

**Summary of Well Water Sampling in California to Detect Pesticide Residues Resulting from Nonpoint-Source Applications**

John Troiano, Don Weaver, Joe Marade, Frank Spurlock, Mark Pepple, Craig Nordmark, and Donna Bartkowiak

## Summary of Well Water Sampling in California to Detect Pesticide Residues Resulting from Nonpoint-Source Applications

John Troiano,\* Don Weaver, Joe Marade, Frank Spurlock, Mark Pepple, Craig Nordmark, and Donna Bartkowiak

### ABSTRACT

This report summarizes well sampling protocols, data collection procedures, and analytical results for the presence of pesticides in ground water developed by the California Department of Pesticide Regulation (DPR). Specific well sampling protocols were developed to meet regulatory mandates of the Pesticide Contamination Prevention Act (PCPA) of 1986 and to provide further understanding of the agronomic, chemical, and geographic factors that contribute to movement of residues to ground water. The well sampling data have formed the basis for the DPR's regulatory decisions. For example, a sampling protocol, the *Four-Section Survey*, was developed to determine if reported detections were caused by nonpoint-source agricultural applications, a determination that can initiate formal review and subsequent regulation of a pesticide. Selection of sampling sites, which are primarily rural domestic wells, was initially based on pesticide use and cropping patterns. Recently, soil and depth-to-ground water data have been added to identify areas where a higher frequency of detection is expected. In accordance with the PCPA, the DPR maintains a database for all pesticide well sampling in California with submission required by all state agencies and with invitations for submission extended to all local and federal agencies or other entities. To date, residues for 16 active ingredients and breakdown products have been detected in California ground water as a result of legal agricultural use. Regulations have been adopted for all detected parent active ingredients, and they have been developed regardless of the level of detection.

IN 1979, residues of 1,2-dibromo-3-chloropropane (DBCP) were detected in California well water. This

Environmental Monitoring and Pest Management Branch, Dep. of Pesticide Regulation, California EPA, 830 K Street Mall, Sacramento, CA 95814-3510. Received 21 Apr. 2000. \*Corresponding author (jtroiano@cdpr.ca.gov).

Published in *J. Environ. Qual.* 30:448-459 (2001).

discovery demonstrated the potential effect that agricultural applications of pesticides could have on California's ground water supplies (Peoples et al., 1980). Prior to this time, movement of pesticides to ground water was considered unlikely because of dilution effects, low water solubility, high vapor pressure, rapid degradation, and binding to soil. After DBCP was detected, the Department of Pesticide Regulation (DPR, formerly the Division of Pest Management in the California Department of Food and Agriculture) conducted well sampling to determine the presence and geographical distribution of high use pesticides in California ground water. These surveys indicated that the contamination was more prevalent than originally anticipated.

The Pesticide Contamination Prevention Act (PCPA) was enacted into law in 1986 (Connelly, 1986). The law resulted in a shift of well sampling objectives because data were now needed to identify and support regulatory activities. Prior to the PCPA, concentrations of DBCP and ethylene dibromide (EDB) in well water were determined to pose a hazard, so the director of the California Department of Food and Agriculture made the decision to suspend statewide use. Subsequent active ingredients detected in well water were subjected to a formal review process that was prescribed in the

**Abbreviations:** ACET, 2-amino-4-chloro-6-ethylamino-*s*-triazine; 1,2-D, 1,2-dichloropropane; DACT, 2,4-diamino-6-chloro-*s*-triazine; DBCP, 1,2-dibromo-3-chloropropane; DHS, California Department of Health Services; DPR, Department of Pesticide Regulation, California Environmental Protection Agency; EDB, ethylene dibromide; MCL, maximum contaminant level; MDL, minimum detection limit; PCPA, Pesticide Contamination Prevention Act; PMZ, pesticide management zones; TPA, 2,3,5,6-tetrachloroterephthalic acid; WIBD, Well Inventory Data Base.

PCPA. The process was triggered when residues of previously undetected pesticide active ingredients were found in ground water and their presence determined to result from legal agricultural use. As defined in the California Food and Agricultural Code Section 11408 and interpreted by the DPR, "agricultural use" includes use on commercial production of plants or animals including fumigation on a grower's property, parks, nurseries, label directions stated as "per acre," irrigation canals and ditches, drainage ditches, ditchbanks and street trees and grass strips owned by municipalities, golf courses, cemeteries, roadsides, power lines, and railroad rights-of-way. The formal review is conducted upon request by the registrant of the detected active ingredient. During the review, formal testimony is given to three representatives from three state agencies, one from the Office of Environmental Health Hazards Assessment, one from the State Water Resources Control Board, and the DPR. Upon conclusion of the public comment period, the panel recommends actions to be taken by the director of the DPR (formerly the Director of the Department of Food and Agriculture). The law does not prescribe a level of a detection that is required to trigger the review process because issues of potential health effects are addressed through the composition of the review panel. To date, pesticides with sufficient data for review are atrazine, simazine, bromacil, diruon, bentazon, prometon, norflurazon, and aldicarb. The regulatory decisions have been tailored to the pesticide under review and they have ranged from prohibition of specific pesticide uses to continued use in vulnerable areas with accompanying mitigation measures. Specific use requirements are listed in the California Code of Regulations (Title 3, Food and Agriculture) Division 6: Pest and Pest Control Operations, Article 4: Use Requirements, Sections 6450-6489. These requirements can be viewed at <http://www.leginfo.ca.gov/calaw.html>.

The objective of this report is to present the well sampling methodologies that have been developed to support the regulatory activities for detected pesticides, to indicate the range in pesticide active ingredients and their breakdown products detected in ground water and as verified by the California Department of Pesticide Regulation, and to discuss how the data have been used to provide a scientific approach for the further development of the ground water regulatory program. Through this review, we hope to characterize the breadth of the task of monitoring pesticides in California's ground water and to indicate how these data relate to the development of a regulatory system that balances environmental protection with economic considerations.

#### **DEPARTMENT OF PESTICIDE REGULATION GUIDELINES FOR WELL SAMPLING AND CHEMICAL ANALYSIS**

Prior to the discussion of specific well studies, we present the evolution for the DPR's current guidelines for sampling wells and for chemical analysis. Since the California Department of Health Services (DHS) was tasked with monitoring municipal wells, the DPR's efforts complemented DHS sampling by focusing on rural, single family, domestic drinking

water wells. A comparison of the data supports the conclusion that rural, domestic wells represent a greater potential for exposure to pesticide residues. Some reasons for higher potential for detection of residues are their close proximity to applications and their shallow construction. Rural domestic wells are generally shallower than municipal or agricultural production wells because of the lower water yield needed to support a single family.

The DPR initiated well sampling studies in the early 1980s. Since information on the geographical distribution of residues was lacking, an initial objective of well sampling was to determine the occurrence of pesticide residues in ground water throughout California. However, limited resources necessitated a low sampling density of wells. For example, in an early survey for the detection of DBCP, EDB, simazine, and carbofuran in well water, the spatial sampling unit was defined as a township, which is a 15.4-km<sup>2</sup> area of land. The U.S. Geological Survey's (USGS) Public Lands Survey Coordinate System was used as the basis for locating study sites because pesticide use reports and the state well numbering system employed this coordinate system. In this system, a section of land is a 2.59-km<sup>2</sup> area of land and a Township is a 6 × 6 square composed of 36 sections (Davis and Foote, 1966). Since only one well was sampled per township in the initial survey, wells could be sorted prior to sampling according to construction details, such as the depth of the well and the perforation depths of the screen intervals (Weaver et al., 1983).

