Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1020 N Street, Room 161
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Protocol for a Pesticide Management Zone (PMZ) Well Monitoring Network in California. March, 1995

I. INTRODUCTION

The Department of Pesticide Regulation (DPR) has adopted regulations to establish Pesticide Management Zones (PMZs) to prevent further contamination of ground water in areas where pesticide contamination has occurred. A PMZ is a geographical area of approximately one square mile which is sensitive to ground water pollution and which corresponds to a section as defined by base meridian, township, range and section, or which is defined by latitude and longitude or other generally accepted geographical coordinates.

All uses of pesticides containing atrazine or prometon are prohibited in the PMZs. Agricultural, outdoor institutional and outdoor industrial uses of pesticides containing bromacil, diuron, and simazine are prohibited in non-crop areas and on rights-of-way in appropriate PMZs. PMZs have been established for the pesticides atrazine, bromacil, diuron, prometon, and/or simazine in one or more of the following counties: Contra Costa, Fresno, Glenn, Los Angeles, Merced, Orange, Riverside, Stanislaus, Tehama, and Tulare. The Department has proposed regulations to establish additional PMZs in Kern, Placer, and Solano Counties.

The first PMZs were put into regulation in 1989, approximately six years ago. Since then, there has not been an evaluation of their effectiveness in preventing further contamination of ground water. This study uses a well monitoring network to measure temporal changes in pesticide residues in known contaminated wells. Since changes in residue concentration in wells in response to regulations in PMZs is unknown, the study is initially planned as a five year monitoring program. Trends may be evident before five years but previous studies indicate that contaminated ground water may require many years before changes can be measured (Gilbert 1987 and Ward et al, 1988).

II. OBJECTIVE

The objectives of this study are: 1) To measure patterns in temporal changes of atrazine concentration in PMZs where use has been banned; 2) To measure patterns in temporal changes of simazine concentration in PMZs where agricultural use is allowed

when advisories are written; and 3) To conduct a survey of agricultural management practices in PMZs in order to determine if ground water advisories have been adopted by growers.

III. PERSONNEL

This study will be conducted by the Environmental Hazards Assessment Program (EHAP) under the general direction of Don Weaver, Senior Environmental Research Scientist. Key personnel are listed below:

Project Leader:	Blanca Rodriguez
Field Coordinator:	Frank Spurlock
Senior Staff Scientist:	John Troiano
Laboratory Liason:	Nancy Miller
Chemical Analysis:	
Experimental Design/Data Analysis:	Terri Barry

Questions concerning this monitoring program should be directed to Peter Stoddard at (916) 324-4100 and FAX (916) 324-4088.

IV. EXPERIMENTAL DESIGN / SAMPLING METHODS

A. Study Design for Objective I to Determine Temporal Concentration of Atrazine in PMZs

Thirty wells will be selected from Glenn and Los Angeles Counties for periodic sampling of atrazine and its breakdown products. These counties were chosen because they contain PMZs that are concentrated in a relatively small geographic area. Wells chosen for this study from the Department's Well Inventory Database must have concentrations high enough at the beginning of the five year sampling period to yield a complete set of concentrations above the detection limit for fitting the trend. Wells with concentrations close to the detection limit at the start of the study may yield non-detects too early in the five year sampling period to fit a trend. However, inclusion of analysis for atrazine degradates may allow the use of some wells that have concentrations of the parent triazine near the detection limit at the beginning of the study. The final selection of network wells will be based on the concentration of atrazine plus degradates found in the well at the initial sampling for this study.

Analysis will also be performed for herbicide active ingredients that are being substituted for use of atrazine in PMZs. The choice of alternative herbicides to be analyzed for will be made based on the Pesticide Use Reports for sections in which network wells are located. The alternate herbicides analyses will be well-specific. There is no requirement that the same back-up herbicide analyses be used for all PMZs

in the study. If possible, the trends in the concentrations of atrazine will be compared to the trend in the alternative herbicide concentrations within each well. This comparison will depend on both the use of an alternate herbicide and the concentrations if an alternate herbicide is found.

Wells will be sampled at quarterly intervals for five years. A minimum of two years of quarterly observations will be required to detect a trend but it may take five years before reliable trends are measured.

B. Study Design for Objective II to Determine Temporal Concentration of Simazine in PMZs

Thirty wells will be selected from Fresno and Tulare Counties for periodic sampling of simazine and its breakdown products. These counties were chosen because they contain PMZs that are concentrated in a relatively small geographic area. In addition, an extensive analysis of the vulnerability of ground water to pesticide pollution in this area has been conducted by DPR scientists (Troiano et al, 1992). Wells chosen for this study from the Department's Well Inventory Database must have concentrations high enough at the beginning of the five year sampling period to yield a complete set of concentrations above the detection limit for fitting the trend. However, inclusion of analysis for simazine degradates may allow the use of some wells that have concentrations of the parent triazine near the detection limit at the beginning of the study. The final selection of network wells will be based on the concentration of simazine plus degradates found in the well at the initial sampling for this study.

