DEPARTMENT OF PESTICIDE REGULATION

EXECUTIVE SUMMARY
Of Report EH 92-01 Entitled
"Survey of Chlorthal-Dimethyl Residues in Well Water of Seven California Counties"

Environmental Monitoring and Pest Management
Department of Pesticide Regulation

PURPOSE:

The Department of Pesticide Regulation (DPR) conducted a well water survey to determine if residues of the pesticide chlorthal-dimethyl or its metabolites (also known as breakdown products) occurred in ground water in agricultural areas in California where chlorthal-dimethyl is used.

BACKGROUND:

Chlorthal-dimethyl is a selective herbicide used on crops such as broccoli and onion as well as on ornamentals and turf to control annual grasses and broadleaf weeds. In 1989, during its National Pesticide Survey, the U. S. Environmental Protection Agency (USEPA) tested 61 wells in California, detecting chlorthal-dimethyl metabolites in two municipal wells, one in Los Angeles County and one in Santa Clara County. Metabolites of chlorthal-dimethyl include monomethyl tetrachloroterephthalate (MTP) and tetrachloroterephthalic acid (TPA).

The Environmental Hazards Assessment Program (EHAP) of DPR conducted follow-up studies in both counties in response to these reported detections. These studies confirmed the presence of the metabolites. Based on these results, it appeared that the presence of these residues in ground water was from non-point sources, such as application of agricultural chemicals to crops which cannot be traced to an isolated location. However, since these two wells were located in what are now predominantly urban areas, the EHAP conducted this more extensive well water survey to sample wells in crop-growing areas of the State where chlorthal-dimethyl is used. Well water samples were collected and analyzed for the herbicides chlorthal-dimethyl and its metabolites, as well as atrazine, bromacil, diuron, prometon and simazine. These five herbicides have previously been detected in California ground water due to normal agricultural use.

STUDY METHODS:

From August 6 through August 23, 1990, EHAP staff sampled 60 wells in seven counties: Fresno, Kern, Los Angeles, Monterey, San Luis

Obispo, Santa Barbara and Tulare. These counties were selected because recent use reports showed that moderate to high amounts of chlorthal-dimethyl were used on crops in these areas. Although Tulare is a low-use county, it was chosen because it is an area where other pesticides have been detected in well water samples and therefore represents an area which is sensitive to pesticide leaching.

Pesticide use information, such as location of use and amount used, from 1986 through 1990, obtained from DPR monthly pesticide use reports and some county agricultural commissioners' records, was transferred to county road maps. These maps served as field guides for locating possible sampling locations. In the field, a well was selected using the following procedure. First, domestic rather than irrigation wells were selected when possible. Secondly, clusters of moderate- to high-use areas were targeted. Wells adjacent to crops for which chlorthal-dimethyl is registered were located. When possible, wells situated near crops reporting high use were selected. Thirdly, attempts were made to distribute well sampling sites throughout the high-use areas.

RESULTS:

Of the 60 wells sampled, 17 (28%) contained confirmed detections of TPA residues. The concentrations ranged from 0.18 to 15 parts per billion. Two wells were located in Fresno County, five were located in Kern County, five wells in Monterey County, one in San Luis Obispo County and four wells in Santa Barbara County. No residues were detected in wells sampled in Los Angeles or Tulare Counties.

Although there are no state or federal maximum contaminant levels, USEPA has issued a lifetime health advisory of 4,000 parts per billion for chlorthal-dimethyl and its metabolites. The USEPA issues health advisories to describe concentrations below which adverse health effects would not be expected to occur during a lifetime of drinking such water. Health advisory levels contain a margin of safety to protect the very young, the elderly, and other susceptible members of the population. These health advisory levels are provided by USEPA as guidance for "safe" levels of contaminants in drinking water.

Simazine detections were confirmed in two wells and diuron in one well in Fresno County only. Atrazine, bromacil and prometon were not detected.

CONCLUSIONS:

The findings from this survey suggest that residues of TPA, a chlorthal-dimethyl metabolite, can occur in ground water as a result

of agricultural use. Physical and chemical properties of TPA indicate it has a high probability for leaching, which is a probable cause for its frequent detection. TPA would probably be the most commonly detected ground water residue in other chlorthal-dimethyl high-use regions of the State.

Pursuant to the mandates of the Pesticide Contamination Prevention Act (section 13149 of the Food and Agricultural Code), the Director is required to initiate a review process when an active ingredient, degradation product or other specified ingredient of an economic poison is found in ground water or in soil under certain conditions. A degradation product is considered "found" in ground water only if it is determined to pose a threat to public health.

At the request of the Department, the registrant submitted all available toxicology studies on TPA. After review of the toxicological data, the Medical Toxicology Branch of DPR has concluded that, at the levels detected in ground water, TPA does not pose a threat to public health.

Since all the conditions specified in section 13149 for degradation products have not been met, TPA will not be regulated under the provisions of the Pesticide Contamination Prevention Act.

Ronald J. Oshima
Branch Chief

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ABSTRACT

Due to the United States Environmental Protection Agency's detection of chlorthal-dimethyl metabolites in ground water in Los Angeles and Santa Clara counties, the California Department of Pesticide Regulation (CDPR) conducted a well water survey to test for chlorthal-dimethyl and its metabolites, monomethyl tetrachloroterephthalate (MTP) and tetrachloroterephthalic acid, (TPA) in agricultural use areas of the state. Seven counties reporting low to high chlorthal-dimethyl use from 1986 to 1990 were selected as study sites. Sixty wells were sampled from August 6 through August 23, 1990, in Fresno, Kern, Los Angeles, Monterey, San Luis Obispo, Santa Barbara, and Tulare counties. Of these wells, seventeen were confirmed positive for TPA with concentrations ranging from 0.18 to 15.00 ppb in five counties (Fresno, Kern, Monterey, San Luis Obispo, and Santa Barbara). No confirmed detections were reported for Los Angeles and Tulare counties.

Well water samples were also analyzed for simazine, atrazine, bromacil, prometon, and diuron. In Fresno County, there were two confirmed simazine and one confirmed diuron detections with concentrations of 0.30, 0.50, and 0.10 ppb, respectively. Confirmed simazine and diuron detections were not reported in Kern, Los Angeles, San Luis Obispo, Santa Barbara, or Tulare counties. Prometon, bromacil, and atrazine were not found in any of the seven counties.

ACKNOWLEDGEMENTS

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DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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INTRODUCTION

Chlorthal-dimethyl (dimethyl tetrachloroterephthalate, DCPA or Dacthal®) is a selective preemergent and postemergent herbicide in the chlorinated benzoic acid family used to control annual grasses and broadleaf weeds. In California, approximately 90% of the reported chlorthal-dimethyl use is applied to Brassica (e.g., broccoli) and Allium (e.g., onion) crops (CDFA, 1986-1988). Applications are also made to ornamental, turf, and field crops, but to a much smaller degree. The compound has been registered in the State for approximately thirty years and formulations currently available include Dacthal® wettable powder 50 and 75% active ingredient (ai) and granular 5% ai.

The average half-life of chlorthal-dimethyl in soil is given as 100 days (Hurto et al., 1979). Dissipation of the parent compound (Figure 1) has been shown to be dependent upon soil microorganisms (Tweedy et al., 1968), soil moisture (Fermenta Plant Protection Co., 1986), and soil temperature (Walker, 1978) to first yield monomethyl tetrachloroterephthalate (MTP), the half-acid ester, and then tetrachloroterephthalic acid (TPA), the diacid, through a two step hydrolysis reaction (Fermenta Plant Protection Co., 1990).

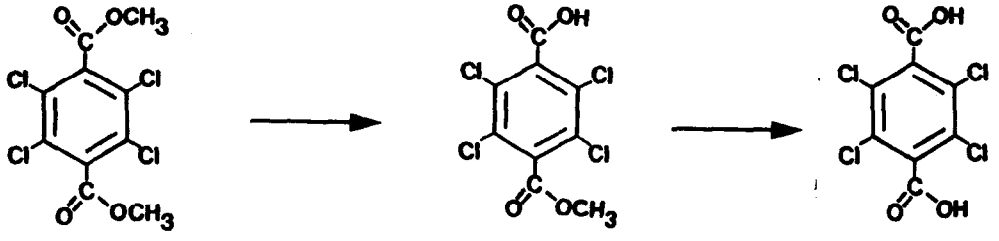

Figure 1. Degradation pathway of chlorthal-dimethyl in the environment.

In 1988, chlorthal-dimethyl was found in three[1] monitoring wells in Monterey County; however, residues from both wells were considered to have originated from point source contaminations (Cardozo, et al., 1988). In 1990, the California Department of Pesticide Regulation (CDPR) was notified that two California municipal wells sampled during the United States Environmental Protection Agency's (EPA) National Pesticide Survey were determined to contain chlorthal-dimethyl metabolites. The CDPR staff conducted four-section well surveys in Los Angeles and Santa Clara counties and confirmed the detections at both well sites, as well as in two other wells in Los Angeles County and five other wells in Santa Clara County. Based on these results, it appears that the presence of TPA in ground water resulted from nonpoint sources.

The detections prompted the CDPR staff to conduct a well water survey to investigate regions of the state where chlorthal-dimethyl is used in agriculture. Water samples were analyzed for chlorthal-dimethyl and its two metabolites, TPA and MTP. Additional backup water samples were screened for the herbicides atrazine, simazine, diuron, prometon, and bromacil. These herbicides are found in regulation on the Ground Water Protection List Part A, which consists of chemicals known to leach in the soil.

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[1] The 1988 Well Inventory Report (Cardozo, et al., 1988) reported in error that chlorthal-dimethyl had been detected in two monitoring wells in Monterey County; it was detected and confirmed in three monitoring wells in Monterey County during sampling conducted by the Central Coast Regional Water Quality Control Board in 1987.

MATERIALS AND METHODS

Site Description and Methods

The well survey was conducted in seven counties. Fresno, Kern, Los Angeles, Monterey, San Luis Obispo, and Santa Barbara counties were selected based upon the moderate to high chlorthal-dimethyl use (lb ai per county) reported for each region (Table 1). Tulare County, although a low use county, was chosen because it represented an area thought to be hydrogeologically sensitive to pesticide leaching.

Table 1. Chlorthal-dimethyl use for seven counties

County	Chlorthal-dimethyl use* lb active ingredient Year 1986	1987	1988
Fresno	75,579	84,735	51,966
Kern	28,109	17,962	14,548
Los Angeles	26,802	19,158	14,661
Monterey	126,554	125,932	107,194
San Luis Obispo	18,148	16,187	15,596
Santa Barbara	37,820	40,225	41,381
Tulare	2,721	1,588	0

* Source: CDFA Monthly Pesticide Use Report (January through December) for 1986, 1987 and 1988.

Pesticide use information from 1986 to 1988 was obtained from the California Department of Food and Agriculture's (CDFA) Monthly Pesticide Use Reports and additional use information for 1989 and 1990 was collected from Fresno, Kern, Los Angeles, and Tulare county agricultural commissioners' records. Use information gathered from both sources was transcribed onto county road maps to pictorially illustrate the quantity and location (township-range-section) of chlorthal-dimethyl applied within the four-year period (Figure 2). These maps served as field guides for locating potential sampling locations.

Well selection within the seven counties was based upon three criteria: The first was preferential sampling of available domestic wells over irrigation wells because domestic wells are usually shallower and therefore of greater value in assessing pesticide movement into ground water. Domestic wells are

also generally less susceptible to point source contamination because they are better sealed than irrigation wells (Sava, 1986). Secondly, clusters of moderate to high use sections were targeted, and wells were located adjacent to commodities where chlorthal-dimethyl use could have occurred. It was preferred that the sampled wells be situated near commodities reporting high use for that specific county (Table 2). An example for Kern County would be the preferential sampling of wells near onion or garlic fields (high reported use) versus sampling wells near broccoli or cabbage fields (no reported use). Finally, attempts were made to spatially distribute well sampling sites throughout the high use areas. All wells sampled required the permission of the well owner.