Implementation of the PCPA resulted in more intensive sampling of a greater number of wells in smaller land areas. It was no longer possible to select wells using well construction information because the data were not easily obtained or frequently not available. Instead, the following guidelines were established to identify suitable wells for sampling during local reconnaissance within an individual section of land (Sava, 1994):

- (i) The well was properly sealed and the pad and cap were in good condition. This ensured that the well was unlikely to be a point source for entry of residues into ground water.
- (ii) The well was not located in close proximity to pesticide sprayer filling stations, washdown areas, or pesticide storage facilities.
- (iii) The elevation and apparent drainage patterns indicated that the well did not intercept runoff water that might contain pesticide residues.
- (iv) The sampling point, which was a faucet, valve, or standpipe, was located between the well and an aboveground water storage tank. Thus, ground water was sampled before it reached a storage tank.

Samples were collected in 1-L amber glass bottles with Teflon-lined caps and usually collected from Schrader valves. Prior to sampling, pumps were run for at least 10 min to clear the casing of standing water and to bring in fresh water from the aquifer. The sample bottles were rinsed with well water and then refilled in a manner that minimized aeration. Field blanks were prepared at each site with deionized water and were analyzed only when pesticide residues were detected in the primary samples. Preservative procedures, such as adjusting the acidity of samples, were conducted as appropriate for each analyte. After sample collection, bottles were stored and transported on wet ice and subsequently stored in a refrigerator at 4°C until analysis.

Quality assurance and quality control (QA/QC) data for each chemical analyte included blind spikes, matrix duplicate spikes, duplicate injections, blank samples, and a reference sample included with each extraction set. Storage studies were

conducted to determine stability of analytes. Initially, detections of residues were confirmed by the primary laboratory using a second detection method or by a second laboratory preferably using a second detection method. Recently, analytical detection methods based on mass spectrometry have been developed and are considered to be unequivocal methods, requiring no second confirmatory analysis. When a residue was detected in a sample, the field blank was always analyzed. Any detection in the field blank would cause the primary analysis to be considered questionable and the well resampled. Since the sampling procedure involved very little handling or sample preparation, detection in field blanks was very rare. In one instance, an apparent detection of molinate in field blanks was attributed to a solvent located in the caps of bottles, which led to a change in the supply of bottles. Sampling procedures that require more handling in the field can be prone to contamination, especially when minimum detection limits (MDLs) are very low, which now can be the low parts per trillion (Martin et al., 1999). In these instances, the data for detection need to be carefully evaluated with respect to QA/QC.

### SPECIFIC WELL SAMPLING STUDY OBJECTIVES

The DPR collects data on occurrence of pesticide residues in wells using a variety of study approaches to address specific objectives. This section summarizes the most commonly used study approaches, along with a few illustrative examples.

#### General Surveys

Weaver et al. (1983) conducted one of the first California studies to quantify the spatial distribution of pesticide residues in wells. The study sampled wells from four ground water basins. DBCP and EDB were chosen because both were soil fumigants with high use and DBCP residues had already been detected in well water samples. Simazine and carbofuran were also chosen because of their widespread use. One observation from the study was a lack of detection in wells sampled from two coastal basins as compared with detections in two inland basins (Table 1). However, in sampling conducted after this study, residues of other pesticide active ingredients have been detected in these coastal areas, such as atrazine detected in Ventura County. Detection in coastal areas have been determined to result from nonpoint-source applications, but their routes of movement to ground water requires further investigation.

#### Four-Section Surveys

The four-section well survey protocol was developed to gather additional information in response to reports

**Table 1. Detections of pesticides in a survey of four ground water basins in California conducted in 1982 (Weaver et al., 1983).**

Ground water basin	Number of wells sampled	Number of wells containing:			
		Carbofuran	DBCP	EDB	Simazine
<b>Coastal basins</b>					
Salinas	21	0	0	0	0
Santa Maria	7	0	0	0	0
<b>Inland basins</b>					
San Joaquin	166	0	21	2	3
Upper Santa Ana	23	1	6	0	2

of active ingredients not previously detected in California's ground water. The objective of the survey was to confirm the detections in the original well and then determine if residues were present in other wells located within approximately one mile (1.61 km) of the original detection. Initially, the well with the reported detection is investigated to rule out the possibility of point-source contamination caused by construction problems such as cracks in the wellhead, or by storage or spillage of pesticides near the well, or by interception of runoff water containing pesticide residues as determined by the location of the well with respect to elevation and drainage patterns. If the well did not appear as a potential point source, then additional wells were sampled in adjoining sections. The number of wells sampled is determined by the density of suitable wells in the surrounding area and by permission from the well owner to sample. The original detection is determined to arise from nonpoint-source contamination if residues are detected in a second well, the pesticide was legally applied, and no other point sources, such as disposal sites, are found. For detection of a new active ingredient, a positive nonpoint-source determination from the four-section survey serves as the basis for further investigation to determine the potential area affected and the relationship of the detection to agronomic factors. For previously detected active ingredients, nonpoint-source determinations form the basis for delineating new vulnerable areas, which currently involves listing the affected section(s) as a Pesticide Management Zone (PMZ).

#### Focused Areal Surveys

When the source of detection in a four-section survey has been determined to result from nonpoint-source applications, expanded sampling may be conducted to determine the extent of the contamination and its relationship to agronomic factors. One example is a 1988 study of bentazon (MDL = 0.1  $\mu\text{g L}^{-1}$ ) in well water (Sitts, 1989). In response to a detection submitted to the DPR by the Regional Water Quality Control Board, bentazon residue was confirmed in a well at 13.7  $\mu\text{g L}^{-1}$ , which was close to the State of California's maximum contaminant level (MCL) of 18  $\mu\text{g L}^{-1}$ . During the four-section survey, residues were detected in four of six additional wells. Three more studies, encompassing areas of increasing geographic coverage, were then conducted to define the extent of the contamination and to determine if contamination was limited to use on rice (*Oryza sativa* L.). In the first follow-up study, residues were detected in 9 of 24 wells sampled in 15 additional sections with concentrations ranging from 0.1 to 13.2  $\mu\text{g L}^{-1}$ . Sampling was eventually broadened to all rice growing areas and residues were detected in 61 of 178 wells with concentrations ranging from 0.1 to 13.7  $\mu\text{g L}^{-1}$  (Table 2). Ten additional wells were sampled in non-rice growing areas where bentazon was used, but residues were not detected.

When possible, analyses for other pesticides are also conducted on a well sample to obtain information on

the co-occurrence of pesticides in ground water. In the bentazon study, samples from a subset of the wells were tested for other commonly used rice herbicides. Nineteen of the wells that contained bentazon residue were also analyzed for the presence of molinate (MDL = 0.2  $\mu\text{g L}^{-1}$ ) or thiobencarb (MDL = 0.2  $\mu\text{g L}^{-1}$ ) but no residues were detected. Additional analyses were conducted for MCPA (MDL = 0.1  $\mu\text{g L}^{-1}$ ) in 35 wells and again residues were not detected.

The bentazon studies resulted in regulatory action. A comparison of the physical-chemical properties for all analytes indicated considerable overlap and provided no clear cause for differentiation in detections (Table 3). In addition, the difference in time between registration and detection for each active ingredient was not sufficient to explain the difference. Bentazon was registered in California in 1977 compared with molinate in 1972, MCPA in 1979, and thiobencarb in 1983. Although the registration of thiobencarb was after bentazon, use on rice was large in previous years because of a conditional registration granted for large acreage in years prior to 1983.

Detection of bentazon in only rice-growing areas indicated that a unique combination of soil properties, herbicide physical-chemical properties, and agricultural practices resulted in movement to ground water. Since mitigation measures were not available and some concentrations were near the California MCL, use of bentazon on rice was prohibited. Use on other crops was allowed because the registrant submitted data that indicated faster field dissipation in surficial layers of soil when used in sprinkler-irrigated beans. One aspect of the decision was a continued monitoring program whereby DPR maintained a biennial well sampling program in dry bean growing areas. To date, bentazon residues have not been detected in areas where use was allowed. The exact cause for bentazon's movement to ground water has yet to be determined, especially in relation to nondetection of other herbicides.

