

PESTICIDE MOVEMENT TO GROUND WATER

**VOLUME I: SURVEY OF GROUND WATER BASINS FOR
DBCP, EDB, SIMAZINE AND CARBOFURAN**

January 1983

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

**STATE OF CALIFORNIA
Department of Food and Agriculture
Division of Pest Management, Environmental Protection
and Worker Safety
Unit of Environmental Monitoring and Pest Management
1220 N Street, Sacramento, California 95814**

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Volume I: Survey of Groundwater Basins
for DBCP, EDB, Simazine, and Carbofuran

by

D.J. Weaver, R.J. Sava,
F. Zalkin, and R.J. Oshima

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Field Monitoring: R. Sava, F. Zalkin, S. Simpson,
D. Duncan, B. Johnson, R. Segawa
I. Carmean, C. Garretson,
J. Pratt, L. Herschberger,
T. C. Poole, Jr., G. Baker

Sampling Methods
and Preparation: T. Mischke, J. Franz, V. Bunac,
and B. Winters

Chemical Analysis: S. Fredrickson, T. Jackson,
S. Margetich, P. Schlocker,
R. Magkoski, J. Echelberg,
E. Wong, and D. Conrad

Data Processing: L. Neher and R. Segawa

Programming and
Graphics: L. Neher, T. Arnold¹

1) Statewide Air Pollution Research Center

ABSTRACT

A study was conducted during the summer of 1982 to determine the spacial distribution of groundwater contamination by certain pesticides in four of California's major agricultural areas. This was the first phase of a broad based project designed to study the mobility of selected pesticides to groundwater. Samples were collected from wells preselected for shallow depth and certain other criteria. Large quantities of the pesticides, carbofuran, DBCP, EDB and simazine had been used in previous years in all four areas. None of the pesticides were detected in water samples from the Santa Maria or Salinas Valley groundwater basins where one well was sampled in each of 7 and 21 6x6 mile cells, respectively. DBCP was detected in six of 23 wells sampled in the Upper Santa Ana groundwater basin. Two of the wells also contained simazine and carbofuran was found in one well, the only positive sample in the entire study. A single well was sampled from each of 166, 6x12 mile cells in the San Joaquin Valley. Twenty-one samples (9 from Fresno County) contained DBCP, three contained simazine and two contained EDB. This is the first report of simazine or EDB contamination of groundwater in California. The results suggest that a reliable estimate of the spacial distribution of groundwater contamination by certain pesticides may be obtained by the methods utilized in this study. Further, groundwater sampling is a useful means of evaluating the downward movement of pesticides after application to soil.

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EPA GROUNDWATER STUDY REPORT

I. INTRODUCTION

Groundwater is contained in geologic formations called aquifers, layers of permeable soil, sand or gravel. Water reaches an aquifer from relatively permeable surface water drainage basins. This recharge, or net flow of water into the earth, can occur at streams and lakes or may occur generally through the soil above the aquifer. The recharge may also occur at a significant horizontal distance from the entry point of the water at the surface. About 40% (15 million acre-feet) of the water used each year in California for irrigation, domestic and industrial purposes is groundwater (6). There are approximately 143 million acre-feet of storage capacity for usable groundwater, about three times the amount of the annual usable surface storage capacity (6).

Industrial waste and municipal waste disposal sites have been considered to present a significant threat to groundwater quality. Groundwater contamination by synthetic organic chemicals from these sources has been extensively documented and remains a serious and on-going concern.

In the past, the amount of pesticides found in groundwater was generally negligible or non-existent. A 1972 Stanford Research Institute article (5) stated that, "Most data collected imply that the

incidence of pesticides in groundwater is low and not a significant environmental contamination factor." It was also generally believed that potential groundwater contamination by pesticides would be negligible because of dilution factors, low water solubility of soil applied pesticides, rapid degradation or binding to soil particles as well as high vapor pressure of certain pesticides.

Perceptions of the possibility of pesticide contamination of groundwater have changed. This has occurred partly because of a better understanding of the mechanisms for transport and degradation and also because of a significant technical improvement in our ability to detect very small concentrations of pesticides. It is now evident that at least the upper layers of some aquifers do have measurable amounts of pesticidal chemicals.