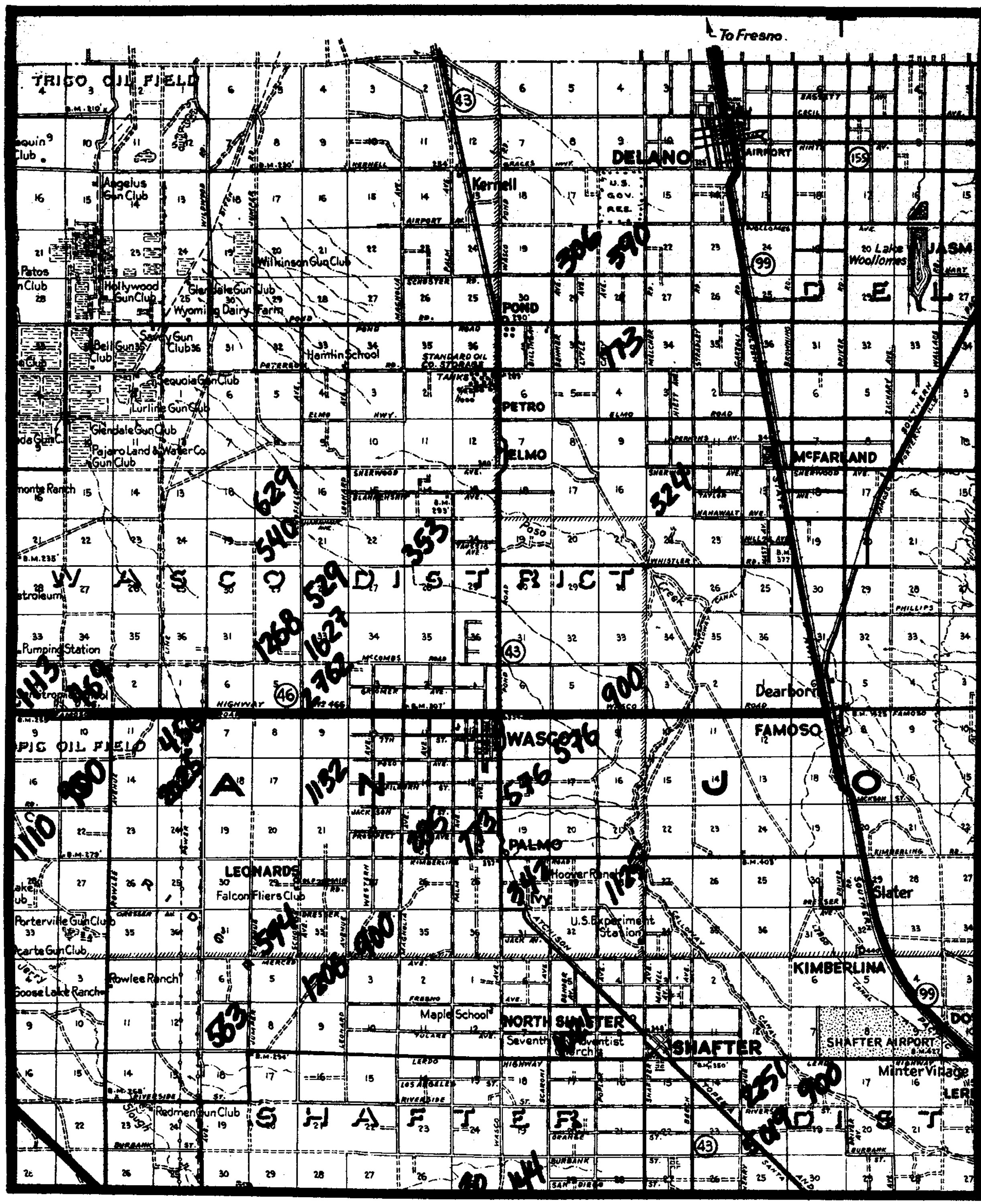

Figure 2. Kern County road map showing chlorthal-dimethyl use. Numbers indicate pounds of active ingredient per section.

Table 2. Major chlorthal-dimethyl use (lb ai) for five agricultural crops*

Crop	Onion	Garlic	Broccoli	Cauliflower	Cabbage
1986					
Fresno	40,256	31,505	3,261	0	0
Kern	24,534	2,667	0	675	0
Los Angeles	23,894	0	0	0	0
Monterey	8,066	1,001	87,115	26,654	0
San Luis Obispo	0	0	14,798	2,886	460
Santa Barbara	0	0	23,955	12,311	0
Tulare	1,509	0	1,206	0	0
1987					
Fresno	67,037	11,649	0	0	0
Kern	16,553	324	540	0	0
Monterey	6,272	0	94,148	20,617	0
Los Angeles	863	0	0	0	0
San Luis Obispo	0	0	12,292	276	572
Santa Barbara	0	0	28,038	10,118	604
Tulare	1,472	0	74	0	0
1988					
Fresno	39,881	8,715	0	0	0
Kern	13,006	324	0	0	0
Los Angeles	13,100	0	0	0	0
Monterey	6,118	0	77,580	19,652	0
San Luis Obispo	0	0	10,880	3,145	1,388
Santa Barbara	0	0	26,683	11,390	1,994
Tulare	0	0	0	0	0

* Source: CDFA Pesticide Use Report for 1986, 1987, and 1988.

Sample Collection

Sixty wells in agricultural areas were sampled for well water from August 6 through August 23, 1990. Water samples were collected after the pump had actively drawn water for 10 min. to remove any standing water in the casing so that a representative ground water sample could be obtained. When possible, samples were collected from a faucet, Schrader valve, or other available orifice prior to entering the pressure tank. Water temperature and pH were recorded at each well location. Additional information concerning well condition (i.e., casing material, existence and condition of well cap, well environment) were collected through observation by CDPR staff and through conversation with the well owner or other person(s) knowledgeable about the well.

Water samples were collected in six 1-liter amber glass bottles which consisted of five replicate well water samples (one primary and four backup) and one field blank filled with de-ionized water at the well site. Samples were placed immediately on wet ice and remained chilled until analyzed.

Laboratory Analytical Methods

Chlorthal-Dimethyl and Breakdown Products. Chemical analyses for chlorthal-dimethyl and metabolite residues were conducted by two laboratories using different analytical methods. The primary and field blank samples were analyzed by the CDFA Chemistry Laboratory Services Branch (Sacramento, California) for chlorthal-dimethyl, MTP, and TPA with minimum detection limits of 0.05, 0.10 and 0.10 ppb, respectively. One replicate backup sample from each well was analyzed by the confirming laboratory, Agriculture Priority and Pollutants Laboratory (APPL) located in Fresno, California. Initially, APPL was to distinguish between chlorthal-dimethyl and total metabolite (MTP and TPA) residues in water samples, however, this was unsuccessful and consequently samples were analyzed for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined) with a minimum detection limit of 0.01 ppb.

Water samples prepared by CDFA were acidified (pH<1) with concentrated sulfuric acid to allow for protonation of the metabolites. Equal volumes of diethyl ether and petroleum ether were used to extract chlorthal-dimethyl,

MTP, and TPA which were collected in the organic phase of the separation process. Anhydrous sodium sulfate was then added to remove any water and the remaining solvent was reduced to 1 to 3 ml by evaporation on a rotary evaporator. Diazopropane was then used to derivatize the residue so that differentiation could be made between tetrachlorterephthalate and its isomer tetrachlorophthalate by gas chromatography and mass spectroscopy. Samples were analyzed on a Hewlett-Packard Model 5890 Gas Chromatograph equipped with a series 5970 Mass Selective Detector. Gas chromatograph conditions (Appendix A) were as follows - Column: HP-1 (25 m x 0.2 mm x 0.33 µm film); carrier: helium at 50 cc/sec; column temperature: initial 60 °C and final 250 °C at 20 °C/min rate; detector and injector temperature: (250 °C) and volume injected: 2 µl.

The analytical procedures employed by APPL were significantly different from those used by CDFA. Interfering compounds were first removed by acidifying the water samples with sulfuric acid, extracting with diethyl ether, adding potassium hydroxide and water (to partition into the aqueous phase), then evaporating the ether. Extraction of the chlorthal-dimethyl and metabolites was accomplished by acidifying with sulfuric acid and partitioning into diethyl ether. The ether extract was dried by adding sodium sulfate and filtering, then concentrated using a Kuderna-Danish apparatus. Diazomethane was used as the derivitizing agent, so differentiation between chlorthal-dimethyl and the metabolites was not possible. The extracts were analyzed on a Hewlett-Packard 5890 gas chromatograph equipped with an electron capture detector. Gas chromatograph conditions were as follows - Column: SPB-5 (30 m x 0.25 mm x 0.25 µm film); carrier: 5% methane in argon at 1-2 cc/sec; column temperature: initial 60 °C and final 280 °C at 16 °C/min rate; injector temperature: 200 °C; detector temperature: 325 °C; and volume injected: 2 µl.

Atrazine, Simazine, Bromacil, Prometon, and Diuron. Residue analysis was conducted by the CDFA laboratory and Enseco-California Analytical Laboratory located in Sacramento, California for atrazine, simazine, bromacil, prometon, and diuron with a minimum detection limit of 0.10 ppb for each compound (Appendix A). Water samples were trapped in a C-18 reversed phase Sep-pak which was then centrifuged to remove any available water. By creating a

vacuum, methanol was brought into the system to condition the Sep-pak, followed by the addition of distilled water. The water sample was then taken up through a glass tube (Sep-pak attached) and the Sep-pak removed and centrifuged for 1 minute. All chemicals were eluted from the Sep-pak using methanol and the vacuum system and were transferred to a test tube to be concentrated using a nitrogen evaporator. Atrazine, simazine, and prometon were analyzed by gas chromatography while diuron and bromacil were analyzed by liquid chromatography. Equipment and operation conditions are included in Appendix A.

Laboratory Quality Control for Chlorthal-Dimethyl and Breakdown Products

Method Validation. Three replicate samples using three spike levels (0.2, 0.5, and 1.0 ppb) for chlorthal-dimethyl, MTP, and TPA were used to calculate the mean percent recovery and standard deviation (SD) to determine warning and control limits (mean $\pm$ 1SD and $\pm$ 3SD) for each compound.

Storage Dissipation. Prior to field sample collection and analysis, well water samples obtained from a source determined to be free of pesticides were each spiked at 2.0 ppb for chlorthal-dimethyl, MTP, and TPA and examined at day 0, 14, 28, 42, and 56 for compound dissipation.

Continuing Quality Control. One blank matrix (de-ionized water) and one blank matrix spike (de-ionized water containing a known concentration of herbicide) were analyzed with each extraction set. Reanalysis of the extraction set would have been required if recovery of the associated blank matrix spike concentration exceeded the established control limits for any of the compounds.

Interlaboratory Quality Control. To compare results obtained between CDFA and APPL laboratories, replicate water samples from seventeen wells were divided between laboratories for TPA residue analysis.

Laboratory Quality Control for Atrazine, Simazine, Bromacil, Prometon, and Diuron

Continuing Quality Control. One blank matrix spike (2.0 or 4.0 ppb) of atrazine, simazine, bromacil, prometon, or diuron was analyzed with each extraction set. Reanalysis of the extraction set would have been necessary if the recovery level associated with the blank matrix spike concentration exceeded the established control limit for the compounds.

Quality control results for all compounds are presented in Appendix B.

Sample Verification

Analytical confirmation of samples by the primary laboratory (CDFA) was done by a second laboratory (APPL) which was able to determine the presence of total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined). Confirmation of samples by CDFA for atrazine, simazine, bromacil, prometon, and diuron was also made by a second laboratory (Enseco-California Analytical Laboratory).

RESULTS

The data presented and discussed in this section, unless otherwise mentioned, refer only to those results obtained by CDFA, the primary laboratory. The CDFA laboratory was able to confirm all findings of TPA to be that of tetrachloroterephthalic acid and not the isomer tetrachlorophthalate.

The analytical results obtained from the three laboratories performing chemical analyses (CDFA, APPL, and Enseco-California Analytical Laboratory) for chlorthal-dimethyl residue, atrazine, simazine, bromacil, prometon, and diuron are presented in table form in Appendix C. These tables include confirmed and unconfirmed values. Each sampled well was assigned an identification number (Appendix C) which can be used to cross reference the well location in maps presented in Appendix D.

Detection of Chlorthal-Dimethyl and Breakdown Products

Of the sixty wells sampled, seventeen wells (28%) in five of seven counties were determined by CDFA laboratory to contain only TPA residue ranging in concentration from 0.18 to 15.00 ppb (Table 3 and Figure 3). APPL laboratory was able to verify these seventeen wells for TPA when it was the only compound detected by the primary laboratory. An additional well which was unconfirmed for TPA was also unconfirmed for chlorthal-dimethyl and MTP residues. Since more than one compound was detected in this well by the primary laboratory, all three compounds were considered to be unconfirmed detections since APPL was unable to speciate between compounds. This well was located in Monterey County and was the only well in the study determined by CDFA laboratory to contain more than one chlorthal-dimethyl residue.

