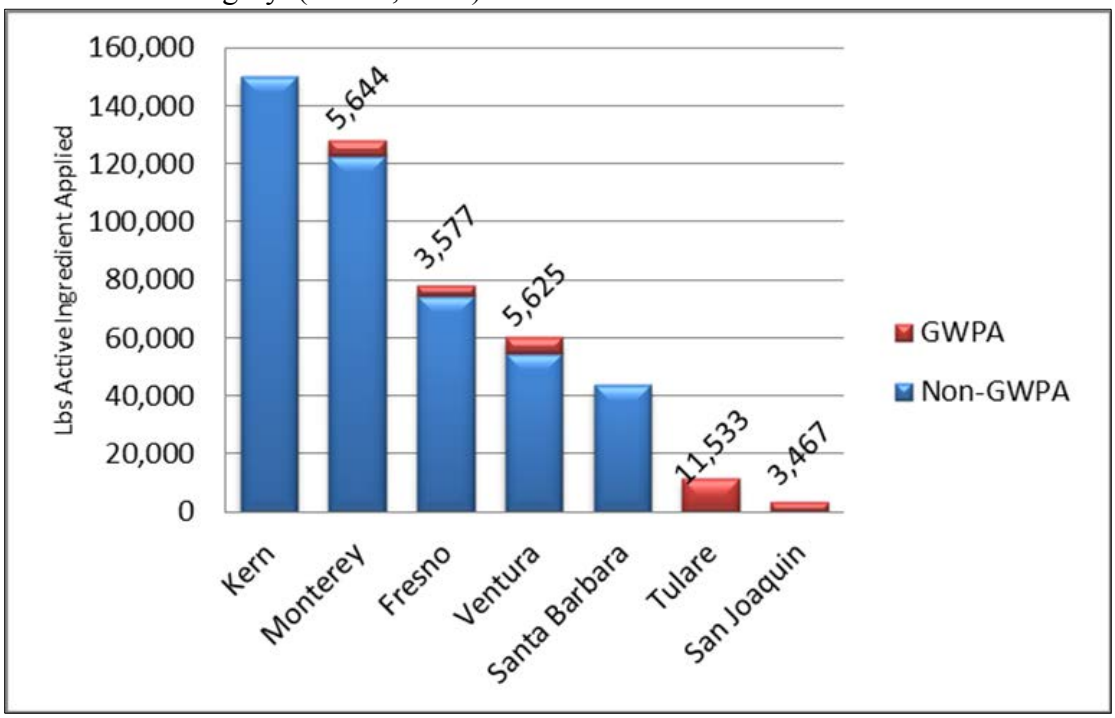


Figure 4. Total Methomyl use from 1990 through 2010 in non-GWPAs and GWPAs for the top 5 counties in each category. (CDPR, 2011).

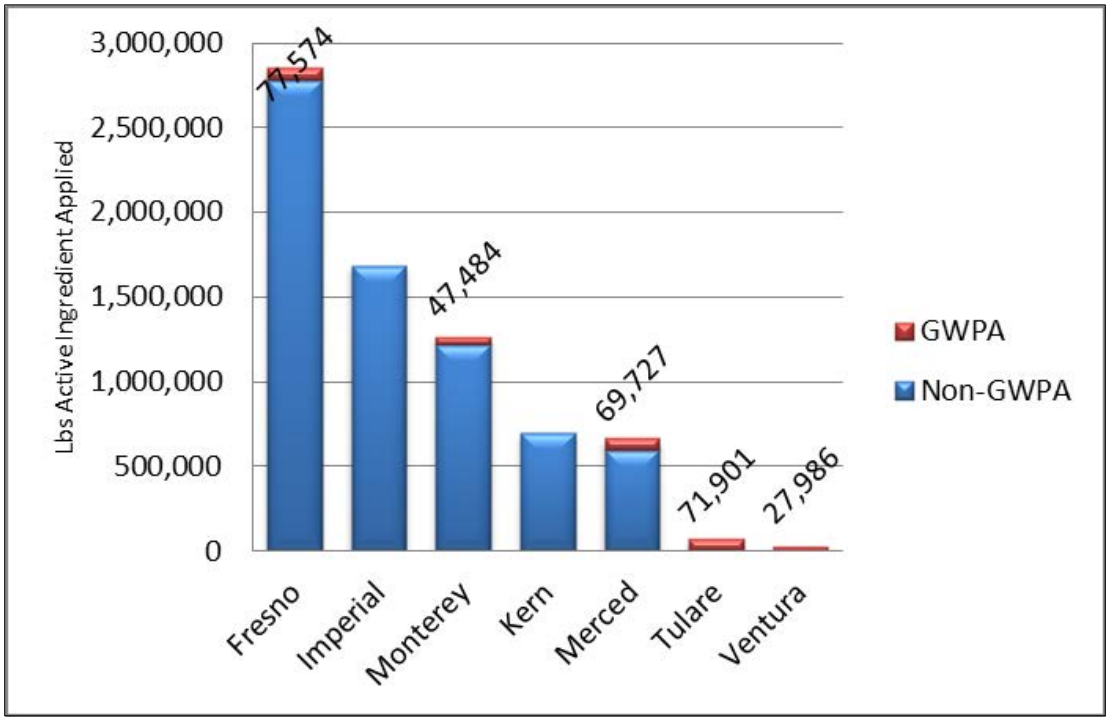

Figure 5. Total Propyzamide use from 1990 through 2010 in non-GWPAs and GWPAs for the top 5 counties in each category. (CDPR, 2011).