One such problem of contamination of groundwater by a pesticide became apparent in California in the late 1970's. DBCP (1,2-dibromo-3-chloropropane), a soil fumigant that had been used for nematode control in vineyards, orchards and annual crops for several years, was detected in well water (3). The water contamination came to light after DBCP had already been banned from further use because it had been linked to temporary sterility, birth defects and cancer. The results of a study recently conducted by the Fresno County Health Department also demonstrated that a high percentage of the shallowest wells in portions of that county were contaminated by DBCP.

Although a great deal of research has been conducted on the interaction, persistence and movement of pesticides in soil, much of the work has been done under laboratory conditions or has been confined to the upper few feet of field soil.

The purpose of the study described in this report was to determine whether certain pesticides are sufficiently mobile to percolate into, and be detectable in, groundwater. The intent was to use groundwater as the sampling medium to determine if pesticides had moved through the soil to the depth sampled. A major objective was to quantify the spacial distribution (geographical) of shallow groundwater contamination by four pesticides in four major California agricultural production regions. The objective focuses on a limited population of wells described in the Materials and Methods section. The pesticides selected for study include DBCP and EDB (ethylene dibromide) which are both used as soil fumigants for the control of plant parasitic nematodes.

The remaining chemicals, selected for their widespread usage, are simazine, an s-triazine herbicide, and carbofuran, a carbamate compound used for insect and nematode control. Originally, atrazine, and not simazine had been selected for inclusion in this study. However, during the analysis of water samples, simazine was detected in some samples and atrazine in none.

This report contains the results of sampling and analysis of water from wells located throughout the four groundwater basins. Part 2 of the study involved the collection and analysis of soil cores from pesticide application sites and will be presented in a separate report (Volume II). Additionally, a third volume will attempt to evaluate the contribution of several variables (land use, soil type, etc.) towards facilitating the mobility of pesticides to groundwater.

II. MATERIALS AND METHODS

A. GROUNDWATER BASINS INCLUDED IN STUDY

Groundwater basins in four of California's major agricultural production areas (see Figure 1 for geographical locations) were selected for this study and include:

1. Salinas Valley - located in Monterey and southern Santa Cruz Counties, covering an area of 740 square miles.
2. San Joaquin Valley - located in Alameda, Contra Costa, Fresno, Kern, Kings, Madera, Merced, San Joaquin, Stanislaus, and Tulare Counties, covering an area of 13,500 square miles.
3. Upper Santa Ana - located in western Riverside and San Bernardino Counties, covering an area of 620 square miles.