### Ground Water Protection List Monitoring

The PCPA addressed the need for retrospective well sampling by directing the DPR to identify and sample for pesticides with the potential to move to ground water. In compliance with the PCPA, Wilkerson and Kim (1986) compiled mobility data defined as values for either soil organic carbon adsorption ( $K_{oc}$ ) or water solubility, and persistence data defined as half-life estimates obtained from field dissipation studies or from labora-

**Table 3. Selected physical-chemical properties of rice herbicides.†**

Active ingredient	Water solubility $\mu\text{g L}^{-1}$	$K_{oc}$ $\text{cm}^3 \text{g}^{-1}$	Estimated half-life for		
			Aerobic degradation	Anaerobic degradation	Hydrolysis
			days		
Bentazon	530	116	40	365	30‡
2,4-D	656 750	45	66	NA§	39
MCPA	1 060 000	26	24	1872	30
Molinate	970	199	NA	105	1560
Thiobencarb	28	530	37	306	160‡

† Data obtained from 1999 annual report to California Legislature (Kollman, 1999).

‡ No hydrolysis occurred during study, so value is greater than listed.

§ NA = data not available.

tory measurements of aerobic, anaerobic, or hydrolysis transformation. The test and choice of physical-chemical properties was crafted after a similar procedure developed by the USEPA (Cohen et al., 1984; Creeger, 1986). In the procedure developed by the DPR, a statistical comparison was conducted for the distribution of each variable between a set of active ingredients that had been detected in ground water and another set that had been sampled for but not detected in ground water in any state of the USA. The test, which has been denoted the Specific Numerical Values (SNVs) test, was updated in 1991 (Johnson, 1991). According to the results of that analysis, a pesticide is determined as a potential leacher if [(water solubility is greater than 3  $\text{mg L}^{-1}$  or  $K_{oc}$  is less than 1900  $\text{L kg}^{-1}$ ) and (soil aerobic metabolism half-life is greater than 610 d, or anaerobic metabolism half-life is greater than 9 d, or hydrolysis half-life is greater than 14 d)]. If the active ingredient is determined to be a potential leacher and if it is applied to soil by ground-based application equipment or chemigation, or if flood or furrow-irrigation occurs within 72 h after application, then it is placed on a list for potential sampling, denoted the 6800(b) list in reference to the section in the California Code of Regulations.

Since 1992, the 6800(b) list of potential leachers has contained more than 50 active ingredients. Resources were available to sample only two to four active ingredients per year, so a protocol was established to rank the pesticides. Initially, higher priority was given to active ingredients with potentially greater human toxicological data. Inclusion of toxicity data caused some relatively low soil use pesticides, such as some insecticides, to be given highest priority. Also, areas that were sampled were identified based on cropping patterns and pesticide use data, when available. Approximately 40 wells were

**Table 2. Detections of bentazon in sequential surveys of increasing land area conducted in 1989 (Sitts, 1989).**

Sampling phase	Number of wells sampled	Number of detections	Range in concentrations† $\mu\text{g L}^{-1}$
<b>Four-section survey</b>			
Phase I; four sections sampled around initial detection	6	4	1.04–13.7
<b>Focused areal sampling</b>			
Phase II; two-square mile area surrounding Phase I sampled	24	9	0.10–13.2
Phase III; 24 additional sections west and south of Phase II sampled	48	20	0.10–4.2
Phase IV; all rice growing areas in 12 counties sampled	100	28	0.10–10.2
<b>Total from all phases</b>	<b>178</b>	<b>61</b>	<b>0.10–13.7</b>

† Minimum detection limit at 0.1  $\mu\text{g L}^{-1}$ .

sampled for each active ingredient with sampling sites located in areas of greatest pesticide use. Eighteen active ingredients have been sampled using this protocol but no residues were detected, even though some had been reported in other state or federal surveys, for example, cyanazine and 2,4-D (Klaseus et al., 1988; Kolpin et al., 1997).

Since issues of toxicology are addressed during hearings conducted after detection, greater emphasis is now placed on choosing pesticide active ingredients that have physical-chemical properties indicative of greater potential to move off-site, that have use patterns with a greater probability of movement to ground water, and that have been detected in sampling conducted in other portions of the USA. In addition, soil and depth-to-ground water data have been used to identify geographic areas with a higher probability for detection (Troiano

et al., 1994, 1997). Results from our first application of this approach have been encouraging. Residues of norflurazon (MDL at  $0.05 \mu\text{g L}^{-1}$ ), the first pesticide chosen under the revised protocol, have been detected in areas delineated as vulnerable according to the empirical model (Troiano et al., 1999).

### Adjacent Section Monitoring

As previously indicated, the DPR has restricted the use of active ingredients in sections (PMZs) where residues have been detected in well water. A protocol was developed, entitled "Adjacent Section Monitoring," with the objective of sampling wells in 10% of the sections surrounding each PMZ. If residue of previously detected active ingredients was detected in a section adjacent to a PMZ, then the section was submitted for addition to the PMZ list. As the number of PMZs in-

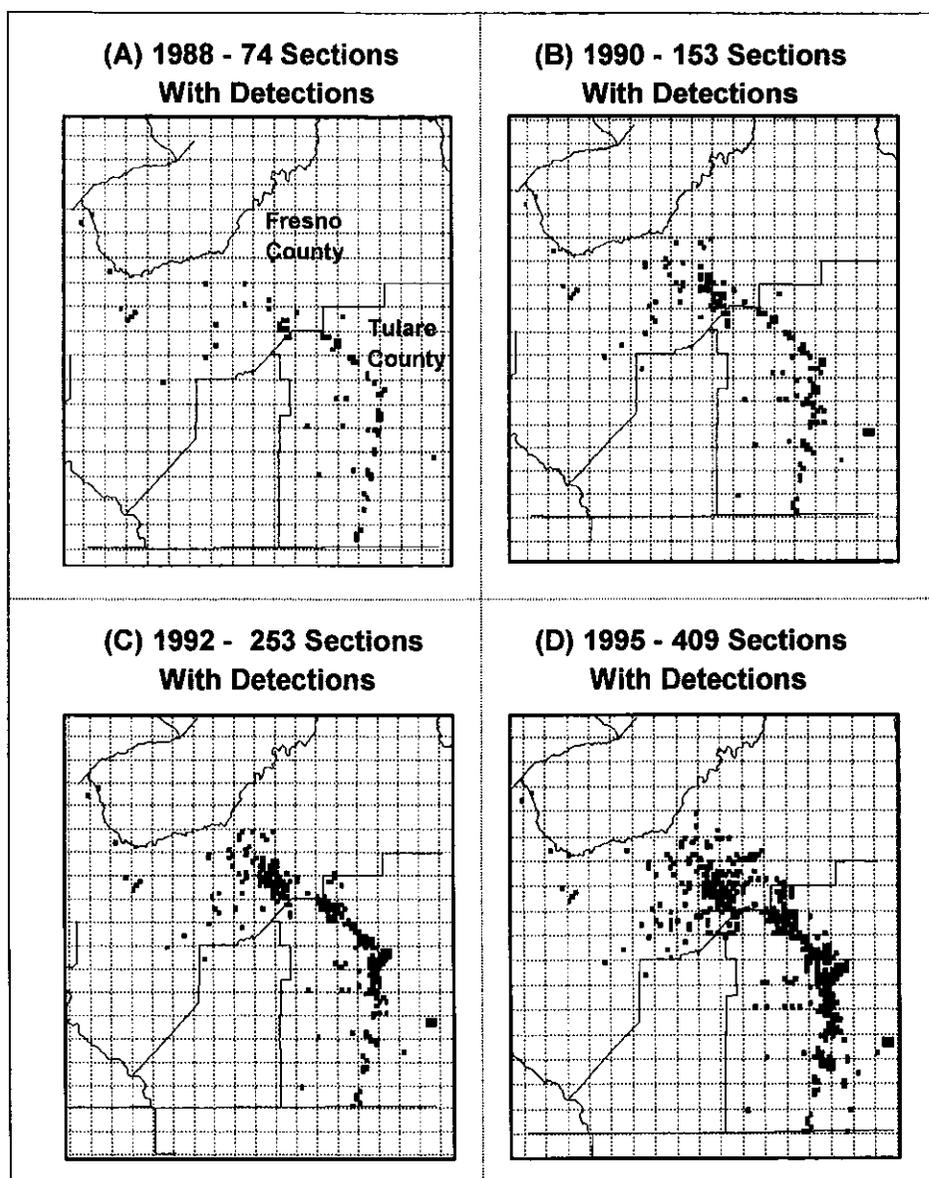


Fig. 1. Sections with pesticide detections in wells sampled in Fresno and Tulare Counties, excluding 1,2-dibromo-3-chloropropane (DBCP), in (A) 1988, (B) 1990, (C) 1992, and (D) 1995.

creased, the number of potential adjacent sections to monitor grew rapidly and the goal of 10% could not be attained (Fig. 1). We have proposed to replace a portion of the PMZs with generalized areas of protection defined through an empirical analysis of spatial vulnerability (Troiano et al., 2000). This approach reduces the need for adjacent section monitoring and is more preventative than the current practice of regulation after detection.