Based upon general observation, the condition of the seventeen confirmed positive wells showed no visible cracks or holes present in either the cap or casing. It also appeared that the wells were located in areas where irrigation water would not pool near the well head.

The predominant region of chlorthal-dimethyl use in Fresno County was located along Interstate 5 from Mendota south to Huron. Lack of available wells in this area resulted in sampling a greater number of wells east of Kerman where use was less concentrated and reported to be much lower. Sampling resulted in the detection of two positive wells located near the city of Fresno with TPA residue levels of 1.10 and 1.50 ppb.

In Kern County, areas located near Mettler, Lamont, Shafter, and Wasco were identified as high use regions. Of the ten wells sampled in these areas, five were positive for TPA with concentrations ranging from 0.80 to 15.00 ppb. At least one positive well was located in each high use region, with the exception of the Mettler area, where no positive wells were detected. The highest TPA level was found from a well near Wasco.

Use of chlorthal-dimethyl in Monterey County was prevalent along Highway 101 from Castroville south to King City. Sampled wells were distributed from Castroville south to Greenfield. TPA detections ranged from 0.43 to 6.90 ppb. A well containing the highest detected TPA concentration in Monterey County was located east of Greenfield. A well sampled near Gonzales contained chlorthal-dimethyl, MTP, and TPA which were considered to be unconfirmed detections as the confirming laboratory was not able to differentiate between compounds.

In San Luis Obispo County, herbicide use was concentrated east of Highway 101 from Arroyo Grande south to the county border. One well located northeast of Guadalupe, near the Santa Maria River contained 1.50 ppb TPA.

Two major chlorthal-dimethyl use regions were identified in Santa Barbara County. One area was near Lompoc and the other was east of Santa Maria, from Guadalupe south to Betteravia. Wells were sampled in both regions and resulted in the following: one positive well near Lompoc (0.18 ppb) and three wells west of Santa Maria containing TPA concentrations ranging from 2.60 to 11.00 ppb.

In Los Angeles County, four wells were sampled near Lancaster, an area reporting significant herbicide use. No wells were found to contain chlorthal-dimethyl residue.

In Tulare County, documented use occurred in three areas (Strathmore, Waukena, and south of Earlimart) and wells were sampled in each region, with no detections.

Table 3. Chlorthal-dimethyl residue well water survey summary data

County	Number of wells sampled	Number of wells confirmed positive	TPA concentration (ppb) Range Low	High
Fresno	15	2	1.10	1.50
Kern	10	5	0.80	15.00
Los Angeles	4	0	ND*	ND
Monterey	15	5	0.40	6.90
San Luis Obispo	3	1	1.50	1.50
Santa Barbara	7	4	0.18	11.00
Tulare	6	0	ND	ND
TOTAL	60	17	--	--

* ND = Not detected, minimum detection limit for TPA is 0.10 ppb.

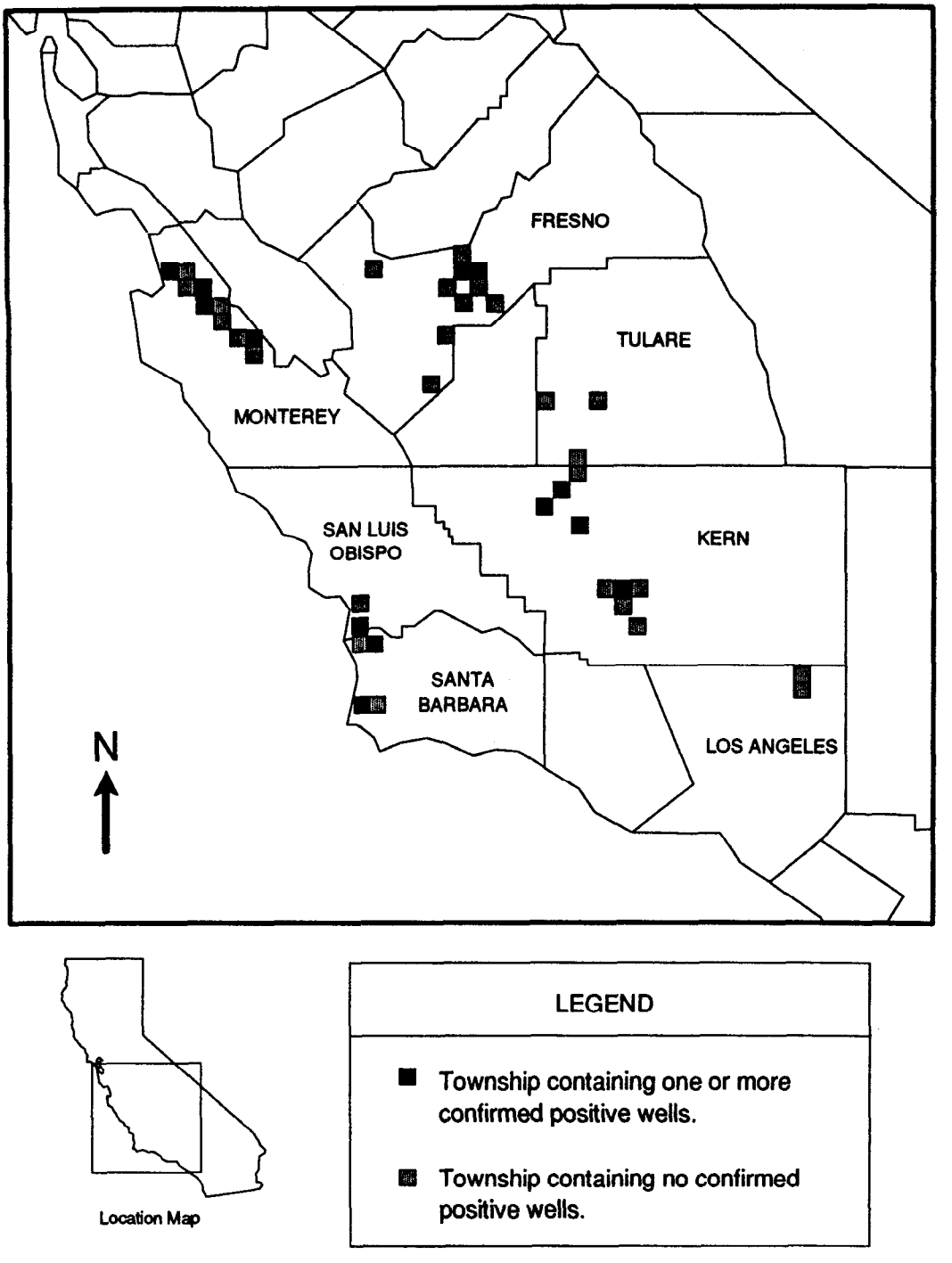

Figure 3. Township location of wells sampled for chlorthal-dimethyl, MTP, and TPA in the seven counties selected for sampling. Each township (square) is 6×6 miles.

Atrazine, Simazine, Bromacil, Prometon, and Diuron

Simazine and diuron were detected in the survey. Since the sampled wells were not selected based on atrazine, simazine, bromacil, prometon, or diuron use patterns in mind, it was not surprising to find only three wells containing these herbicide residues. Prometon, bromacil, and atrazine were not found in any of the seven counties.

Fresno County was reported to have two confirmed simazine and one confirmed diuron detections. Two wells which were located west of Selma contained simazine at levels of 0.30 and 0.50 ppb and were not positive for additional pesticides. The well confirmed positive for diuron was located west of the city of Fresno. This well contained 0.10 ppb diuron and had no detectable levels of other pesticide residues. There were no confirmed simazine or diuron detections reported for wells sampled from Kern, Los Angeles, Monterey, San Luis Obispo, Santa Barbara, and Tulare counties.

Laboratory Quality Control for Chlorthal-Dimethyl and Breakdown Products

Method Validation. The average percent recovery for chlorthal-dimethyl, MTP, and TPA at three spike levels (0.2, 0.5, and 1.0 ppb) were 112, 98, and 79%, respectively. Coefficients of variation for the three compounds were very similar, ranging from 6.9 to 8.6% (Appendix B, Tables B1, B2, and B3).

Storage Dissipation. Results in Tables B7, B8, and B9 (Appendix B) indicate that the degradation of chlorthal-dimethyl, MTP, and TPA was not an important factor when samples were stored up to two months.

Continuing Quality Control. The average percent recoveries for chlorthal-dimethyl, MTP, and TPA were 105, 96, and 83%, respectively (Appendix B, Tables B4, B5, and B6). The coefficients of variation for the three compounds ranged from 6.8 to 9.7%.

Interlaboratory Quality Control. The average relative percent difference between laboratories for TPA analysis in seventeen samples was 13.9% (Table B10, Appendix B).

Laboratory Quality Control for Atrazine, Simazine, Bromacil, Prometon, and Diuron

Continuing Quality Control. The mean percent recoveries for atrazine, simazine, bromacil, prometon, and diuron ranged from 96 to 98%. Coefficients of variation ranged from 7.4 to 13.7% (Appendix B, Tables B11, B12, B13, B14, and B15). All sample values fell within control limits (Appendix A).

DISCUSSION

The presence of the single unconfirmed chlorthal-dimethyl detection in the survey may be attributed to its low water solubility (0.5 ppm), a physical property which affects the magnitude of soil pesticide movement (Menges and Hubbard, 1970). Miller et al. (1978) and Ross et al. (1989) also reported minimal movement of chlorthal-dimethyl residues in soil.

The single unconfirmed detection of MTP may be due to the fact that the half-life of this metabolite is reported to be very short under aerobic soil conditions. The rapid conversion of MTP to TPA (Fermenta Plant Protection Co., 1986) may explain the lack of MTP detections in this study.

TPA was the only chlorthal-dimethyl residue whose presence was confirmed. TPA was the predominant residue detected and was found in ground water in the high chlorthal-dimethyl use counties. Laboratory leaching studies showed TPA to be the major residue detected in leachate when radiolabeled chlorthal-dimethyl was applied to a sandy loam soil (Fermenta Plant Protection Co., 1986). TPA's ability to leach more easily than chlorthal-dimethyl or MTP may explain why it was more frequently detected in the well survey.

The findings from this survey suggest that residues of the chlorthal-dimethyl metabolite (TPA) in ground water is the result of agricultural use and that leaching is a probable means for explaining these herbicide detections in ground water. TPA was the predominant residue detected in the study and would probably be the most commonly detected ground water residue in other high use regions.

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APPENDIX A

ANALYTICAL METHODS

ANALYSIS OF TOTAL CHLORTHAL-DIMETHYL RESIDUES (CHLORTHAL-DIMETHYL, MTP, AND TPA) IN GROUNDWATER

Solvent Cleanup:

Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4 °C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into a 250-mL Erlenmeyer flask, and pour the organic layer into a 125-mL Erlenmeyer flask containing about 0.5 g of acidified sodium sulfate. Repeat the extraction twice more the 10-mL aliquots of diethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hrs.

Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Preset the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60 -65 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and preset the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

Determine the original sample volume by refilling the sample bottle to the mark with water and transferring to a 1-liter graduated cylinder. Record the sample volume to the nearest 5 mL.

Esterification:

The Diazald Kit may be used for the generation of diazomethane. The Diazald Kit method is good for large quantities of samples needing esterification. The diazomethane derivatization (U.S. EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use a mechanical pipetting aides.
- Do not heat above 90 °C -- EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers -- EXPLOSION may result.
- Store away from alkali metals -- EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

Diazald kit method: Instructions for preparing diazomethane are provided with the generator kit.

Add 2 mL of diazomethane solution and let sample stand for 10 min. with occasional swirling.

Rinse inside wall of ampule with several hundred uL of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

Dissolve the residue in 5 mL of hexane. Analyze by gas chromatography.

Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 min.

Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions may occur. Analyze by gas chromatography. Minimum detection limit for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined) is 0.01 ppb.