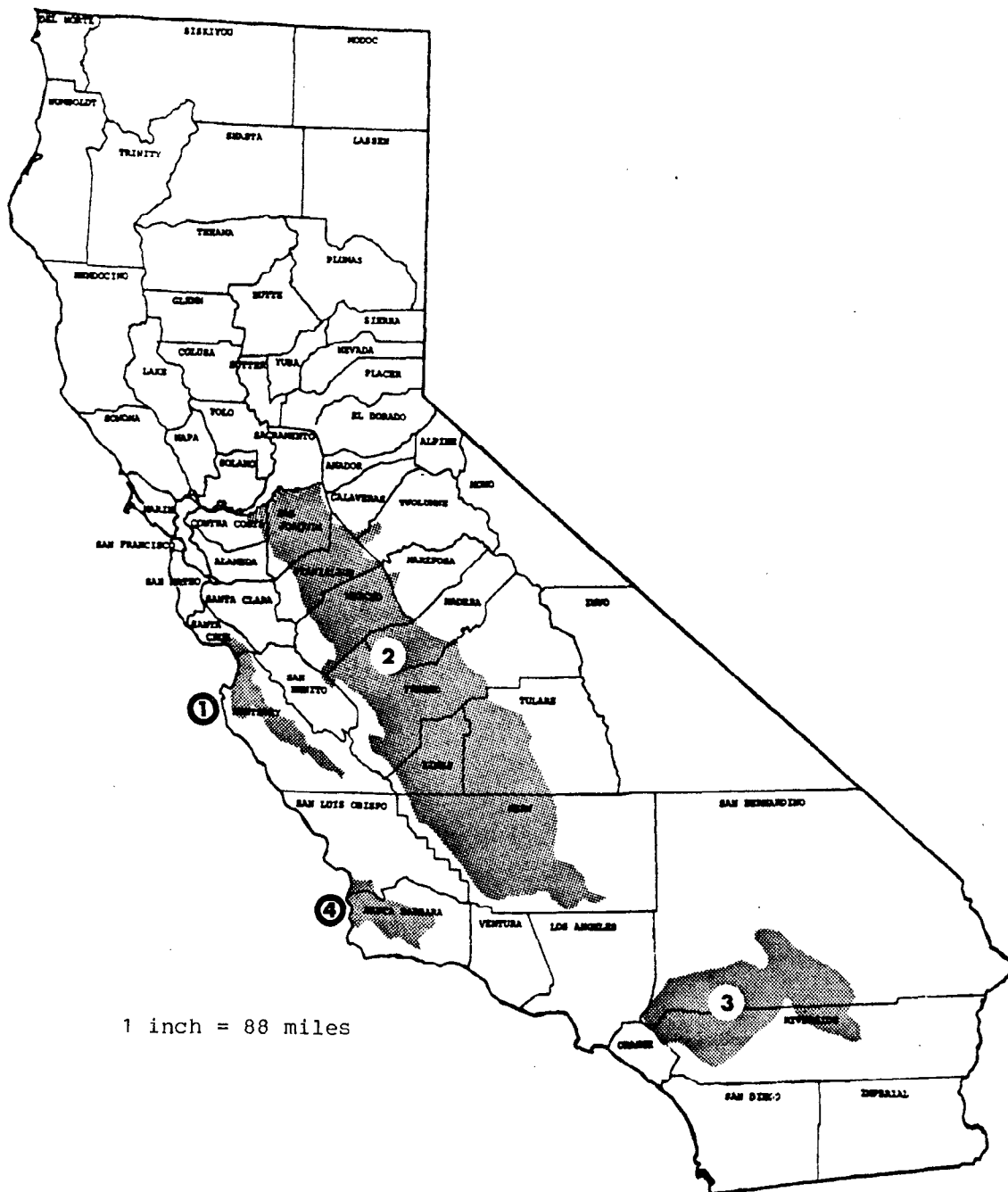


FIGURE 1. Geographical locations (shaded areas) of the 1) Salinas Valley, 2) San Joaquin Valley, 3) Upper Santa Ana, and 4) Santa Maria groundwater basins.

4. Santa Maria - located in San Luis Obispo and Santa Barbara Counties, covering an area of 240 square miles.

Total quantities of carbofuran, DBCP, EDB and simazine that were reported as used between 1970 and 1981 in the counties that encompass each groundwater basin are presented in Table 1.

B. SAMPLE CELL SIZE

In order to insure that the groundwater basin was sampled with a representative spacial distribution of wells, a matrix system was established utilizing township and range boundaries to establish sample cells. Each cell was 6 x 6 miles (36 square miles) for the Salinas, Santa Maria and Santa Ana aquifers but for the larger San Joaquin Valley, two adjacent 6 x 6 mile cells were combined to form cells 6 x 12 miles (72 square miles). All cells were numbered sequentially and referred to by cell number or township-range location.

C. SELECTION OF WELLS FOR SAMPLING

Well logs filed by local well drillers provided the information used to select wells to be sampled in each cell of the four aquifers. Access to well log information was provided mainly by the Department of Water Resources; other sources of information included County Health Departments, Flood Control Districts and Municipal water

TABLE 1. Total pounds of four pesticides applied from 1970 to 1981 in California counties that encompass the upper Santa Ana, Santa Maria, Salinas and San Joaquin Valley groundwater basins.

Groundwater Basin	County	Pounds of Pesticide applied, 1970-1981 ^{a/}			
		Carbofuran	DBCP ^{b/}	EDB	Simazine
Upper Santa Ana	Riverside	30,780	206,352	320,569	131,201
	San Bernardino	3,862	44,668	17,881	82,622
Santa Maria	Santa Barbara	3,917	205,310	239,211	62,100
	San Luis Obispo	16,409	92,521	67,176	28,698
Salinas	Monterey	7,831	320,837	65,828	109,145
	Santa Cruz	28	11	0	23,494
San Joaquin	Alameda	1,562	2,420	2,490	142,352
	Contra Costa	1,199	6,039	0	88,552
	Fresno	61,129	575,768	32,963	255,213
	Kern	61,758	183,764	40,042	210,794
	Kings	13,387	8,573	2,160	8,371
	Madera	23,841	188,122	8,000	114,019
	Merced	41,534	163,788	139,021	100,328
	Sacramento	18,162	2,122	15,519	89,799
	San Joaquin	112,336	1,220,753	619,485	75,126
	Stanislaus	25,615	272,329	1,379,810	94,133
Tulare	49,402	256,281	71,136	268,275	

^{a/} Data obtained from compilations of pesticide use reports, California Department of Food and Agriculture; reported as pounds of commercial formulation.