### Targeted Well Studies

Targeted well studies have also been conducted to provide information on the geographical and agricultural factors that determine patterns of detection. For example, a recent cooperative study with U.S. Geological Survey staff was conducted to estimate the time between preemergence herbicide application and subsequent detection in shallow, rural domestic wells (Spurlock et al., 2000). Samples were collected from domestic wells that had a history of simazine contamination and that were located in sections with shallow ground water at less than 15 m depth. Based on chlorofluorocarbon dating and one-dimensional transport modeling, more than half of the detections were associated with applications made within the previous decade. A comparison of grower surveys conducted a decade apart indicated that agricultural practices had been stable within the same estimated period of recharge. This data provided support for adoption of DPR's mitigation measures that aim to prevent pesticide movement to ground water in vulnerable areas.

### Repeated Well Sampling

To date, the sampling studies conducted by the DPR have focused on identifying new active ingredients in well water and on delineating the geographic extent of contamination. Consequently, there has been little repeated sampling of wells over time. Regulations adopted in response to the PCPA decision-making process for aldicarb and bentazon directed the DPR to conduct well sampling in areas where use was allowed. To date, no residues have been detected.

Proposed changes in implementation of the PCPA provide for increased regulation of detected pesticides in delineated vulnerable areas. As an indication of the success of this program, a subset of domestic wells will be routinely sampled in the areas where the best management practices (BMPs) will be imposed. Although the proposed changes in regulations have not yet been finalized, sampling was initiated in October 1999 with samples drawn from approximately 40 wells located in each of two vulnerable soil conditions in Fresno and Tulare counties. Each of these wells had previous detection of one or multiple residues of simazine, bromacil, diuron, and/or triazine degradates. Since these wells are located in the same area where the age-dating study was conducted, a minimum sampling period of 5 yr is expected in order to detect changes in concentration that can be related to proposed changes in management practices.

Some agencies have submitted data from long-term monitoring studies for inclusion into California's Well Inventory Data Base (discussed in next section). Data for DBCP and aldicarb provide interesting case studies of the changes in residue concentrations in wells after cessation of pesticide use and for comparison between ground water basins. The North Coast Regional Water Quality Control Board has conducted long-term monitoring for aldicarb in wells in Del Norte and Humboldt counties (Warner et al., 1989). Aldicarb transformation products were detected in 19 wells and the residues were determined to be from nonpoint sources arising from agricultural applications to lily (*Lilium* spp.) bulbs. As a result, use of aldicarb was suspended in these counties in 1982 and the registrant subsequently removed this use from the label. The pattern for aldicarb sulfoxide and aldicarb sulfone indicated a substantial decrease in concentrations over time after suspension of use (Fig. 2). Data from this well were similar to other wells sampled from this area. The prominent decrease in residues over the 4-yr period is probably due to a combination of high annual rainfall at 1500 to 2500 mm yr<sup>-1</sup> and coarse soils, which contribute to relatively rapid movement of shallow ground water. In contrast, data for DBCP submitted by the DHS for wells sampled in the San Joaquin Valley paint a more complicated scenario. Even though use was suspended in 1979, trends measured in three wells sampled in three different sections, appear to have decreased (Fig. 3a, T/R/S-14S22E23), remained stable (Fig. 3b, T/R/S-13S21E16), or even increased over time (Fig. 3c, T/R/S-15S23E26). Factors that have resulted in a much more complicated regional movement of DBCP-contaminated ground water include widespread use of DBCP at application rates that were more than 45 kg ha<sup>-1</sup>, instability in the movement of ground water due to local influences of large pumping depressions created by irrigation and municipal wells, and stability of residues once they are moved out of the root zone to ground water (Burlinson et al., 1982; Deeley et al., 1991; Schmidt, 1986).

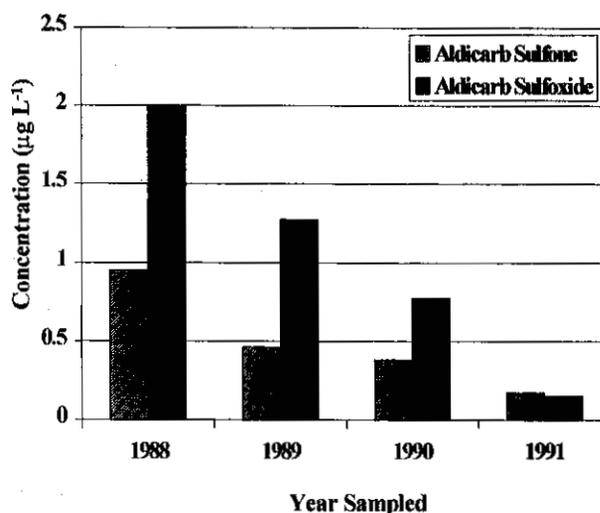


Fig. 2. Concentrations of aldicarb sulfoxide and aldicarb sulfone (minimum detection limit [MDL] at 0.1–0.4 µg L<sup>-1</sup>) in a well sampled in northwestern California after aldicarb use was suspended in 1984.