INSTRUMENT PARAMETERS

I. Interpreter Parameters:

* Zero = 10
* Attenuation = 8
* Chart speed = 0.1 cm/min
* Peak Width = 0.04
* Threshold = 5
* Area reject = 5
* Time (front)
  i. Chart speed 0.5 at 10 min
  Time (back)
  i. Chart speed 0.5 at 9 min
  ii. Stop time at 24.0 min

II. G.C. Parameters:

* GC Hewlett Packard 5890 equipped with an electron capture detector
* Initial oven temp = 60 °C
* Initial time = 1.0 min.
* Equilibrium time = 1.0 min.
* Oven tem. ramp = 16 °C/min.
* Final oven temp = 280 °C
* Final time = 9.25 min.
* Run length = 24. 0 min.
* Injector temp = 200 °C
* Detector temp (ECG) = 325 °C
* Signal range = 2
* Zero = 10
* Attenuation = 8
* Purge
  1) initial off
  2) on at 0.7 min.
  3) off at 23.9 min.
* Injection sample size: 2 ul; splitless mode with splitless inserts
* Front column: SPB-608 30m x 0.25mm ID w/ 0.25 m film thickness
* Rear column: SPB-5 30m x 0.25mm ID w/ 0.25 m film thickness
* Flow rates/Gas types
  - Carrier gas: 5% methane in Argon @ 1-2 cc/min
  - Auxiliary gas: Grade 4.7 helium @ 30 cc/min
  - Detection limit: 0.01 ug/L

CALIFORNIA DEPT. OF FOOD & AGRIC.
CHEMISTRY LABORATORY SERVICES
ENVIROMENTAL MONITORING SECTION
3292 Meadowview Road
Sacramento, CA 95832
(916)+427-4408

Original Date:August 1, 1990
Supersedes: none
Current Date:December 18, 1990
Method #:Dacthal 90-1

DCPA (DACTHAL), MTP and TPA in Groundwater by GC/MSD

SCOPE:

This method is for the determination of dimethyl tetrachloroterephthalate (DCPA) and its degradation products monomethyltetrachloroterephthalate (MTP) and tetrachloroterephthalate (TPA) in groundwater samples. The detection limit of this method is 0.05 ppb for DCPA and 0.1 ppb for TPA and MTP.

PRINCIPLE:

The water sample is acidified below pH 1. DCPA, with the protonated MTP and TPA, are all extracted with diethyl ether. The residues are derivatized with diazopropane, and analyzed by gas chromatography on a capillary column using a mass selective detector (MSD).

REAGENTS AND EQUIPMENT:

1. *Reagents:*

Petroleum ether, grade suitable for pesticide residue analysis.

Diethyl ether, grade suitable for pesticide residue analysis. (grade not Suitable should be redistillated).

Sulfuric acid, concentrated, A.C.S. reagent grade.

Hydrochloric acid, concentrated, A.C.S. reagent grade.

Ethanol, 95%.

Potassium hydroxide, A.C.S reagent grade.

3-Nitro-1-nitroso-1propylguanidine, 98%, Aldrich 14319-7.

Sodium sulfate, anhydrous, suitable for pesticide residue analysis.

Diazopropane (see below)

PREPARATION OF DIAZOPROPANE:

Diazopropane is prepared from 3-Nitro-1-nitroso-1-propylguanidine. Assemble a distillation apparatus according to the Aldrich Technical Information Bulletin number AL-131 (cat #Z10,025-0).

The reaction flask is placed in a 65°C water bath on a hot plate with a magnetic stirring control. A 0.5-inch stirring bar is placed in the reaction flask and a 1-inch stirring bar is placed in the water bath. Both magnetic bars should be stirring. Place a separatory funnel in the side arm of the Claisen adaptor. Add 10 mL of 95% ethanol to a solution of 5 g KOH in 8 mL water in the reaction flask. 5 grams of 3-Nitro-1-nitroso-1-propylguanidine crystals are carefully transferred into the separatory funnel. Add 100 mL ether into the separatory funnel. The crystals are sparsely soluble in ether. Carefully open the stopcock of the funnel to allow the crystals and ether to drain into the reaction flask at a slow rate of about 1 hour for the entire 5 gm of crystals. Add an additional 50 mL of ether to rinse the separatory funnel and drain it into the reaction flask.

Diazopropane formed in the reaction is distilled, condensed and collected into a 500 ml flask in an ice bath. After completing the distillation, transfer the diazopropane solution to a 4-ounce brown bottle with a teflon-lined cap and store it in the freezer. This solution should be good for about a month in the freezer. (Diazopropane is explosive and a carcinogen, use with care)

2. Equipment:

Rotary evaporator (Buchi/Brinkmann, R110).

Nitrogen evaporator (Organomation Model #12).

Distillation kit (Aldrich Z10025-0)

Hotplate with magnetic stirrer, 10"x10"

ANALYSIS:

Sample Preparation:

1. Wash all glassware with 10% HCl, rinse them with deionized water and dry them in a 110°C oven.

2. Allow sample to equilibrate to ambient temperature. Measure 800 mL (or by weight) of the sample to be analyzed into a one-liter separatory funnel and record the volume or the weight to one decimal point.

3. Add 2.5 mL of the concentrated sulfuric acid to the water and mix it well.

4. Add 150 mL of 1:1 petroleum ether : diethyl ether (v/v). Shake it vigorously for 1.5 minutes. Vent frequently as pressure builds rapidly.

5. Allow the phase to separate. Drain the aqueous layer into a 1-liter beaker.

6. Pour the organic phase from the top of the separatory funnel into a 500-mL acid-washed beaker. Transfer the aqueous phase back to the separatory funnel.

7. Repeat steps 4 thru 6 twice. Combine the extracts.

8. Add approximately 20 mL of anhydrous sodium sulfate to the solvent extracts and immediately stir with a teflon rod to remove any water.

9. Pour the dried solvent to an acid-washed 500-mL flat bottom flask.

10. Rinse the beaker with 20 mL of the 1:1 ether mix and combine in the flask.

11. Evaporate the solvent to about 1-3 mL on a rotary evaporator at 35° and 20 inches of vacuum.

Derivatization of the Residues:

12. Add 1-3 mL of the diazopropane solution to the residue in the 500-mL flask.

13. Allow the reagent to contact the inside surface of the flask by swirling gently and let the reaction mixture sit in fume hood covered with aluminum foil for 20 minutes. (If the brownish color has disappeared within 20 minutes, add additional diazopropane and let the reaction mixture sit for another 20 minutes.)

14. Evaporate the solvent and the excess reagent to just dryness at ambient temperature using a gentle stream of nitrogen.

15. Pipet 5 mL hexane into the flask and swirl. The extract is ready for GC analysis.

Instrument Conditions:

Hewlett-Parkard Model 5890 Gas Chromatograph equipped with a series 5970 Mass Selective Detector, a Model 9000-340 Computer System Model 9000-340, and a Model 7673A Autosampler.

Column: HP-1 (cross-linked methyl silicon), 25 m X 0.2 mm X 0.33 um film.

Carrier:	Helium, 50 cm/sec
Column Temperature:	Initial 60°C 0.5 minute Program Rate 20°C/min Final 250°C 5 minutes
Injector Temperature:	250°C
Detector Temperature:	250°C
Ions Selected for SIM Acquisition:	221, 223, 282, 285, 299, 301, 304, 318, 329, 332, 360, 388.
Retention time:	DCPA, 12.5 min. MTP, 14.7 min. TPA, 17.2 min.
Volume Injected:	2 microliter

CALCULATIONS:
Report data in ppb.

$$\text{Analyte (ppb)} = \frac{PA1}{PA2} \times \frac{FV}{W} \times SC \times 1000$$

Where:

PA1 = peak area of analyte from injected sample volume
PA2 = peak area of analyte standard
FV = final volume of sample extract (in mL)
W = sample weight (in grams)
SC = standard concentration (in ng/mcL)

RESULTS and DISCUSSION:

Recovery:

Chemical Name	Spike Levels (ppb)	Recovery (%)	Standard Deviation	n
DCPA	1.0	108	2.3	3
	0.5	110	5.0	3
	0.2	115	12.5	3
MTP	1.0	99	7.0	3
	0.5	92	8.0	3
	0.2	100	7.5	3
TPA	1.0	81	5.0	3
	0.5	78	4.0	3
	0.2	75	11.5	3

Storage Stability:

Spike Level (ppb)	Storage Period (Week)	Recovered (in ppb) DCPA	MTP	TPA
2.0	0	2.15	2.07	1.51
2.0	0	2.10	2.08	1.44
2.0	2	2.02	1.98	1.77
2.0	2	2.05	2.10	1.45
2.0	4	2.00	2.10	1.59
2.0	4	2.00	2.10	1.55
2.0	6	2.16	2.10	1.53
2.0	6	2.20	2.10	1.54
2.0	8	2.12	2.04	1.31
2.0	8	2.10	2.00	1.50

pH 8 water: Water for storage stability study was provided by EHAP (labelled as drawn from "Joni's well"), prepared by adding 1 gram of Sodium bicarbonate per liter, and adjusted to pH 8 with 1 N Sodium hydroxide.

Storage stability samples of DCPA, MTP and TPA were fortified at 2.0 ppb by diluting 20 mL of 1 ng/mcL DCPA, MTP and TPA respectively in water to 10 liters with the pH 8 water. Each fortification was stored in 10 one-liter brown bottles which were kept in a refrigerator at 3-4^{o}C.

Discussion:

Our experience indicated that with this method all glassware must be rinsed with acid to ensure a decent recovery. We also noticed that the diethyl ether should be redistilled. The presence of many high background peaks were due to the impurity in the ether.

Recovery of DCPA is beyond 100%, ranging from 106% to 130% at 0.2 ppb to 1.0 ppb. This is probably due to the effect of solvent impurities. To verify this we performed an experiment by extracting a blank water sample according to the procedure described in this method. The only change was in step #15: 5 mL of hexane was replaced by 5 mL of 0.2 ng/uL DCPA in hexane. This resulted in a 20% higher peak area in the sample than in the standard. Further investigation of adding standard solution to the residue of evaporated solvents revealed the same high recovery. Therefore, we conclude that solvent impurities enhance the response of DCPA on the MSD when operated on selective ion monitor mode. This is also true for TPA and MTP. However, the final results of the analysis do not reveal this, due to the high polarity and low extraction efficiency of these two compounds.

We chose 12 ions for our detection throughout the entire analysis. Among them 4 ions were chosen from each of the three compounds, which are: 221, 299, 301, 332, (DCPA); 285, 318, 329, 360, (MTP); 223, 282, 304, 388, (TPA). The expected ratio of the ion intensities were confirmed, giving a high degree of confidence. Further confirmation with a full mass spectrometric scan always agreed with the initial selective ion detection whenever the residue level was greater than 1.0 ppb.

ACKNOWLEDGEMENTS:

I thank Mike Papathakis of the CDFA Chemistry Laboratory Services for his suggestion of using the mass selective detector, so that the low detection limit and better selectivity were achieved.

WRITTEN BY: PAUL LEE

Paul Lee

TITLE: AGRICULTURAL CHEMIST III

REVIEWED BY: CATHERINE COOPER

Catherine Cooper

TITLE: SUPERVISING CHEMIST

APPROVED BY: MARK LEE

Mark Lee

TITLE: AGRICULTURAL RESEARCH CHEMIST

APPROVED BY: TERRY JACKSON

Terry Jackson

TITLE: QUALITY ASSURANCE OFFICER

CALIFORNIA DEPT. OF FOOD & AGRIC.
CHEMISTRY LABORATORY SERVICES
ENVIRONMENTAL MONITORING SECTION
3292 Meadowview Road
Sacramento, CA 95832
(916)+427-4998/4999

Original Date:03/24/1990
Supercedes: NEW
Current Date:04/10/1990
Method #:

MULTIPESTICIDE RESIDUE ANALYSIS: ATRAZINE, BROMACIL, DIURON, PROMETON, SIMAZINE IN WELL WATER.

SCOPE:

This method is developed to analyze Atrazine, Bromacil, Diuron, Prometon, and Simazine in well water.

PRINCIPLE:

A conditioned C 18 reversed phase Sep-pak is used to trap Atrazine, Bromacil, Diuron, Prometon and Simazine from water samples. The Sep-pack is then centrifuged to eliminated any remaining water. Methanol is then used to elute all chemicals. The eluant is then concentrated and analyzed for Diuron and Bromacil by LC, for Atrazine, Prometon, Simazine by GC.

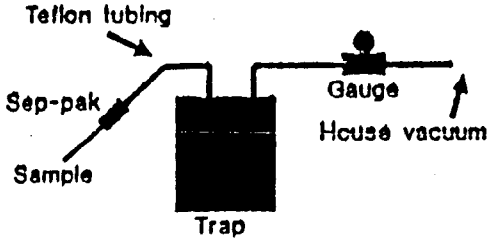
REAGENTS AND EQUIPMENT:

Methanol, pesticide grade or equivalent.
Distilled water.
Working standards in Methanol (Diluted from stock standard.)
In house vacuum manifold.
In house aspiration system.
C18 reversed phase Sep-pak, ® Water Division of Millipore.
Nylon acrodisc, 0.2 micron, Gelman Sciences.
Centrifuge: Clay Adams.
Beakers, 600 mL.
Graduated test tubes, 10 mL.
Micro-Mate Syringes, 10 cc - Popper & Sons Inc.
N-EVAP - Meyers Organomation Associates Incorporated
Vibrating mixer.
Sodium Sulfate, anhydrous, granular (ACS).