^{b/} Use of DBCP was suspended in 1977.

suppliers.

A preliminary survey of the data bases characterizing the well populations within the four study areas indicated the following:

1. The total population of wells was far too large to adequately sample with existing procedures.
2. Most privately owned wells were poorly characterized in terms of documented, verifiable well measurements.
3. A significant population of deep wells drawing from multiple aquifers existed in each groundwater basin. Water samples drawn from these wells would not be useful in determining the location of soil coring sites.

Based on this information, the study design was altered to address limited objectives which would only apply to a small, artificially selected population of wells but would allow the greatest potential for developing the information needed to conduct the soil core sampling. The study design was developed to apply to the shallowest wells available that were homogeneously distributed over the study areas. It was not intended to characterize the entire well population or the full groundwater basin associated with each of the four study areas. The spacial distribution of interest was a one-dimensional surface (geographical distribution) to aid in selecting the soil core

sampling locations and to define general areas of water contamination.

The following factors, listed in order of importance, were used to select the three or four most "suitable" wells from the well logs for each sample cell:

1. Draws from the shallowest unconfined groundwater.
2. Depth and location of perforations.
3. Central location within a cell.
4. Ease of obtaining an unaerated sample.
5. Ease of access during the sampling period.
6. Proper seal on well.
7. Steel casing rather than PVC when possible.

Using the suitability ordering sequence as a guide, attempts were made to locate the wells in the field and obtain owner permission for sampling. Once two wells had been secured, the more suitable was designated as the sampling well and the other was designated as the alternate.

D. TEN WELL CELLS

In order to determine the variability among wells within a cell, 10 wells were selected for sampling in each of two different cells. One cell (6 x 6 miles) in the Salinas Valley and one cell (6 x 12 miles) in the San Joaquin Valley were designated as 10 well cells based upon the availability of wells with the desired characteristics. The same procedures for selecting wells and obtaining permission to sample as described in section C were used. Before sampling began, one well was designated as the primary well to represent the cell in the study and the remaining nine wells were designated as wells sampled as part of the 10 well cell. Additionally, a statistical comparison of the mean of two wells and the mean of the remaining eight wells was undertaken to determine whether a larger sample size would have improved cell characterizations.

E. TYPES OF WELL PUMPS AND SAMPLING PORTS

Three general categories of well pumping equipment with various types of sampling ports were encountered in the wells selected for sampling.

1. Turbine motors with a submerged pump were found on many irrigation wells, deep wells and older domestic wells. These pumps usually had a discharge line with a sampleable port, faucet, removable

plug, removable pressure gauge, pressure release valve or an outlet on the discharge pipe.

2. Submersible motors and pumps were found on most domestic wells that drew water from 200 feet deep or less. A delivery line connecting the well head and storage tank incorporated sampling ports that included a Schrader valve, removable plug, faucet, or pressure release valve.
3. Jet pumps with above ground motors and pumps were found on domestic wells drawing water from 50 feet or less. These generally had a removable discharge line, plug or pressure release valve.

F. COLLECTION OF WATER SAMPLES

Water samples were collected between 27 May and 8 July 1982. The period of sampling for individual aquifers was as follows:

Salinas Valley - 27 May thru 3 June

San Joaquin Valley - 2 June thru 1 July

Upper Santa Ana Valley - 7 July thru 8 July

Santa Maria - 30 June thru 1 July

Before samples were taken, certain procedures were followed to insure that the sample came from fresh recharge water from the aquifer and not from water that had already been in the casing. Whenever possible, well log information was used to calculate the volume of

standing water in the well casing using the formula $\pi \times r \times h$ (where: r = the radius of the casing; h = height of standing water above the water table in the casing). Then the volume of water being pumped per minute from the well was estimated after opening a discharge port. This information was used to calculate the number of minutes the pump should run in order to flush out three volumes of standing water from the well casing. Pumps were run for the required amount of time and then a sample was taken. When insufficient information was available or when conditions did not allow for running a pump sufficiently long to flush the casing before sampling, the pump was run for as long as conditions would permit. All samples were collected while pumps were still running.

Samples were collected using a 2-foot-long piece of 1/4 inch I.D. Teflon tubing to keep sample aeration to a minimum. The tubing was inserted directly into the sampling port or, if necessary, into the stream of water. When Schrader valves were used as sampling ports, it was necessary to use a 2-inch-long piece of 5/16 inch I.D. Tygon tubing to cover both the valve and the Teflon tubing and keep the Teflon tubing butted tightly against the valve. Water contact with Tygon tubing was minimal and a new length of Teflon tubing (and Tygon tubing when necessary) was used at each well.