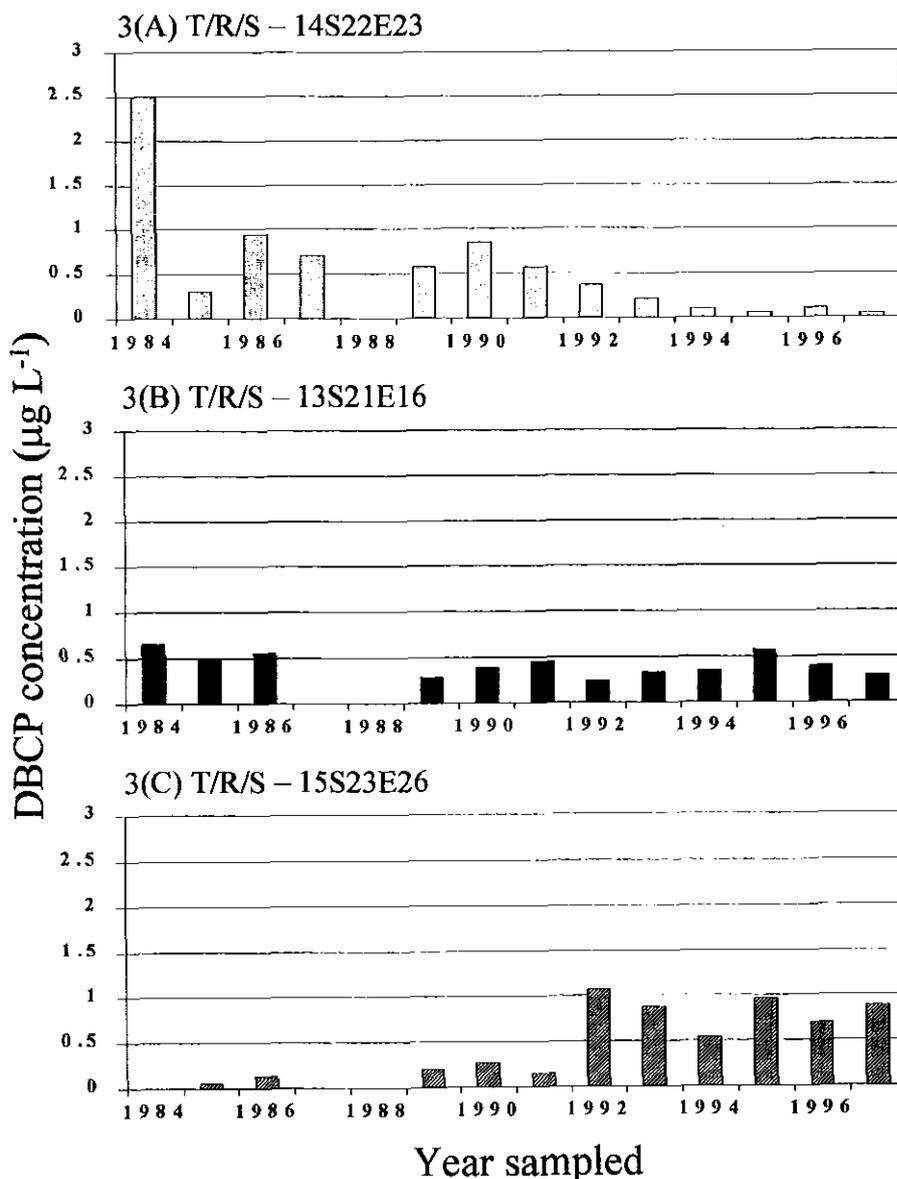


Fig. 3. Concentration of 1,2-dibromo-3-chloropropane (DBCP) (minimum detection limit [MDL] at  $0.01 \mu\text{g L}^{-1}$ ) in wells sampled in three different townships, in (A) T/R/S-14S22E23, (B) T/R/S-13S21E16, and (C) T/R/S-15S23E26. Wells were sampled after agricultural use was suspended in 1979.

### WELL INVENTORY DATA BASE

The PCPA required the DPR to maintain a statewide database of the results for well water samples that have been analyzed for pesticides. All state agencies are required to submit sampling data but invitations for submission have been extended to all federal, local, or other groups that conduct well sampling. The following set of minimum qualifications were developed to assure consistency and analytical quality of the information added to the data base:

- Well number, denoted by County/Township/Range/Section
- Descriptive address
- Agency or group that conducted the sampling
- Date the sample was obtained
- Date the sample was analyzed (optional)

- Chemical analyte(s) reported
- Concentration of each analyte
- Minimum detection limit for each analyte
- Sample type, such as primary, confirmation, or blank
- Laboratory that conducted the analysis (optional)
- Analytical method such as "EPA Method #", "GC/MS" (optional)

Although the Well Inventory Data Base (WIDB) is a valuable resource, the data must be interpreted cautiously. The WIDB contains data derived from many different studies that have varied objectives and chemical analytical procedures. For example, the California Department of Health Services (DHS) provides data from municipal wells. Municipal wells are usually much deeper than private, domestic wells so results between

**Table 4. Occurrence of pesticide active ingredients or breakdown products in wells sampled in California as of December 1999 and resulting from nonpoint-source applications (Bartkowiak et al., 1999).**

Pesticide active ingredient†	Agricultural use or action	Status	Unique wells sampled	Wells with detections	Range in detections	MDL‡ range	MCL§
			#		µg L <sup>-1</sup>		
DBCP	soil fumigant	not registered	10 692	2820	0.001–166.0	0.001–100.0	0.2
Simazine	preemergence herbicide	regulated in PMZs¶	10 403	693	0.020–4.5	0.01–13.6	4.0
Diuron	preemergence herbicide	regulated in PMZs	6 624	387	0.050–4.5	0.009–50.0	NA#
Atrazine	preemergence herbicide	regulated in PMZs	9 820	256	0.020–8.5	0.01–12.3	3.0
Bromacil	preemergence herbicide	regulated in PMZs	7 489	208	0.030–23.0	0.00–20.0	NA
ACET	triazine breakdown product	parent regulated	692	171	0.050–6.0	0.01–0.2	NA
EDB	soil fumigant	not registered	6 606	146	0.006–4.3	0.001–2.0	0.05
1,2-D	soil fumigant	not registered	10 363	125	0.010–160.0	0.02–20.0	5.0
Bentazon	postemergence herbicide	regulated statewide	3 824	85	0.070–13.7	0.01–200.0	18.0
Prometon	preemergence herbicide	regulated in PMZs	4 086	49	0.050–2.0	0.02–50.0	NA
DACT	triazine breakdown product	parent regulated	75	47	0.050–6.9	0.05–0.1	NA
DEA	triazine breakdown product	parent regulated	656	40	0.052–2.0	0.01–0.1	NA
TPA	dacthal breakdown product	parent not detected	274	35	0.100–15.0	0.01–0.1	NA
Aldicarb sulfone	breakdown product	parent regulated	2 898	19	0.050–4.9	0.01–5.0	NA
Aldicarb sulfoxide	breakdown product	parent regulated	2 842	19	0.060–13.2	0.01–5.0	NA
Norflurazon	preemergence herbicide	regulated in PMZs	254	9	0.070–0.79	0.05–0.36	NA

† Chemical names for abbreviations listed in the Abbreviations section.

‡ Minimum detection limit.

§ MCL = California maximum contaminant level which was obtained from the DHS website at <http://www.dhs.gov/ps/ddwem/chemicals/mcl/mclindex.htm>.

¶ PMZ = pesticide management zone.

# NA = data not available.

them may not be comparable. In addition, the municipal well studies usually employ broad chemical analytical screens, providing data for pesticides in areas where they have not been applied. These data, especially with respect to nondetections, have limited application in determining geographical distribution of residues or to analysis of spatial vulnerability. First, pesticide use patterns may not coincide with the areas sampled. Pesticide use data must be superimposed upon the detections to infer whether or not nondetection is simply due to lack of applications. Prior to 1991, spatial data for pesticide use in California was only required for restricted materials. Mandatory use reporting was initiated in 1991, which now enables a more complete analysis of geographic patterns of use.

Second, nondetections may result from agricultural management practices and, thus, are not necessarily reflective of intrinsic spatial vulnerability. In the aldicarb example, residues of aldicarb sulfoxide and aldicarb sulfone were detected in the high rainfall counties of Del Norte and Humboldt, located in the northwestern portion of California. In contrast, residues have not yet been detected in wells sampled in cotton (*Gossypium hirsutum* L.) growing areas of the southern San Joaquin Valley in California (Marade and Weaver, 1994). The difference in detection was due to the placement of residue relative to the production of downward percolating water. Residues in Del Norte and Humboldt counties were exposed to percolating water produced from rainfall, which averages between 1500 and 2500 mm yr<sup>-1</sup> and is a major source for ground water recharge. In contrast, aldicarb use in the southern San Joaquin Valley was mainly in cotton where it is banded beneath the seed in a berm. Average rainfall in the southern San Joaquin Valley is very low at 254 mm or less per year so percolation produced from irrigation is the major source for ground water recharge (Gronberg et al., 1998). The placement of the residues in cotton exposed residues to water from furrow irrigations that

wicked up the berm and not to water that percolated downward from the furrow bottoms. In this case, aldicarb was being applied in a potentially vulnerable area but the combination of weather and agricultural management practices mitigated the potential for movement to ground water (Jones, 1986).