ANALYSIS:

1. For each sample, weigh 500.0 grams of water sample into two separated 600ml beakers.
2. Connect a C 18 reversed phase Sep-pak to the in house vacuum manifold as follows in diagram #1.

Diagram #1



ANALYSIS:

3. Condition the Sep-pak with about 5 mL of methanol followed by about 10 mL of distilled water by applying in house vacuum. Do not let the sep-pak go to dryness.
4. Attach the conditioned Sep pak to a 15 mm glass tubing and dip into the beaker containing the 500g of sample. Adjust the flow rate to about 3-5 ml/minute (about 6 in Hg).
5. After all 500g of water sample has passed through the Sep-pak, leave the vacuum on for few minutes.
6. Remove the Sep-pak and insert the sep-pak into a centrifuge tube and centrifuge for 1 minute at 1200 rpm by setting the dial at 4 on the centrifuge.
7. Elute all chemicals with 8 mL of methanol by using the in house aspiration system into a 10 mL graduate test tube.
8. Concentrate the eluting solvent to 1.0 mL by using the Nitrogen evaporator. Mix it well for 30 seconds by using the vibrating mixer. Filter through a 0.2 um acrodisc into three separated micro vials.

Analyze by gas chromatograph and liquid chromatograph

EQUIPMENT CONDITIONS:

A. Gas chromatograph: HP 3700 with TSD.
Column: HP-17 10 m x 0.53 mm. Film thickness: 2.0 um.
Temperature program: Isothermal 175°C.
Injector: 220°C, detector: 220°C.
Carrier gas: Helium. Flow rate: 20 mL/min.
Sample injected: 2 ul.
Retention times: Prometon ~ 2.40 minutes
Atrazine ~ 2.82 minutes
Simazine ~ 3.04 minutes

B. Liquid chromatography: Perkin Elmer Series 4.
Column: BECKMAN ODS, 5.0 um, 4.6 mm x 15.0 cm.
Guard column: BECKMAN ODS, 5.0 um, 4.6 mm x 4.5 cm.
Detector: Varian 2550 UV.
Flow rate: 1.0 ml/min.
Sample injected: 60 ul.

For Diuron analysis:
Mobile phase: 55% water, 45% acetonitrile.
Wave length: 254 nm.
Retention time: ~ 5.60 minutes.

For Bromacil analysis:
Movile phase: 70% water, 30% acetonitrile.
Wave length: 280 nm.
Retention time: ~ 5.14 minutes.

CONFIRMATION:Atrazine, Promoton and Simazine are confirmed by Varian 6000 with TSD. Column: 20 m x 0.53 mm x 1.3 um Carbowax.
Injector: 220°C, detector: 220°C.
Temperature program: Int:150°C.
Int time: 0 min.
Rate: 15°C/min.
Final time: 9 min.
Carrier gas: Helium. Flow rate:25 mL/min.

Retention times: Prometon ~ 5.7 minutes.
Atrazine ~ 7.8 minutes.
Simazine ~ 9.3 minutes.

Bromacil is confirmed by TSD/DB-1301 30 m x 0.53 mm x 1.0 um column.
Carrier gas: Helium. Flow rate: 25 mL/min.
Isothermal 190°C, injector: 220°C, detector: 220°C.
Retention time:~ 8.9 minutes.
Diuron *is not confirmed at MDL level.*

CALCULATIONS:

$$PPB = \frac{\text{Peak height of sample x Amount of std(ng) x 1,000ul}}{\text{Peak height of std x volume injected x sample weight(g)}}$$

DISCUSSION:

Minimum detection limit (Signal to noise ratio is 5 to 1.) for these chemicals by this method was 0.1ppb.

DIODE ARRAY DETECTOR was tried to analyze bromacil and diuron. However, the sensitivity did not meet the requirement.

The diagram #1 is a in house system. If you have any question about it, please contact the above address.

The following results were obtained from different spike levels by multipoints calibration method:

Chemical	Spike level (ppb)	Number of analysis (n)	Mean % Recovery	Standard deviation (+/-)
Atrazine	4.0	5	102.7	7.9
Prometon	4.0	5	105.5	9.6
Simazine	4.0	5	107.4	8.8
Bromacil	4.0	5	103.5	6.2
Diuron	4.0	5	102.2	4.7

DISCUSSION:

Chemical	Spike level (ppb)	Number of analysis (n)	Mean % Recovery	Standard Deviation (+/-)
Atrazine	2.0	5	90.4	3.5
Prometon	2.0	5	91.5	4.8
Simazine	2.0	5	89.4	6.6
Bromacil	2.0	5	87.7	6.8
Diuron	2.0	5	88.2	7.2
Atrazine	0.5	10	106.8	13.3
Prometon	0.5	10	103.0	6.9
Simazine	0.5	10	105.6	15.6
Bromacil	0.5	10	92.0	9.7
Diuron	0.5	10	99.6	14.8

REFERENCES:

WRITTEN BY: Duc Tran

TITLE: Agricultural Chemist I

REVIEWED BY: Catherine Cooper

TITLE: Agricultural Chemist III

APPROVED BY: S. Mark Lee

TITLE: Principal Investigator

APPENDIX B

QUALITY CONTROL

Table B1. Method validation data (% recoveries) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Dacthal
MDL: 0.05 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
651	0.23	0.2	115			
650	0.26	0.2	130			
649	0.21	0.2	105			
648	0.58	0.5	116			
647	0.53	0.5	106			
646	0.55	0.5	110			
645	1.10	1.0	110			
644	1.06	1.0	106			
643	1.10	1.0	110			
			OVERALL:	112	7.76	6.93

Table B2. Method validation data (% recoveries) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: MTP
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
663	0.22	0.2	110			
662	0.20	0.2	100			
661	0.19	0.2	95			
666	0.43	0.5	86			
665	0.45	0.5	90			
664	0.50	0.5	100			
669	1.04	1.0	104			
668	0.93	1.0	93			
667	1.01	1.0	101			
			OVERALL:	98	7.4	7.6

Table B3. Method validation data (% recoveries) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: TPA
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
660	0.14	0.2	70			
659	0.18	0.2	90			
658	0.14	0.2	70			
657	0.39	0.5	78			
656	0.38	0.5	76			
655	0.41	0.5	82			
654	0.80	1.0	80			
653	0.87	1.0	87			
652	0.78	1.0	78			
			OVERALL:	79	6.8	8.6

Table B4. Continuing quality control data for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Dacthal
MDL: 0.05 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
25, 55, 265, 337, 343, 349, 379, 391, 541-2	345	0.50	0.5	100			
13, 49, 235, 283, 289, 319, 355	384	0.56	0.5	112			
31, 121, 127, 151, 181, 241, 259, 277, 367, 373, 415	449	0.54	0.5	108			
15, 421, 433, 481, 495, 499, 511, 523, 535, 545,-6	447	0.52	0.5	104			
397, 403, 457, 475, 505, 529	557	0.48	0.5	96			
79, 109, 361, 439	553	0.56	0.5	112			
1, 97, 103, 115, 139, 157, 193, 199, 203	555	0.56	0.5	112			
37, 73, 85, 175, 253, 307	550	0.55	0.5	110			
18, 30, 60, 240, 288, 342, 348, 354, 360, 384	548	0.55	0.5	110			
162, 180, 258, 438, 486, 492-3, 504, 516, 522	547	0.56	0.5	112			
36, 126, 132, 156, 186, 246, 264, 282, 372, 378	545	0.52	0.5	104			
42, 108, 120, 204, 408, 426	577	0.49	0.5	98			
6, 54, 198, 210, 270, 294, 324, 396, 480, 510	575	0.46	0.5	92			
312, 366, 420, 444, 462, 540	573	0.48	0.5	96			
				OVERALL:	105	7.13	6.81

Table B5. Continuing quality control data for the 1990 Dacthal Well Survey.

Study: 98
Analyte: MTP
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
25, 55, 265, 337, 343, 349, 379, 391, 541-2	345	0.51	0.5	102			
13, 49, 235, 283, 289, 319, 355	384	0.54	0.5	108			
31, 121, 127, 151, 181, 241, 259, 277, 367, 373, 415	449	0.49	0.5	98			
15, 421, 433, 481, 495, 499, 511, 523, 535, 545,-6	447	0.45	0.5	90			
397, 403, 457, 475, 505, 529	557	0.51	0.5	102			
79, 109, 361, 439	553	0.44	0.5	88			
1, 97, 103, 115, 139, 157, 193, 199, 203	555	0.49	0.5	98			
37, 73, 85, 175, 253, 307	550	0.49	0.5	98			
18, 30, 60, 240, 288, 342, 348, 354, 360, 384	548	0.52	0.5	104			
162, 180, 258, 438, 486, 492-3, 504, 516, 522	547	0.52	0.5	104			
36, 126, 132, 156, 186, 246, 264, 282, 372, 378	545	0.43	0.5	86			
42, 108, 120, 204, 408, 426	577	0.48	0.5	96			
6, 54, 198, 210, 270, 294, 324, 396, 480, 510	575	0.42	0.5	84			
312, 366, 420, 444, 462, 540	573	0.40	0.5	80			
				OVERALL:	96	8.6	9.0

Table B6. Continuing quality control data for the 1990 Dacthal Well Survey.

Study: 98
Analyte: TPA
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
25, 55, 265, 337, 343, 349, 379, 391, 541-2	345	0.43	0.5	86			
13, 49, 235, 283, 289, 319, 355	384	0.44	0.5	88			
31, 121, 127, 151, 181, 241, 259, 277, 367, 373, 415	449	0.42	0.5	84			
15, 421, 433, 481, 495, 499, 511, 523, 535, 545,-6	447	0.41	0.5	82			
397, 403, 457, 475, 505, 529	557	0.34	0.5	68			
79, 109, 361, 439	553	0.40	0.5	80			
1, 97, 103, 115, 139, 157, 193, 199, 203	555	0.49	0.5	98			
37, 73, 85, 175, 253, 307	550	0.42	0.5	84			
18, 30, 60, 240, 288, 342, 348, 354, 360, 384	548	0.45	0.5	90			
162, 180, 258, 438, 486, 492-3, 504, 516, 522	547	0.42	0.5	84			
36, 126, 132, 156, 186, 246, 264, 282, 372, 378	545	0.36	0.5	72			
42, 108, 120, 204, 408, 426	577	0.45	0.5	90			
6, 54, 198, 210, 270, 294, 324, 396, 480, 510	575	0.36	0.5	72			
312, 366, 420, 444, 462, 540	573	0.41	0.5	82			
				OVERALL:	83	8.0	9.7

Table B7. Storage dissipation analyses for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Dacthal
MDL: 0.05 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
670	0	7/17/90	7/18/90	2.15	2.0	108			
671	0	7/17/90	7/18/90	2.10	2.0	105	107	2.12	1.99
696	14	7/30/90	7/31/90	2.02	2.0	101			
695	14	7/30/90	7/31/90	2.05	2.0	103	102	1.41	1.39
676	28	8/14/90	8/15/90	2.00	2.0	100			
678	28	8/14/90	8/15/90	2.00	2.0	100	100	0	0
683	42	8/27/90	9/5/90	2.16	2.0	108			
684	42	8/27/90	9/5/90	2.20	2.0	110	109	1.41	1.30
689	56	9/14/90	9/17/90	2.12	2.0	106			
690	56	9/14/90	9/17/90	2.10	2.0	105	106	0.71	0.67
						OVERALL:	105	3.53	3.38

Table B8. Storage dissipation analyses for the 1990 Dacthal Well Survey.

Study: 98
Analyte: MTP
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
672	0	7/17/90	7/18/90	2.07	2.0	104			
673	0	7/17/90	7/18/90	2.08	2.0	104	104	0	0
698	14	7/30/90	7/31/90	1.98	2.0	99			
697	14	7/30/90	7/31/90	2.10	2.0	105	102	4.24	4.16
679	28	8/14/90	8/15/90	2.10	2.0	105			
680	28	8/14/90	8/15/90	2.10	2.0	105	105	0	0
685	42	8/27/90	9/5/90	2.10	2.0	105			
686	42	8/27/90	9/5/90	2.10	2.0	105	105	0	0
691	56	9/14/90	9/17/90	2.04	2.0	102			
692	56	9/14/90	9/17/90	2.00	2.0	100	101	1.41	1.40
						OVERALL:	103	2.27	2.20

Table B9. Storage dissipation analyses for the 1990 Dacthal Well Survey.