Analysis will also be performed for herbicide active ingredients that are being substituted for use of simazine in PMZs. The choice of alternative herbicides to be analyzed for will be made based on the Pesticide Use Reports for sections in which network wells are located. The alternate herbicides analyses will be well-specific. There is no requirement that the same back-up herbicide analyses be used for all PMZs in the study. If possible, the trends in the concentrations of simazine will be compared to the trend in the alternative herbicide concentrations within each well. This comparison will depend on both the use of an alternate herbicide and the concentrations if an alternate herbicide is found.

Previous analysis of the geography of the Fresno-Tulare county area indicated that contaminated wells occurred in two separate soil types (Troiano et al. 1994). Contaminated wells occurred in coarse soils where leaching would be a predominant process for pesticide movement to ground water. Contamination also occurred in soils where hardpan was a dominant feature and where dry are constructed to aid in drainage of water from these poorly-drained soils. The 30 will be divided between these two clusters to determine if the differences in the pathway of contamination potentially affects temporal trends that may be measured.

Wells will be sampled at quarterly intervals for five years. A minimum of two years of quarterly observations will be required to detect a trend but it may take five years before reliable trends are measured.

C. Study Design for Objective III to Survey Agricultural Management Practices in PMZs

Simazine use has been allowed on agricultural crops in PMZs if the user obtains a written advisory from a certified Pest Control Advisor. The advisories contain suggestions for changes in agricultural practices that would decrease the risk of off-site movement and for protection of wells against contact with water that contain agricultural residues. In order to determine the extent to which advisories have been adopted, a survey will be conducted through the County Agricultural Commissioners offices first to determine if the users were aware of the need for advisories in the PMZ and then to determine if any of the advisories had been adopted by the user. These data will aid in interpreting any trends measured in objectives 1 and 2.

V. CHEMICAL ANALYSIS / QUALITY CONTROL

VI. DATA ANALYSIS

A. Methods of Statistical Analysis for Objective I

Normal distribution based statistical methods such as least squares regression and the covariance test for homogeneity of slopes could be used to analyze this data. However, if there are many non-detects (ND) or missing values these methods may perform poorly. Therefore, it is anticipated that the data will be analyzed using nonparametric methods of analysis for detection and comparison of trends as discussed in Gilbert (1987), Hollander and Wolfe (1973) and Ward and Loftis (1988). These statistical methods include the tests discussed below:

Mann-Kendall Test - a nonparametric test for trend will be performed for each chemical in each well. Missing values are allowed and no particular underlying distribution of the data is assumed. Data reported as a trace or less than the detection limit can be used by assigning those data a common value smaller than the smallest measured value in the remainder of the data set. The Mann-Kendall test uses only the relative magnitudes of the data rather than the measured value. The Mann-Kendall Test is a nonparametric test for zero slope of the linear regression of time-ordered data versus time.

Sen's Nonparametric Estimator of Slope - This procedure is not greatly affected by outliers and missing data. No particular underlying distribution is assumed. It is closely

related to the Mann-Kendall test. The slope and a 95% confidence interval will be calculated for each chemical in each well.

Homogeneity of Slopes - The test for homogeneity of slopes will use the Mann-Kendall statistics to ascertain whether atrazine and alternative herbicide concentrations exhibit different trends within a single well. A general statement about the presence or absence of monotonic trends will be meaningful if the trends for atrazine and the alternate herbicides are in the same direction. A comparison of the concentrations of atrazine in wells in PMZs and the concentrations of atrazine in wells in adjacent sections will also be performed.

The proportion of sampled wells with the trend of atrazine significantly different from an alternate herbicides will be compared to the proportion of wells that show no difference in trend. In addition, the proportion of wells that show concentrations of alternative herbicides will be compared to the proportion of wells that show no alternative herbicide concentrations.

B. Methods of Statistical Analysis for Objective II

Same as for Objective I

C. Methods of Statistical Analysis for Objective III

There will be no statistical analysis for this objective. The results of the survey will be evaluated qualitatively and any changes in practices that may have resulted from PMZ regulation will be determined.

VII. TIMETABLE

Sample Collection	April, July, October, and January, 1995-2000.
Chemical Analysis	April, July, October, and January, 1995-2000.
Data Analysis	April, July, October, and January, 1995-2000.
Interim Reports	Due dates to be determined.