

**California Environmental Protection Agency
Department of Pesticide Regulation
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**STUDY 226: PROTOCOL TO DETERMINE DISTRIBUTION OF
ATRAZINE/SIMAZINE PARENT AND BREAKDOWN PRODUCT RESIDUES
IN MUNICIPAL WELLS**

I. Introduction

The Department of Pesticide Regulation (DPR) has previously conducted well surveys for the presence of triazine pre-emergence, herbicide residues in primarily domestic wells (Schuette et. al., 2002). Simazine residues have been detected in 659 wells in 24 different counties and atrazine residues have been detected in 203 wells in 21 counties. Atrazine detections are expected to be lower than simazine because use of atrazine is less than that of simazine in California. During the 1990's DPR added the atrazine/simazine breakdown products deethyl-simazine (ACET), deethyl-atrazine (DEA) and diamino chlorotriazine (DACT) to the standard pesticide analytical screen conducted on all well water samples. Since 1996, when all breakdown products were included in the screen, 248 wells contained atrazine, simazine and/or breakdown product residues. 66% of these wells had both parent and breakdown product residues, 25% had only breakdown product residues and 9% had only parent residues. Where both parent and breakdown products were present in the same sample, the total degradate residue levels exceeded the parent residue levels in 82% of the samples.

Since the objective of DPR's sampling is to detect residues in ground water, domestic wells have been targeted for sampling because they are more often situated in shallow ground water aquifers where the probability of detection is greatest. Municipal wells, on the other hand, are more often situated in deeper ground water aquifers so data obtained from domestic well sampling are not necessarily representative of the detection frequency and concentration experienced by municipal well systems. The California Department of Health Services (CDHS) routinely receives results from tests of water samples from municipal and other community wells in California. Since July 1996, CDHS has received no reports of atrazine detections and only two wells were reported with simazine residues. The triazine breakdown products are not included in the standard chemical analysis conducted for CDHS monitored wells.

DPR, however, has sampled some municipal wells for triazine parent and breakdown products. Residues were detected in seven of 19 community wells sampled in the Fresno-Tulare-Kern County area. DACT was not reported but in some cases it was not included in the screen for sampling conducted prior to 1996. Three wells sampled by

DPR in the Sanger area contained simazine and DEA or ACET residues. Two of these wells were reported by CDHS to contain DBCP (1,2-dibromo-3-chloropropane) residues as recently as 2002. CDHS continues to report DBCP in numerous wells throughout the state. DBCP has been banned in California since the late 1970's and was originally used for nematode control in vineyards, orchards and annual crops. Simazine is currently used for pre-emergent weed control in orchards, cane berries, corn and vineyards in many of the same areas of the state where DBCP use eventually contaminated ground water. The area of the state with the most detections of simazine by DPR and DBCP by CDHS is located from Fresno County through Tulare to northern Kern County.

II. Study Objective

The objective of this study is two fold. The first objective is to develop data on the presence and distribution of triazine residues in the deeper aquifers of the state that have previously shown to be vulnerable to pesticide contamination based on the reported presence of DBCP. The second objective will be to compare the frequency and concentration of detections between parent and breakdown products for atrazine and simazine in the deeper wells with the data for other wells, previously sampled by DPR, in the surrounding area. This study would target municipal or community wells with consistent DBCP detections that are also located in areas where simazine has been used heavily and where DPR has previously detected triazine residues in shallow ground water. This data will provide a basis for determining the extent of potential contamination in municipal wells, and provide data on the ability of the triazine breakdown products to migrate from shallower to deeper ground water aquifers.

III. Personnel

Study personnel from the Environmental Monitoring Branch of DPR include:

Project Leader:	John Troiano
Field Coordinator:	Craig Nordmark
Senior Scientist:	Bruce Johnson
Additional Field Personnel:	Jeff Schuette, Murray Clayton
Laboratory Liaison:	Carissa Ganapathy
Agency/Public Contact:	Mark Pepple

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IV. Study Design

Study Area: The study will focus on the Fresno through northern Kern County area because there is already an extensive history of triazine detections in shallow ground water and because many of the community wells in that area have reported continued detections of DBCP. The area selected for the study extends from the City of Fresno in the northwest to the Delano in the south. It is bounded on the west by Highway 99 and on the east by the Sierra foothills in a line roughly defined by Orange Cove to Woodlake to Porterville. This area is underlain with vulnerable shallow ground water as indicated

by the location of many Ground Water Protection Areas. Simazine use from 1993-2002 has been heavy along the eastern boundary with most of the area having at least some simazine applied. DPR has found over 500 wells in this area with residues of atrazine, simazine or degradates present, and CDHS has reported detections of DBCP residues in 150 large water system wells since 2000.

Well Selection: Municipal, small water system and community wells will be selected based on previous recent detections of DBCP by CDHS, and on their proximity to wells where DPR has detected triazine residues. The use of simazine will be another geographic layer that will determine well selection. Well selection is also contingent on obtaining permission from the wells owner and whether a desired well is currently in operation. If a desired well is unavailable, another well may be substituted. All available well data such as hole depth, pump depth and screening intervals will be obtained at the time of sampling.

Well Sampling: This study will provide a snapshot of the presence of residues in municipal wells. Monitoring the change in residue levels over time is not part of the scope of this study. Wells will be sampled using the standard DPR well sampling protocol with up to 50 wells sampled. One primary sample, two backup samples and one field blank will be collected from each well in one-liter amber bottles. Samples will be stored on wet ice for transport and will be refrigerated until analysis.

Sampling Schedule: This study will be conducted in two phases beginning in early October. The initial phase will sample up to 12 of the highest priority wells, those that we predict have the highest chance for finding residues based on the factors mentioned above. The second phase will sample up to an additional 38 wells but will only go forward if detections are made in some of the original 12 wells. The predicted delay between the two samplings is estimated to be four weeks, depending on the analyzing laboratory.

Date	Primary Samples Collected	Sites (Cities)
October 11-14	12	3
November 1-19	38	9

V. Chemical Analysis and Quality Control

The California Department of Food and Agriculture (CDFA) laboratory has established analytical methods of analysis of atrazine, simazine and the breakdown products DEA, ACET and DACT in well water using LC/MS/MS. Additionally, the pesticides diuron, prometon, bromacil, hexazinone and norflurazon are included in the analytical method. The reporting limit for analytes is 0.05 parts per billion (ppb). Turn around time from the submission of the initial samples until the return of preliminary results is planned for less than four weeks. Quality control for this analytical method will follow SOP QAQC001.00 for Chemistry Laboratory Quality Control (Segawa 1995).

V. References

Marade, J. 1996. Well Sampling: Obtaining Permission to Sample, Purging, Collection, Preservation, Storage and Documentation. Environmental Monitoring Branch, Department of Pesticide Regulation, California Department of Environmental Protection. [**SOP FSWA001.00**](#). Available at:

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