Study: 98
Analyte: TPA
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Paul Lee

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
674	0	7/17/90	7/18/90	1.51	2.0	76			
675	0	7/17/90	7/18/90	1.44	2.0	72	74	2.8	3.8
700	14	7/30/90	7/31/90	1.77	2.0	89			
699	14	7/30/90	7/31/90	1.45	2.0	73	81	11	14
681	28	8/14/90	8/15/90	1.59	2.0	80			
682	28	8/14/90	8/15/90	1.55	2.0	78	79	1.4	1.8
687	42	8/27/90	9/5/90	1.53	2.0	77			
688	42	8/27/90	9/5/90	1.54	2.0	77	77	0	0
693	56	9/14/90	9/17/90	1.31	2.0	66			
694	56	9/14/90	9/17/90	1.50	2.0	75	71	6.4	9.0
						OVERALL:	76	5.9	7.8

Table B10. Replicate/Confirmation (TPA) Analyses for the 1990 Dacthal Well Survey.

Study: 98
Analyte: TPA
Detection Limit: 0.10 (CDFA)
Detection Limit: 0.01 (APPL)

Lab: CDFA, APPL
Chemist: Paul Lee (CDFA)
Chemist: Steve Tallman (APPL)

EHAP CDFA #	EHAP APPL #	Lab/Method #1 CDFA (ppb)	Lab/Method #2 APPL (ppb)	$\bar{X}$	Relative Percent Difference
25	26	0.43	0.44	0.435	2.30
31	32	11	10.9	10.95	0.91
37	38	0.8	0.6	0.7	28.57
109	110	1.1	1.2	1.15	8.70
127	128	1.5	1.29	1.395	15.05
139	140	15	10.6	12.8	34.38
151	152	0.18	0.16	0.17	11.76
193	194	1.5	1.6	1.55	6.45
259	260	8	6.1	7.05	26.95
283	284	5.9	6.66	6.28	12.10
349	350	3	2.75	2.875	8.70
355	356	6.9	7.46	7.18	7.80
361	362	5.05	3.7	4.375	30.86
367	368	2.6	2.12	2.36	20.34
379	380	0.61	0.59	0.6	3.33
415	416	1.1	1.25	1.175	12.77
535	536	1.5	1.42	1.46	5.48
				OVERALL:	13.91

Table B11. Continuing quality control data (atrazine) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Atrazine
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Duc Tran

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
17, 27, 51, 57, 267, 285, 287, 291, 321, 334	729	1.79	2.0	89.5			
159, 177, 255, 309, 345, 351, 357, 381, 393, 418	747	4.30	4.0	107.5			
423, 436, 441, 483, 490, 501, 514, 519, 526, 538	748	4.00	4.0	100			
39, 81, 87, 111, 141, 195, 201, 207, 263	785	1.89	2.0	94.5			
3, 33, 75, 99, 117, 153, 183, 243, 261, 279	792	1.82	2.0	91			
123, 129, 369, 375, 399, 405, 459, 477, 507, 531	794	1.81	2.0	90.5			
237, 363	841	1.93	2.0	96.5			
				OVERALL:	96	6.42	6.71

Table B12. Continuing quality control data (simazine) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Simazine
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Duc Tran

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
17, 27, 51, 57, 267, 285, 287, 291, 321, 334	729	1.83	2.0	91.5			
159, 177, 255, 309, 345, 351, 357, 381, 393, 418	747	4.50	4.0	112.5			
423, 436, 441, 483, 490, 501, 514, 519, 526, 538	748	4.10	4.0	102.5			
39, 81, 87, 111, 141, 195, 201, 207, 263	785	1.93	2.0	96.5			
3, 33, 75, 99, 117, 153, 183, 243, 261, 279	792	1.75	2.0	87.5			
123, 129, 369, 375, 399, 405, 459, 477, 507, 531	794	1.85	2.0	92.5			
237, 363	841	1.99	2.0	99.5			
				OVERALL:	98	8.33	8.54

Table B13. Continuing quality control data (diuron) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Diuron
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Duc Tran

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
17, 27, 51, 57, 267, 285, 287, 291, 321, 334	729	1.87	2.0	93.5			
159, 177, 255, 309, 345, 351, 357, 381, 393, 418	747	3.90	4.0	97.5			
423, 436, 441, 483, 490, 501, 514, 519, 526, 538	748	3.90	4.0	97.5			
39, 81, 87, 111, 141, 195, 201, 207, 263	785	1.87	2.0	93.5			
3, 33, 75, 99, 117, 153, 183, 243, 261, 279	792	1.88	2.0	94			
123, 129, 369, 375, 399, 405, 459, 477, 507, 531	794	1.60	2.0	80			
237, 363	841	2.30	2.0	115			
				OVERALL:	96	10.31	10.76

Table B14. Continuing quality control data (bromacil) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Bromacil
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Duc Tran

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
17, 27, 51, 57, 267, 285, 287, 291, 321, 334	729	1.88	2.0	94			
159, 177, 255, 309, 345, 351, 357, 381, 393, 418	747	3.70	4.0	92.5			
423, 436, 441, 483, 490, 501, 514, 519, 526, 538	748	3.50	4.0	87.5			
39, 81, 87, 111, 141, 195, 201, 207, 263	785	2.11	2.0	105.5			
3, 33, 75, 99, 117, 153, 183, 243, 261, 279	792	2.14	2.0	107			
123, 129, 369, 375, 399, 405, 459, 477, 507, 531	794	1.52	2.0	76			
237, 363	841	2.30	2.0	115			
				OVERALL:	97	13.27	13.71

Table B15. Continuing quality control data (prometon) for the 1990 Dacthal Well Survey.

Study: 98
Analyte: Prometon
MDL: 0.1 ppb

Sample Type: Well Water
Lab: CDFA
Chemist: Duc Tran

Extraction Set #	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
17, 27, 51, 57, 267, 285, 287, 291, 321, 334	729	1.83	2.0	91.5			
159, 177, 255, 309, 345, 351, 357, 381, 393, 418	747	4.40	4.0	110			
423, 436, 441, 483, 490, 501, 514, 519, 526, 538	748	4.20	4.0	105			
39, 81, 87, 111, 141, 195, 201, 207, 263	785	1.99	2.0	99.5			
3, 33, 75, 99, 117, 153, 183, 243, 261, 279	792	1.80	2.0	90			
123, 129, 369, 375, 399, 405, 459, 477, 507, 531	794	1.89	2.0	94.5			
237, 363	841	1.92	2.0	96			
				OVERALL:	98	7.28	7.42

APPENDIX C

ANALYTICAL RESULTS OF WELL SURVEY

The following analytical results presented for Fresno, Kern, Los Angeles, Monterey, San Luis Obispo, Santa Barbara, and Tulare Counties represent confirmed and unconfirmed values obtained by CDFA and APPL laboratories for chlorthal-dimethyl, MTP, and TPA, and for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined), respectively. APPL laboratory was able to detect the presence of total chlorthal-dimethyl residue in single samples from 34 additional wells (including the Monterey County well containing chlorthal-dimethyl, MTP, and TPA as determined by CDFA); however, these detections were unconfirmed.

Chemical results reported by CDFA laboratory and Enseco-California Analytical Laboratory for atrazine, simazine, prometon, bromacil, and diuron are presented in the following tables. These results include confirmed and unconfirmed data.

Chemical Analyses Summary Table for Fresno County

County	Well[a] Number	Herbicide Detected	Herbicide Concentration (ppb) and Analyzing Laboratory		
			CDFA	APPL	ENSECO
Fresno	1	ND[b]	ND	ND	NA
	2	ND	ND	ND	NA[d]
	3	Total Residue[c]	ND	0.10	NA
	4	Total Residue	ND	0.16	NA
	5	Total Residue	ND	0.14	NA
	6	ND	ND	ND	NA
	7	Diuron	0.10	NA	0.15
	8	TPA;Total Residue[e]	1.10	1.25	NA
	9	TPA;Total Residue	1.50	1.42	NA
	10	Total Residue	ND	0.09	NA
	11	Total Residue	ND	0.11	NA
	12	Total Residue	ND	0.08	NA
	13	Total Residue	ND	0.15	NA
		Simazine	0.50	NA	0.48
	14	Total Residue	ND	0.16	NA
		Simazine	0.30	NA	0.30
	15	Total Residue	ND	0.11	NA

[a]Numerical assignment given by EHAP.

[b]None detected. CDFA minimum detection limit for chlorthal-dimethyl, MTP, and TPA is 0.05, 0.10, and 0.10 ppb, respectively. APPL minimum detection limit for total chlorthal-dimethyl residue is 0.01 ppb. CDFA and Enseco minimum detection limit for atrazine, simazine, diuron, prometon, and bromacil is 0.10 ppb for all compounds.

[c]CDFA analyzed samples for chlorthal-dimethyl, MTP, and TPA. APPL analyzed samples for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined).

[d]Not analyzed.

[e]TPA residue detected by CDFA; APPL only detected total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined), not individual analytes.

Chemical Analyses Summary Table for Kern County

County	Well[a] Number	Herbicide Detected	Herbicide Concentration (ppb) and Analyzing Laboratory CDFA	APPL	ENSECO
Kern	1	Total Residue[b]	ND[c]	0.15	NA[d]
	2	Total Residue	ND	0.12	NA
	3	Total Residue	ND	0.14	NA
	4	TPA;Total Residue[e]	1.10	1.20	NA
	5	Total Residue	ND	0.12	NA
	6	TPA;Total Residue	0.80	0.60	NA
	7	TPA;Total Residue	15.00	10.60	NA
	8	Total Residue	ND	0.08	NA
	9	TPA;Total Residue	5.05	3.70	NA
	10	TPA;Total Residue	1.50	1.60	NA

[a]Numerical assignment given by EHAP.

[b]CDFA analyzed samples for chlorthal-dimethyl, MTP, and TPA. APPL analyzed samples for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined).

[c]None detected. CDFA minimum detection limit for chlorthal-dimethyl, MTP, and TPA is 0.05, 0.10, and 0.10 ppb, respectively. APPL minimum detection limit for total chlorthal-dimethyl residue is 0.01 ppb. CDFA and Enseco minimum detection limit for atrazine, simazine, diuron, prometon, and bromacil is 0.10 ppb for all compounds.

[d]Not analyzed.

[e]TPA residue detected by CDFA; APPL only detected total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined), not individual analytes.

Chemical Analyses Summary Table for Los Angeles County

County	Well[a] Number	Herbicide Detected	Herbicide Concentration (ppb) and Analyzing Laboratory		
			CDFA	APPL	ENSECO
Los Angeles	1	Total Residue[b]	ND[c]	0.11	NA[d]
	2	Total Residue	ND	0.14	NA
	3	Total Residue	ND	0.09	NA
	4	Total Residue	ND	0.08	NA

[a]Numerical assignment given by EHAP.

[b]CDFA analyzed samples for chlorthal-dimethyl, MTP, and TPA. APPL analyzed samples for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined).

[c]None detected. CDFA minimum detection limit for chlorthal-dimethyl MTP, and TPA is 0.05, 0.10, and 0.10 ppb, respectively. APPL minimum detection limit for total chlorthal-dimethyl residue is 0.01 ppb. CDFA and Enseco minimum detection limit for atrazine, simazine, diuron, prometon, and bromacil is 0.10 ppb for all compounds.

[d]Not analyzed.

Chemical Analyses Summary Table for Monterey County

County	Well[a] Number	Herbicide Detected	Herbicide Concentration (ppb) and Analyzing Laboratory CDFA	APPL	ENSECO
Monterey	1	Total Residue [b]	ND[c]	0.03	NA[d]
	2	Total Residue	ND	0.04	NA
	3	TPA;Total Residue[e]	0.61	0.59	NA
	4	Total Residue	ND	0.06	NA
	5	TPA;Total Residue	3.00	2.75	NA
	6	TPA;Total Residue	0.43	0.44	NA
	7	Total Residue	ND	0.06	NA
	8	Total Residue	ND	0.09	NA
	9	Total Residue	ND	0.06	NA
	10	TPA;Total Residue	5.90	6.66	NA
	11	Total Residue	ND	0.03	NA
	12[f]	Chlorthal-dimethyl	0.68/0.60	NA	NA
		MTP	2.55/2.41	NA	NA
		TPA	0.86/0.83	NA	NA
		Total Residue	NA	7.14/3.20	NA
		Simazine	0.25	NA	NA
		Diuron	0.30	NA	NA
	13	Total Residue	ND	0.04	NA
	14	Total Residue	ND	0.05	NA
	15	TPA;Total Residue	6.90	7.46	NA

[a]Numerical assignment given by EHAP.