Two, 1 liter, amber glass, narrow-necked bottles were completely filled with water from each well that was sampled. The Teflon tube was inserted all the way to the bottom of the bottle to reduce

aeration as the bottle filled with water. After the bottle became filled, the opening was sealed with aluminum foil and the cap was screwed on tightly. The bottles were immediately placed in an ice chest in styrofoam holders to prevent breakage and maintained at approximately 4°C. The samples were transported to the California Department of Food and Agriculture facility in Sacramento within 3 days after collection and were then stored at 4°C until analyzed. All bottles used in the study were cleaned with detergent, rinsed with distilled water, and dried in an oven before use.

G. CHAINS OF CUSTODY

Each water sample was accompanied by a chain of custody which was filled out at the time of sample collection. Included on the chain of custody was the date and time of sampling, location of the well, number of minutes that the pump was run before a sample was taken, the type of well, type of sampling port, the persons who collected the sample and any comments pertinent to the sampling of that particular well (such as vineyard located nearby, etc.).

H. CHEMICAL ANALYSES OF WATER SAMPLES

All chemical analyses were performed by the Chemistry Laboratory Services Unit of the California Department of Food and Agriculture at the Unit's main laboratory in Sacramento. Documentation of analytical methods is presented in Appendices III - VI.

I. COMPARATIVE ANALYSES OF DUPLICATE SAMPLES (INTERLABORATORY QUALITY CONTROL)

In order to insure the accuracy of the analytical results, both 1 liter samples collected from selected wells were analyzed, each by a different laboratory. One sample was analyzed by the CDFA laboratory and the other was sent to an independent laboratory for analysis. California Analytical Laboratories in Sacramento received 16 samples and the State of California, Department of Health Services, Hazardous Materials Laboratory in Berkeley received 10 samples. In a few cases the samples for quality control were chosen to confirm positive results by the CDFA laboratory. However, most of the samples chosen for quality control were selected at random from all the samples collected.

J. EFFECT OF STORAGE ON PESTICIDE CONCENTRATIONS IN SPIKED SAMPLES

A separate study was conducted to insure that the water sample storage regime used in this study did not affect the analytical results. Four sets of four water samples each containing either DBCP at 2 ppb, EDB at 2 ppb, atrazine at 4 ppb or carbofuran at 4 ppb were prepared by California Analytical Laboratories. The water used for all of the samples was collected from an agricultural well located in the San Joaquin Valley. All samples were stored at 4°C until analyzed.

One sample from each set was analyzed by the CDFA laboratory immediately after preparation. One week later another sample from each set was analyzed. All of the remaining samples were analyzed 2 days later, a total of 9 days after sample preparation. Once the collection of well samples began, all samples were analyzed within 7 to 9 days after being taken from the wells.

III. RESULTS

A. ANALYSES OF WATER SAMPLES

Blanks using laboratory distilled water were run for all analyses before any well samples were analyzed. Further, spikes were run for carbofuran, atrazine and simazine at the 5 ppb level with 90% recoveries. EDB and DBCP spikes of 0.1, 1, and 5 ppb were recovered at greater than 90% in all cases.

Water samples were collected from a total of 217 wells in the four groundwater basins during the period 27 May to 8 July 1982.

Quantities of DBCP ranging from 0.1 to 10.5 ppb were found in 27 (12.4%) of the samples, EDB at 0.1 to 0.2 ppb was found in 2 (0.9%) samples, simazine at 0.5 to 3.5 ppb was found in 5 (2.3%) samples, and carbofuran was found in 1 sample at a concentration of 0.5 ppb (Table 2). Atrazine was not detected in any of the samples.

TABLE 2. Pesticide contamination of wells in California counties that encompass the Upper Santa Ana, Santa Maria, Salinas, and San Joaquin Valley groundwater basins.