As of December 1999, the WIDB contained 782 921 records, which represent 20 042 wells (Bartkowiak et al., 1999). Data have been submitted from 45 state, federal, and local agencies and from registrants. Wells have been sampled in all 58 California counties with 32 counties containing residues that were determined to result from nonpoint-source applications. Table 4 contains the number of wells that have a record of at least one analysis conducted for each analyte, the number of wells with detections, and the range in detections for active ingredients or breakdown products. Table 4 reports only those residues that have been determined to be present due to nonpoint-source applications. Many wells had been examined according to the protocols outlined in the well sampling section but data submitted by the DHS, of which most are DBCP detections, have been determined as nonpoint source because most of the data are derived from municipal well systems. The soil fumigants, 1,2-dichloropropane (1,2-D), DBCP, and EDB were initially detected. They were the first active ingredients that were regulated because maximum contaminant levels (MCLs) developed for these were low, and the levels detected in wells were indicative of potential problems. As data became available, some of the MCLs, such as for DBCP, decreased over time. Use of the fumigants was suspended and registrations were not renewed because of drinking water concerns and the absence of mitigation measures.

Active ingredients detected in well water subsequent to the fumigants were subjected to the decision-making process that was previously outlined in the discussion of the PCPA act. Even though MCLs have been rarely exceeded, regulations have been adopted to modify the

agricultural use of each subsequently detected pesticide. Use is allowed if alternative pesticides are not economically advantageous and if mitigation measures are available. Currently, use restrictions apply in sections of land designated as pesticide management zones (PMZs), which are sections with wells that contain pesticide residue. Mitigation measures were developed for crop uses of simazine, bromacil, diuron, aldicarb, norflurazon, and bentazon. The decision to regulate has been based on any level of detection rather than on a health level due these reasons:

- (i) As indicated in Table 4, health levels have not been determined for all pesticides.
- (ii) When analyzed, detection of breakdown products has accompanied the parent, but there was, and still is, no specific guidance on how to view the breakdown products with respect to MCLs developed for parent pesticides. For example, the Food Quality Protection Act has indicated that total residue could be appropriate for tri-

azines, but this is just being considered under the triazine re-registration decision, which has not been finalized.

- (iii) Well samples usually contain multiple residues and the potential interaction on health effects between residues has not yet been addressed.

The frequency distributions of concentration for simazine, bromacil, and diuron and total triazine are presented in order to compare their ranges and distributions (Fig. 4). Data have been taken only from DPR studies because these wells were visually inspected for potential point sources and the detections determined to be from nonpoint-source applications. In addition, the minimum detection limits were consistent between studies, set at 0.05 or 0.1  $\mu\text{g L}^{-1}$ . The distributions reflect only positive data, because, as indicated in the previous discussion of the WIDB, the significance of nondetection is difficult to determine, especially as it relates to pesticide use patterns and to management practices. We are not inferring that nondetection data is useless: To

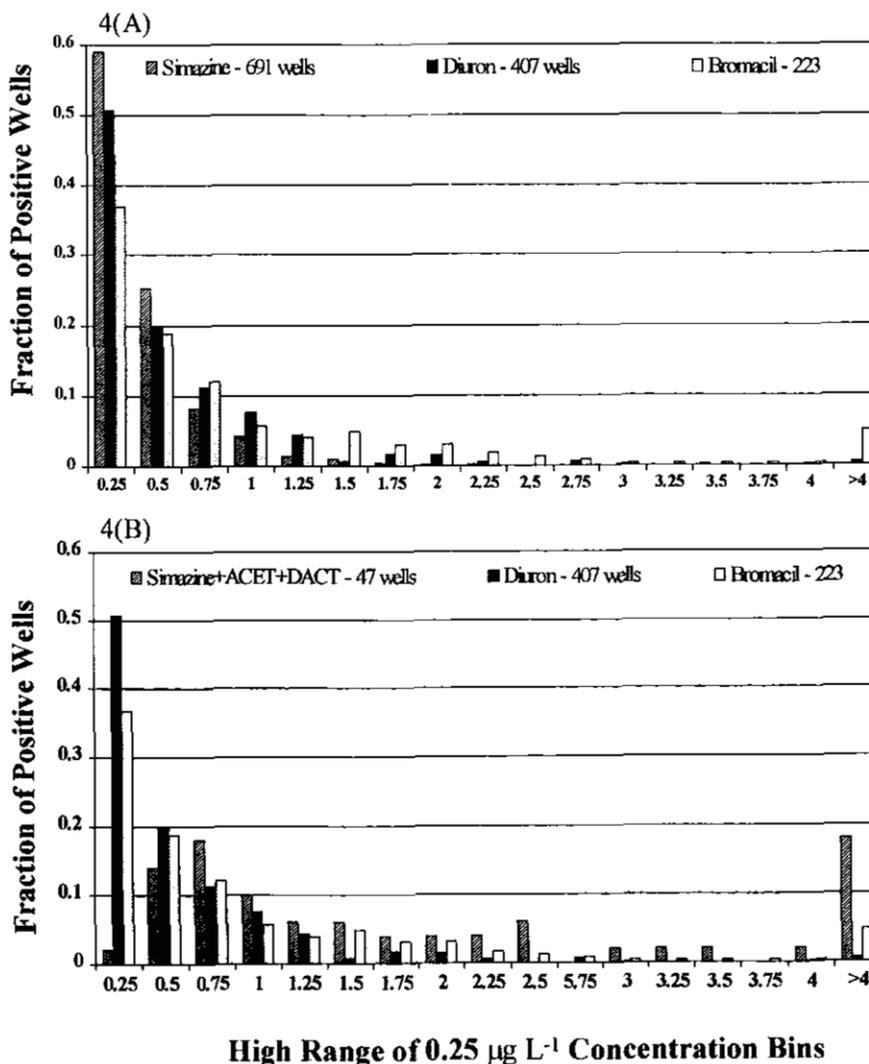


Fig. 4. Comparison of the frequency distributions for concentrations of preemergence herbicide residues detected in California well water samples and attributed to nonpoint-source applications. (A) Simazine compared with bromacil and diuron; (B) simazine + 2-amino-4-chloro-6-ethylamino-s-triazine (ACET) + 2,4-diamino-6-chloro-s-triazine (DACT) compared with bromacil and diuron. Detection above minimum detection limits [MDLs], which range from 0.05 to 0.1  $\mu\text{g L}^{-1}$ .

the contrary, it was quite important in analyzing the pattern for aldicarb. Rather, the sheer amount of information required for analysis of the whole data base currently limits investigations to a case-by-case basis.

Based on the distribution in Fig. 4a, one might conclude that simazine concentrations tend to have a higher frequency of lower concentrations as compared with the distribution for bromacil and diuron. Recently, chemical analyses have included triazine breakdown products. Data for combined simazine parent and two breakdown products, 2-amino-4-chloro-6-ethylamino-*s*-triazine (ACET) and 2,4-diamino-6-chloro-*s*-triazine (DACT), are compared with diuron and bromacil in Fig. 4b. These degradation products are related to simazine because the majority of DPR sampling has occurred in areas where use of simazine is much greater than atrazine, and detection of simazine is much more prevalent than atrazine. Although analyses were conducted at fewer sites for total triazine residues (47 wells) than for simazine alone (691 wells), the frequency distribution for total triazine residue becomes more strongly skewed toward greater concentrations, producing a much different comparison with the bromacil and diuron distributions (Fig. 4b). Concern and detection of transformation products for triazines and other active ingredients is gaining greater attention and indicates the relatively modest state of our knowledge about the occurrence and frequency of pesticide residues in well water (Kolpin et al., 1998).

## DISCUSSION

Results from domestic well sampling in other states have illustrated that patterns of detection reflect the predominant agricultural uses (Hallberg, 1989). California has a diverse array of crops, many of which are high value per acre crops such as citrus, grape (*Vitis* spp.), and tree fruit crops. This pattern contrasts with much of the Midwestern USA, which is predominated by corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.]. These cropping patterns have very different use patterns, especially for preemergence herbicides. In the Midwest, use of atrazine, alachlor, metolachlor, and now acetochlor is dominant, whereas in California, simazine, diuron, and bromacil have been used extensively for decades. While this observation supports the development of regional or local programs tailored to local off-site movement problems, it also reinforces our observation that herbicide substitution will not prevent movement to ground water. Although there are some exceptions, the majority of preemergence herbicides are persistent (long half-lives) and mobile (low attraction to soil) because they are applied before plant emergence and, as plants emerge, residues are absorbed from the soil solution by plant roots. In California, climate and agricultural factors have facilitated development of a generic approach to mitigate off-site movement. For example, on coarse soils that are located in low rainfall areas, irrigation management practices that minimize percolation also reduce leaching of residues (Troiano et al., 1993). Implementation of a similar approach may be difficult in areas where rainfall occurs throughout

the year and is the predominant source of recharge to ground water.