[b]CDFA analyzed samples for chlorthal-dimethyl, MTP, and TPA. APPL analyzed samples for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined).

[c]None detected. CDFA minimum detection limit for chlorthal-dimethyl, MTP, and TPA is 0.05, 0.10, and 0.10 ppb, respectively. APPL minimum detection limit for total chlorthal-dimethyl residue is 0.01 ppb. CDFA and Enseco minimum detection limit for atrazine, simazine, diuron, prometon, and bromacil is 0.10 ppb for all compounds.

[d]Not analyzed.

[e]TPA residue detected by CDFA; APPL only detected total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined), not individual analytes.

[f]Since more than one chlorthal-dimethyl compound was detected in this well by CDFA, the primary laboratory, all three chlorthal-dimethyl compounds were considered to be unconfirmed detections since APPL was unable to speciate between compounds (from p. 11).

Chemical Analyses Summary Table for San Luis Obispo County

County	Well[a] Number	Herbicide Detected	Herbicide Concentration (ppb) and Analyzing Laboratory		
			CDFA	APPL	ENSECO
San Luis Obispo	1	Total Residue[b]	ND[c]	0.05	NA[d]
	2	Total Residue	ND	0.12	NA
	3	TPA;Total Residue[e]	1.50	1.29	NA

[a]Numerical assignment given by EHAP.

[b]CDFA analyzed samples for chlorthal-dimethyl, MTP, and TPA. APPL analyzed samples for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined).

[c]None detected. CDFA minimum detection limit for chlorthal-dimethyl, MTP, and TPA is 0.05, 0.10, and 0.10 ppb, respectively. APPL minimum detection limit for total chlorthal-dimethyl residue is 0.01 ppb. CDFA and Enseco minimum detection limit for atrazine, simazine, diuron, prometon, and bromacil is 0.10 ppb for all compounds.

[d] Not analyzed.

[e]TPA residue detected by CDFA; APPL only detected total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined), not individual analytes.

Chemical Analyses Summary Table for Santa Barbara County

County	Well[a] Number	Herbicide Detected	Herbicide Concentration (ppb) and Analyzing Laboratory		
			CDFA	APPL	ENSECO
Santa Barbara	1	TPA;Total Residue[b]	2.60	2.12	NA[c]
	2	TPA;Total Residue	0.18	0.16	NA
	3	Total Residue[d]	ND[e]	0.09	NA
	4	Total Residue	ND	0.14	NA
	5	TPA;Total Residue	11.00	10.90	NA
	6	TPA;Total Residue	8.00	6.10	NA
	7	Total Residue	ND	0.10	NA

[a]Numerical assignment given by EHAP.

[b]TPA residue detected by CDFA; APPL only detected total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined), not individual analytes.

[c]Not analyzed.

[d]CDFA analyzed samples for chlorthal-dimethyl, MTP, and TPA. APPL analyzed samples for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined).

[e]None detected. CDFA minimum detection limit for chlorthal-dimethyl, MTP, and TPA is 0.05, 0.10, and 0.10 ppb, respectively. APPL minimum detection limit for total chlorthal-dimethyl residue is 0.01 ppb. CDFA and Enseco minimum detection limit for atrazine, simazine, diuron, prometon, and bromacil is 0.10 ppb for all compounds.

Chemical Analyses Summary Table for Tulare County

County	Well[a] Number	Herbicide Detected	Herbicide Concentration (ppb) and Analyzing Laboratory		
			CDFA	APPL	ENSECO
Tulare	1	Total Residue[b]	ND[c]	0.06	NA[d]
	2	ND	ND	ND	NA
	3	Simazine	0.10	NA	NA
	4	ND	ND	ND	NA
	5	Simazine	0.10	NA	NA
	6	Simazine	0.10	NA	NA

[a]Numerical assignment given by EHAP.

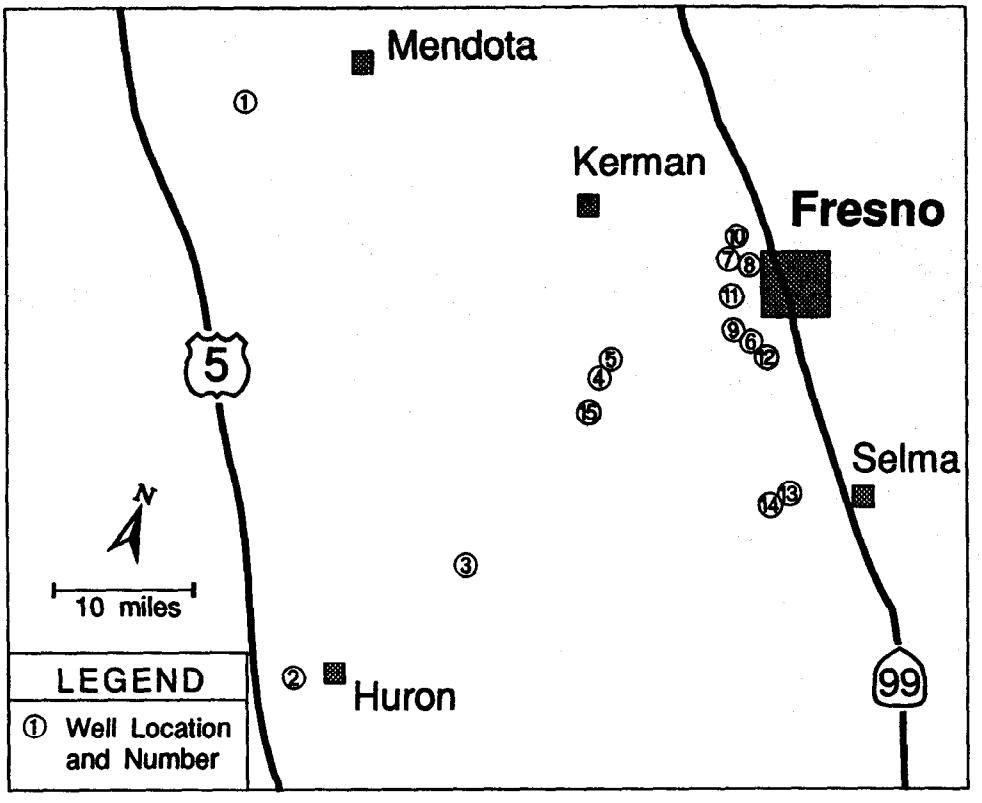
[b]CDFA analyzed samples for chlorthal-dimethyl, MTP, and TPA. APPL analyzed samples for total chlorthal-dimethyl residue (chlorthal-dimethyl, MTP, and TPA combined).

[c]None detected. CDFA minimum detection limit for chlorthal-dimethyl, MTP, and TPA is 0.05, 0.10, and 0.10 ppb, respectively. APPL minimum detection limit for total chlorthal-dimethyl residue is 0.01 ppb. CDFA and Enseco minimum detection limit for atrazine, simazine, diuron, prometon, and bromacil is 0.10 ppb for all compounds.

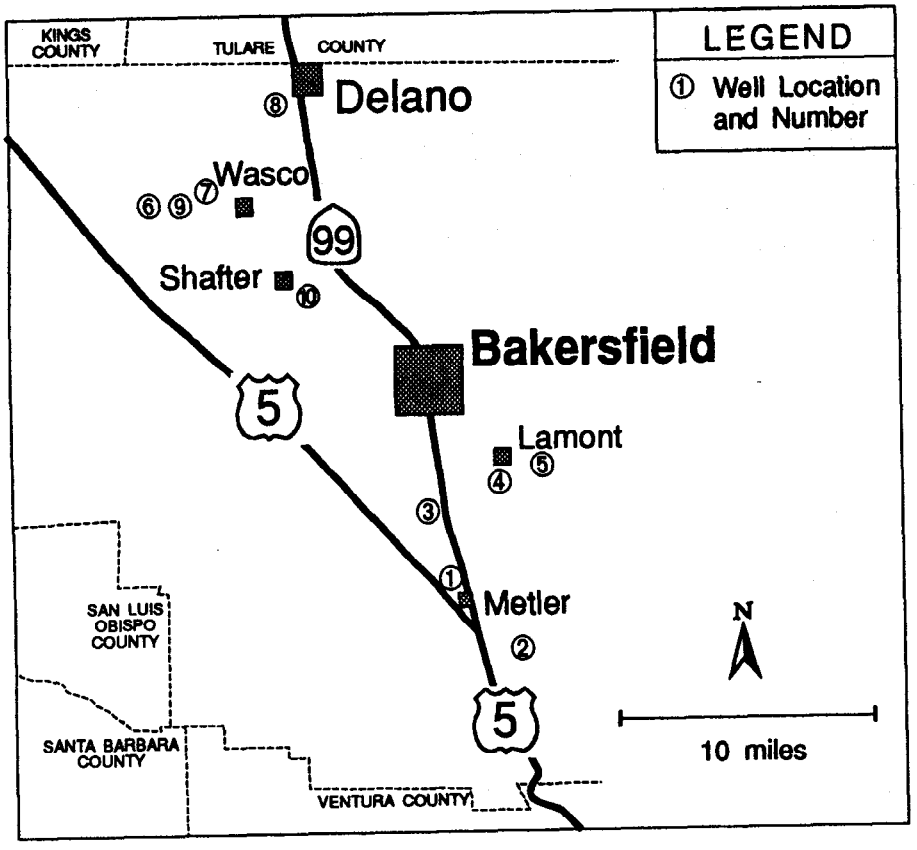
[d]Not analyzed.

APPENDIX D

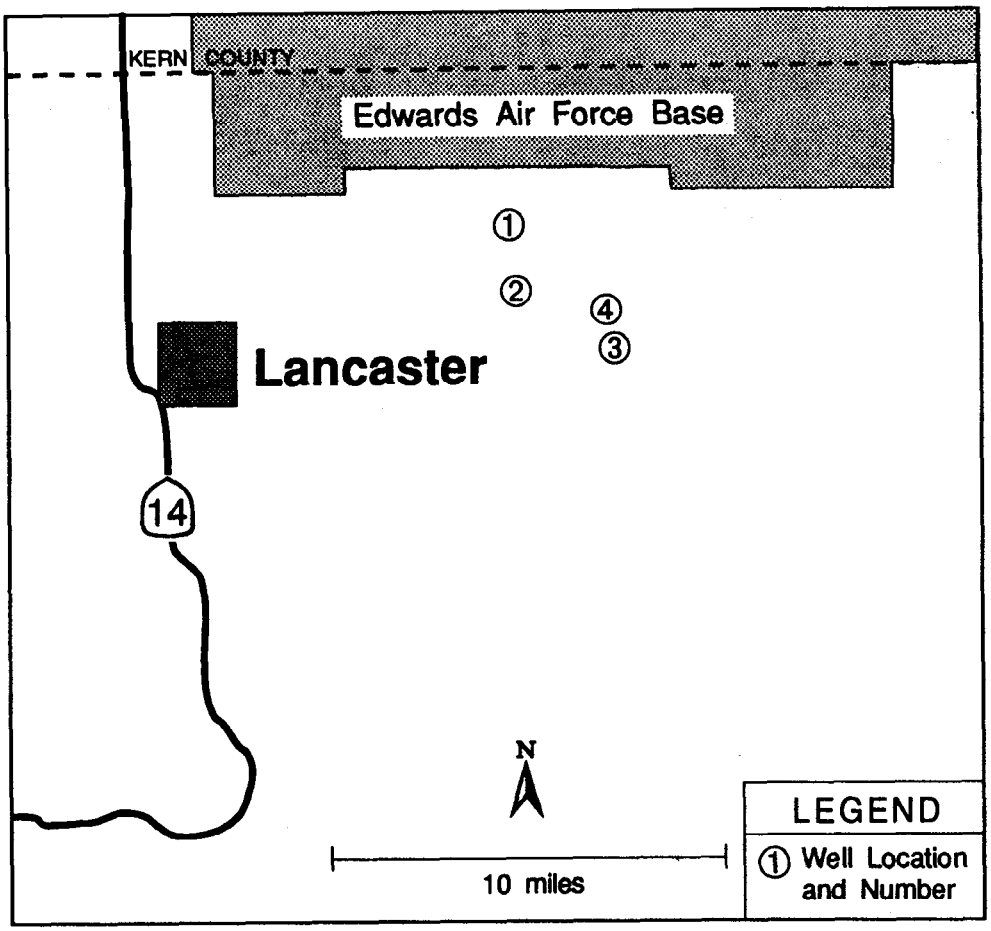
LOCATION OF SAMPLED WELLS



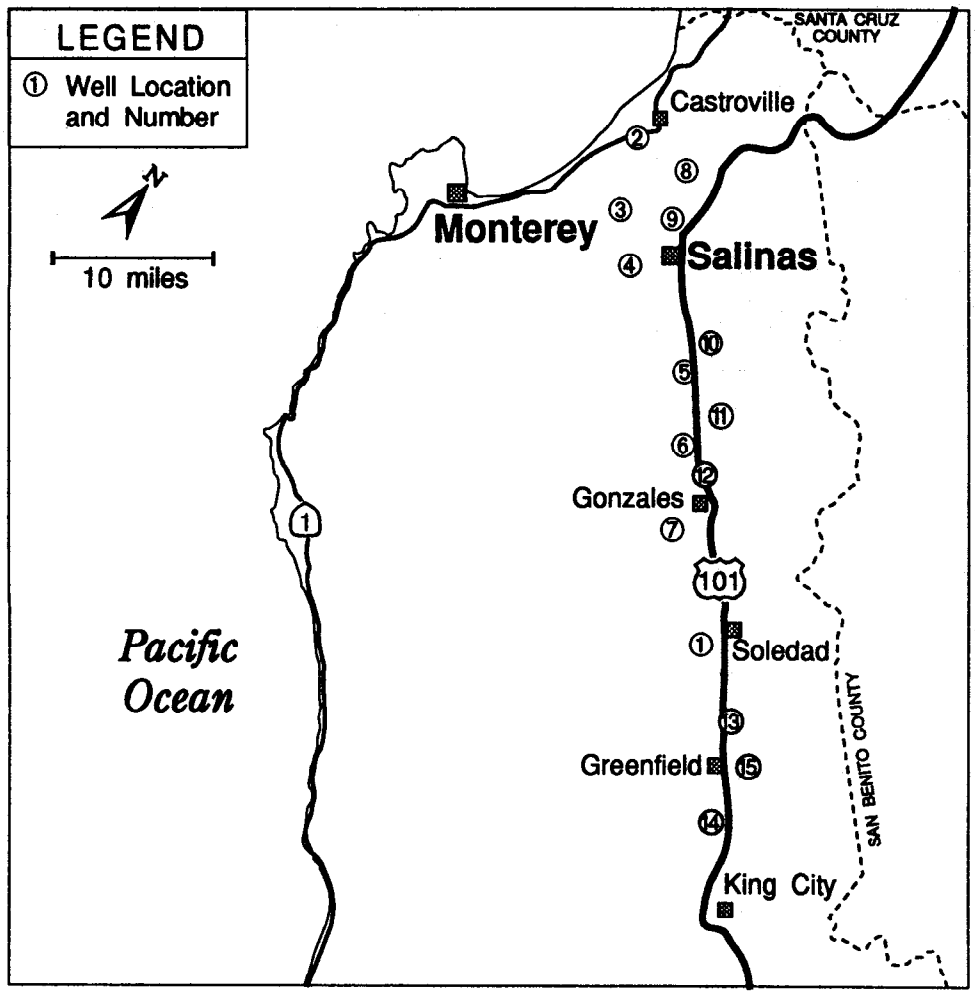
Location of sampled wells in Fresno County.



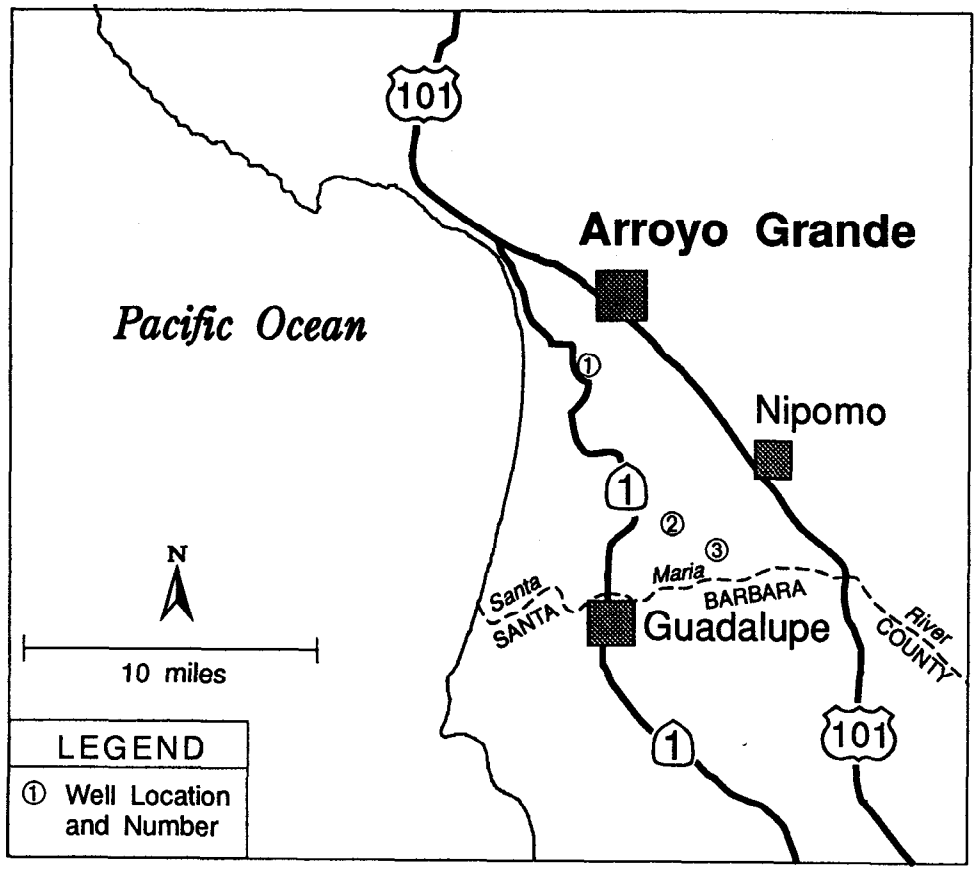
Location of sampled wells in Kern County.



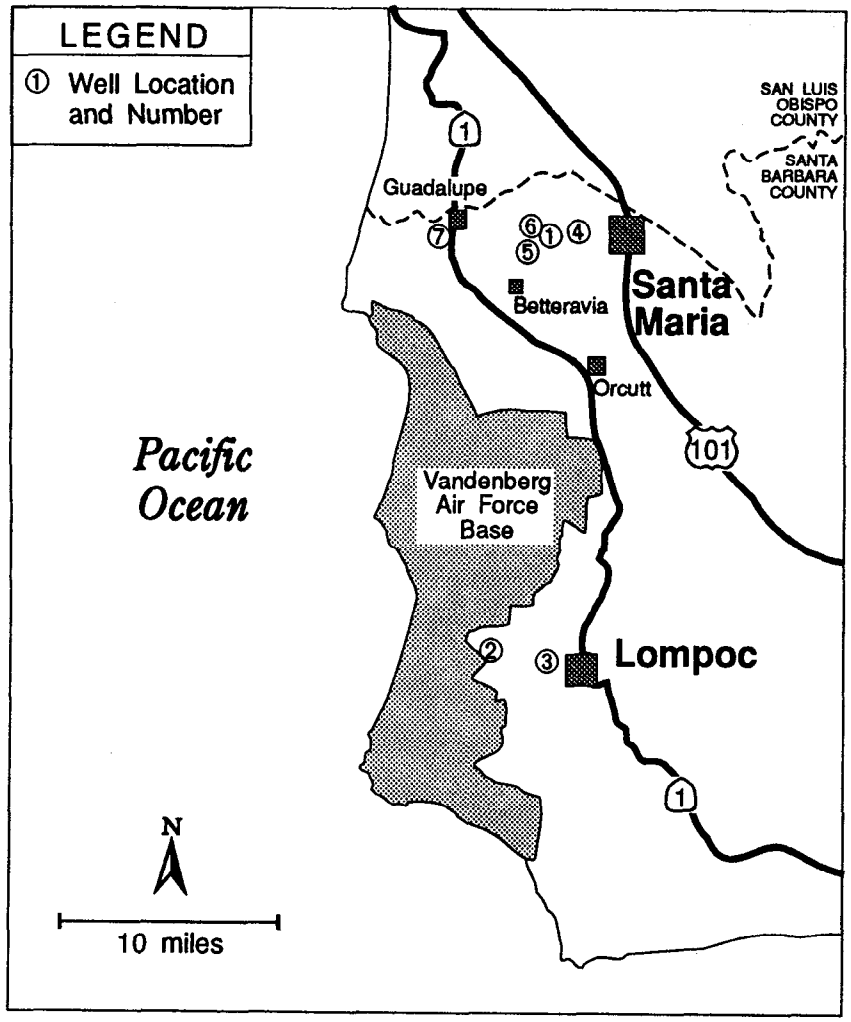
Location of sampled wells in Los Angeles County.



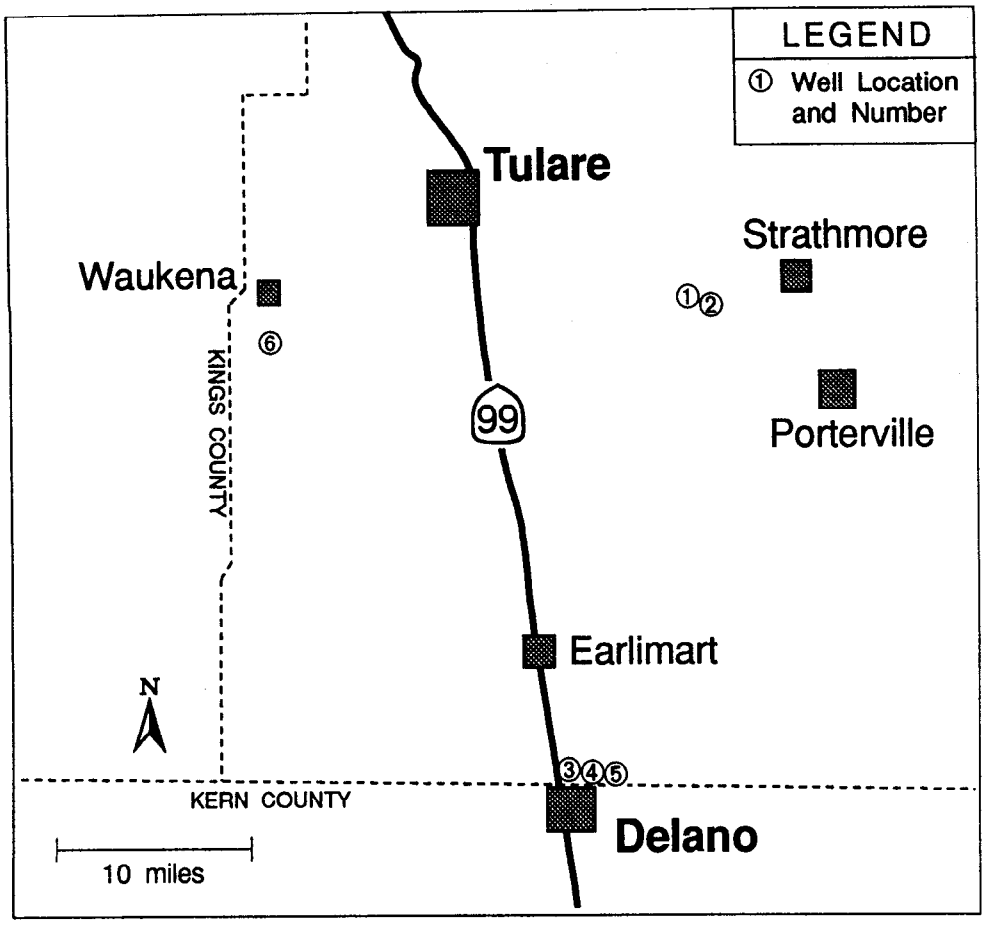
Location of sampled wells in Monterey County.



Location of sampled wells in San Luis Obispo County.



Location of sampled wells in Santa Barbara County.



Location of sampled wells in Tulare County.