The methods developed to comply with the PCPA contrast with sampling designs implemented by other state and federal agencies where, in many studies, sites have been chosen a priori based on a predetermination of vulnerability (USEPA, 1993). One model used for this purpose has been DRASTIC and in some applications, the estimates appeared to have provided useful information (Aller et al., 1985; Kalinski et al., 1994; Meeks and Dean, 1990). In contrast, other tests have shown little correlation between vulnerability indices and frequency of detection (Balu and Paulsen, 1991; USEPA, 1992; Holden et al., 1992; Wade et al., 1998). For the protocols developed to implement the PCPA, sampling sites were originally located based on analysis of cropping or use patterns without determination of vulnerability, or on detections reported to DPR by other agencies for inclusion into the WIDB. Data obtained from adjacent section monitoring and focused-areal survey protocols provided further delineation of contaminated areas. Together, this information produced a relatively large data set of wells containing residues that were determined to arise from nonpoint-source pesticide applications. Observation of the spatial distribution of contaminated wells indicated a wide range in climatic and physiographic factors: Residues have been detected in areas of high and low rainfall, and in areas with clayey as well as coarse, sandy soil conditions (Fig. 5). Since

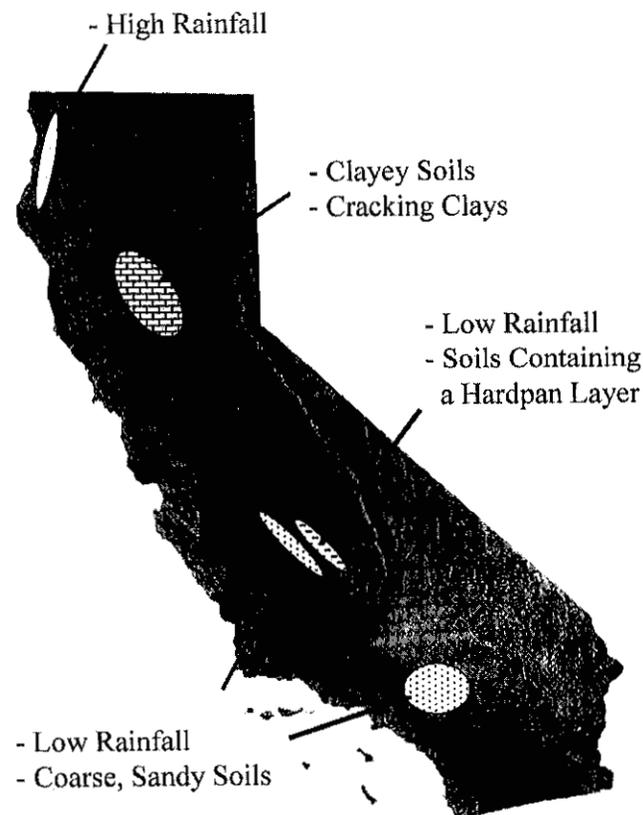


Fig. 5. Areas where pesticide residues have been detected in California and their presence has been determined to result from nonpoint-source applications.

detections covered a wide range in conditions, we have little confidence in declaring an area as invulnerable or in describing an *invulnerable condition*. Instead we have focused our efforts on describing the geographic conditions that are associated with contamination and on conducting studies to understand the processes for movement to ground water. Identification of processes enables further investigations for developing management practices that prevent movement of residues to ground water.

In order to understand factors associated with a vulnerable condition, an empirical approach has been taken to describe contaminated areas. Multivariate statistical methods, such as cluster analysis and canonical discriminant analysis, have been used, first to determine geographic factors that group contaminated sections of land, and then to classify sections of land that do not contain well sampling information (Troiano et al., 1994, 1997). The approach is flexible because additional information can be added to more accurately describe vulnerable conditions or to add new profiles of vulnerable conditions not yet described. As reported in the retrospective well study for norflurazon, initial application of this approach appeared to indicate areas with a higher probability of detection (Troiano et al., 1999). One observation from the statistical analysis is that sections with coarse soil conditions only account for approximately 20% of total contaminated sections (Troiano et al., 2000). In addition to coarse soils, soil features such as the presence of a hardpan or clayey soil conditions have been identified as important factors. For hardpan soils, runoff has been identified as a major route to ground water (Braun and Hawkins, 1991). Routes for movement to ground water have yet to be identified in certain soil clusters, further demonstrating the difficulty in identification of vulnerable conditions a priori. The vulnerability analysis forms the basis for proposed changes in the DPR's ground water regulations where best management practices will be required in vulnerable areas. Information on the regulatory program is available at the DPR website at [http://www.cdpr.ca.gov/docs/empm/gwp\\_prog/gwp\\_prog.htm](http://www.cdpr.ca.gov/docs/empm/gwp_prog/gwp_prog.htm).

## SUMMARY

The evolution of the DPR's ground water program has progressed through a mixture of scientific investigations and regulatory-driven well sampling programs. The enactment of a regulatory statute (PCPA) resulted in the development of well sampling protocols and studies to determine the extent of local ground water contamination in California. The act also mandated that the DPR maintain a data base of all well sampling conducted for pesticide residues in California, where reporting from other state agencies was mandatory and invitations for submission have been extended to all known entities. The DPR conducts sampling to verify detections in wells and then to determine if they result from nonpoint-source, legal agricultural applications. If the pattern of detections for a residue is determined as nonpoint source, it is entered into a decision-making

process. Any level of detection triggers the process. Regulations have been developed for all pesticides that have been entered into the PCPA decision-making process with some modifications of use applying statewide and others to well-defined areas of detection. To date, 16 pesticide active ingredients or breakdown products have been detected in ground water from legal agricultural applications and, hence, from nonpoint-source applications (Table 4). The detections cover such a wide range in climatic and geographic conditions that we have little confidence in declaring an invulnerable condition. Instead, we have focused on understanding the geographic factors that determine vulnerable conditions and on conducting studies that describe the various processes by which pesticides move offsite to ground water.

## ACKNOWLEDGMENTS

We are most grateful and appreciative for the efforts of all who have been associated with the Environmental Hazards and Assessment Program, and the Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, California, whose chemists have participated in the analysis of our well water samples. The evolution of the program was due to their high level of enthusiasm and integrity.

## REFERENCES

- Aller, L., T. Bennett, J.H. Lehr, and R.J. Petty. 1985. DRASTIC: A standardized system for evaluating ground water pollution potential using hydrogeologic settings. EPA/600/2-85/018. USEPA, Washington, DC.
- Balu, K., and R.T. Paulsen. 1991. Interpretation of atrazine in ground water data using a geographic information system. p. 431-446. In D.L. Weigmann (ed.) Pesticides in the next decade: The challenges ahead. Proc. of the 3rd Natl. Res. Conf. on Pesticides, Brookfield, VA. 8-9 Nov. 1990. Virginia Water Resour. Res. Center, Virginia Polytechnic Inst. and State Univ., Blacksburg.
- Bartkowiak, D., K. Newhart, M. Pepple, J. Troiano, D. Weaver, and SWRCB Staff. 1999. Sampling for pesticide residues in California well water. 1999 update of the Well Inventory Database. EH 00-04. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.
- Braun, A.L., and L.S. Hawkins. 1991. Presence of bromacil, diuron, and simazine in surface water runoff from agricultural fields and non-crop sites in Tulare County, California. PM 91-1. Environ. Monitoring and Pest Management Branch, Dep. of Pesticide Regulation, California EPA, Sacramento.
- Burlinson, N.E., L.A. Lee, and D.H. Rosenblatt. 1982. Kinetics and products of hydrolysis of 1,2-dibromo-3-chloropropane. Environ. Sci. Technol. 16:627-632.
- Cohen, S.Z., S.M. Creeger, R.F. Carsel, and C.G. Enfield. 1984. Potential pesticide contamination of groundwater resulting from agricultural uses. p. 297-325. In R.R. Krueger and J.N. Seiber (ed.) Treatment and disposal of pesticide wastes. Am. Chem. Soc. Symp. Ser. 259. ACS, Washington, DC.
- Connelly, L. 1986. AB2021-Pesticide Contamination Prevention Act. Article 15, Chapter 2, Revision 7, Food and Agricultural Code, Sacramento, California [Online]. Available at <http://www.leginfo.ca.gov/calaw.html/> (verified 24 July 2000).
- Creeger, S. 1986. Considering pesticide potential for reaching ground water registration of pesticides. p. 548-557. In W.Y. Garner, R.C. Honeycutt, and H.N. Nigg (ed.) Evaluation of pesticides in ground water. Am. Chem. Soc. Symp. Ser. 315. ACS, Washington, DC.
- Davis, R.E., and F.F. Foote. 1966. Surveying theory and practice. 5th ed. McGraw-Hill Book Company, New York.
- Deeley, G.M., M.R. Reinhard, and S.M. Stearns. 1991. Transformation and sorption of 1,2-dibromo-3-chloropropane in subsurface samples collected at Fresno, California. J. Environ. Qual. 20:547-556.

- Gronberg, J.A.M., N.M. Dubrovsky, C.R. Kratzer, J.L. Domagalski, L.R. Brown, and K.R. Burow. 1998. Environmental setting of the San Joaquin-Tulare Basins, California. Rep. 97-4205. U.S. Geological Survey, Water-Resources Investigations, Sacramento, CA.
- Hallberg, G.R. 1989. Pesticide pollution of groundwater in the humid United States. *Agric. Ecosyst. Environ.* 26:299-367.
- Holden, L.R., J.A. Graham, R.W. Whitmore, W.J. Alexander, R.W. Pratt, S.K. Liddle, and L.L. Piper. 1992. Results of the national alachlor well water survey. *Environ. Sci. Technol.* 26:935-943.
- Johnson, B. 1991. Setting revised specific numerical values. EH 91-6. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.
- Jones, R.L. 1986. Field, laboratory, and modeling studies on the degradation and transport of aldicarb residues in soil and ground water. p. 197-218. *In* W.Y. Garner et al. (ed.) *Evaluation of pesticides in ground water*. Am. Chem. Soc. Symp. Ser. 315. ACS, Washington, DC.
- Kalinski, R.J., W.E. Kelly, I. Bogardi, R.L. Ehrman, and P.D. Yamamoto. 1994. Correlation between DRASTIC vulnerabilities and incidents of VOC contamination of municipal wells in Nebraska. *Ground Water* 32:31-34.
- Klaseus, T.G., G.C. Buzicky, and E.C. Schneider. 1988. Pesticides and groundwater: Surveys of selected Minnesota wells. Prepared for the Legislative Commission on Minnesota Resources, February 1988. Minnesota Dep. of Agric., St. Paul.
- Kollman, W. 1999. Report on economic poisons exceeding specific numerical values pursuant to the Pesticide Contamination Prevention Act. EH 99-04. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.
- Kolpin, D.W., S.J. Kalkhoff, D.A. Goolsby, D.A. Sneek-Fahrer, and E.M. Thurman. 1997. Occurrence of selected herbicides and herbicide degradation products in Iowa's ground water, 1995. *Ground Water* 35:679-688.
- Kolpin, D.W., E.M. Thurman, and S.M. Linhart. 1998. The environmental occurrence of herbicides: The importance of degradates in ground water. *Arch. Environ. Contam. Toxicol.* 35:385-390.
- Marade, S.J., and D.J. Weaver. 1994. Monitoring for aldicarb residues in ground water of the central valley of California. *Bull. Environ. Contam. Toxicol.* 52:1924.
- Martin, J.D., R.J. Gilliom, and T.L. Schertz. 1999. Summary and evaluation of pesticides in field blanks collected for the national water-quality assessment program, 1992-1995. Open File Rep. 98-412. U.S. Geological Survey, National Water Quality Assessment Program, Indianapolis, IN.
- Meeks, Y.J., and J.D. Dean. 1990. Evaluating ground-water vulnerability to pesticides. *J. Water Resour. Plan. Manage.* 116:693-707.
- Peoples, S.A., K.T. Maddy, W. Cusick, T. Jackson, C. Cooper, and A.S. Frederickson. 1980. A study of samples of well water collected from selected areas in California to determine the presence of DBCP and certain other pesticide residues. *Bull. Environ. Contam. Toxicol.* 24:611-618.
- Sava, R. 1994. Guide to sampling air, water, soil, and vegetation for chemical analysis. EH 94-04. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.
- Schmidt, K.D. 1986. DBCP in ground water of the Fresno-Dinuba area, California. p. 511-529. *In* Proc. of the Agric. Impacts on Ground Water: National Water Well Assoc. Conf., Omaha, NE. 11-13 Aug. 1986. National Water Well Association, Dublin, OH.
- Sitts, J.A. 1989. Survey for bentazon in well water of 15 California counties, December 1988-May 1989. EH 89-10. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.
- Spurlock, F., K. Burow, and N. Dubrovsky. 2000. Chlorofluorocarbon dating of herbicide containing well waters in Fresno and Tulare Counties, California. *J. Environ. Qual.* 29:474-483.
- Troiano, J., C. Garretson, C. Krauter, and J. Brownell. 1993. Influence of amount and method of irrigation water application on leaching of atrazine. *J. Environ. Qual.* 22:290-298.
- Troiano, J., B.R. Johnson, S. Powell, and S. Schoenig. 1994. Use of cluster and principal component analyses to profile areas in California where ground water has been contaminated by pesticides. *Environ. Monit. Assess.* 32:269-288.
- Troiano, J., J. Marade, and F. Spurlock. 1999. Empirical modeling of spatial vulnerability applied to a norflurazon retrospective well study in California. *J. Environ. Qual.* 28:397-403.
- Troiano, J., C. Nordmark, T. Barry, and B. Johnson. 1997. Profiling areas of ground water contamination by pesticides in California: Phase II—Evaluation and modification of a statistical model. *Environ. Monit. Assess.* 45:301-318.
- Troiano, J., F. Spurlock, and J. Marade. 2000. Update of the California vulnerability soil analysis for movement of pesticides to ground water: 14 Oct. 1999. EH 00-05. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.
- USEPA. 1992. ANOTHER LOOK: National Pesticide Survey Phase II Report. USEPA 570/9-91-020. U.S. Gov. Print. Office, Washington, DC.
- USEPA. 1993. A review of methods for assessing aquifer sensitivity and ground water vulnerability to pesticide contamination. USEPA 813-R-93-002. U.S. Gov. Print. Office, Washington, DC.
- Wade, H.G., A.C. York, A.E. Morey, J.M. Padmore, and K.M. Rudo. 1998. The impact of pesticide use on groundwater in North Carolina. *J. Environ. Qual.* 27:1018-1026.
- Warner, S.A., H. Lundborg, D. Whyte, M.J. Heassler, and S. Gergus. 1989. Groundwater pollution by pesticides on the Smith River Plains, Del Norte County. Regional Water Quality Control Board, North Coast Region, Santa Rosa, CA.
- Weaver, D.J., R.J. Sava, F. Zalkin, and R.J. Oshima. 1983. Pesticide movement to groundwater. Volume I: Survey of groundwater basins for DBCP, EDB, simazine, and carbofuran. EH 83-01. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.
- Wilkerson, M.R., and K.D. Kim. 1986. The pesticide contamination prevention act: Setting specific numerical values. EH 86-02. Environ. Monitoring and Assessment Program, Dep. of Pesticide Regulation, California EPA, Sacramento.