Groundwater Basin	No. of sample cells	County	No. of ^{a/} sample cells	Total No. of wells containing: ^{b/}			
				Carbofuran	DBCP	EDB	Simazine ^{c/}
Salinas	21 (6x6 miles)	Monterey	19	0	0	0	0
		Santa Cruz	2	0	0	0	0
Santa Maria	7 (6x6 miles)	San Luis Obispo	2	0	0	0	0
		Santa Barbara	5	0	0	0	0
Upper Santa Ana	23 (6x6 miles)	Riverside	11	1	4	0	2
		San Bernardino	12	0	2	0	0
San Joaquin	166 ^{d/} (6x12 miles)	Contra Costa	3	0	0	0	0
		Fresno	38	0	9	2	1
		Kern	32	0	3	0	0
		Kings	11	0	0	0	0
		Madera	10	0	1	0	0
		Merced	20	0	1	0	0
		San Joaquin	19	0	3	0	0
		Stanislaus	11	0	1	0	0
Tulare	<u>22</u>	<u>0</u>	<u>3</u>	<u>0</u>	<u>2</u>		
TOTALS	217		217	1	27	2	5

^{a/} Equivalent to the number of wells sampled

^{b/} Results from additional wells in two 10 well cells are not included

^{c/} No atrazine was detected in the water samples

^{d/} A total of 188 sample cells were included in the San Joaquin Valley but wells suitable for sampling were found in only 166 of the cells

Minimum detectable levels of the four pesticides during analysis of water samples were 0.1 ppb for DBCP, 0.1 ppb for EDB, 1.0 ppb^{1/} for carbofuran and 0.5 ppb for simazine. All positive results were confirmed using two different gas chromatography columns employing the same detector. Additionally, positive carbofuran and simazine results were confirmed by gas chromatograph/mass spectrometry; positive DBCP and EDB samples were not confirmed by this method due to low levels.

A more detailed discussion of pesticide contamination of well water and characterization of wells for each groundwater basin is presented in the pages that follow.

1. SALINAS VALLEY GROUNDWATER BASIN

One well in each of 21 cells (6x6 miles) was sampled in the Salinas Valley but none of the samples contained detectable concentrations of the pesticides under consideration (Table 2). The majority of the wells selected for sampling were domestic (61.9%) or agricultural (23.8%) (Table 3). The depths of wells that were sampled ranged from less than 50 feet to more than 300 feet but over 90% of the wells were in the 51 to 300 foot range (Table 4).

^{1/} Average minimum detectable value based on total samples. The minimum detectable level varied on a sample basis with a range of 0.5 to 1.5 ppb. Due to the large number of samples analyzed, the minimum detectable level is reported as an average.

TABLE 3. Characterization by type of use of all wells sampled in four groundwater basins

Groundwater Basin	County	Number of wells sampled	Number of wells by type of use ^{a/}			
			Domestic	Municipal	Agricultural	Industrial
Upper Santa Ana	Riverside	11	4	4	2	1
	San Bernardino	<u>12</u>	<u>1</u>	<u>7</u>	<u>3</u>	<u>1</u>
	TOTAL	23	5	11	5	2
Santa Maria	Santa Barbara	5	2	2	1	0
	San Luis Obispo	<u>2</u>	<u>1</u>	<u>0</u>	<u>1</u>	<u>0</u>
	TOTAL	7	3	2	2	0
Salinas	Monterey	19	12	1	5	1
	Santa Cruz	<u>2</u>	<u>2</u>	<u>0</u>	<u>0</u>	<u>0</u>
	TOTAL	21	14	1	5	1
San Joaquin	Contra Costa	3	3	0	0	0
	Fresno	38	27	2	9	1
	Kern	32	29	0	3	0
	Kings	11	7	0	4	0
	Madera	10	9	0	0	1
	Merced	20	19	0	0	1
	San Joaquin	19	16	0	2	1
	Stanislaus	11	9	1	0	1
	Tulare	<u>22</u>	<u>22</u>	<u>0</u>	<u>0</u>	<u>0</u>
TOTAL	166	141	3	18	5	

^{a/} Excludes additional wells from two 10 well cells

TABLE 4. Characterization by well depth of all wells sampled in four groundwater basins.

Groundwater basin	County	Number of wells sampled	Number of wells in various depth (ft) ranges ^{a/}				
			20-50	51-100	101-200	201-300	>300
Upper Santa Ana	Riverside	11	0	4	2	3	2
	San Bernardino	12	0	0	3	0	9
	TOTAL	23	0	4	5	3	11
Santa Maria	Santa Barbara	5	0	0	1	2	2
	San Luis Obispo	2	0	0	0	0	2
	TOTAL	7	0	0	1	2	4
Salinas	Monterey	19	1	4	6	7	1
	Santa Cruz	2	0	1	1	0	0
	TOTAL	21	1	5	7	7	1
San Joaquin	Contra Costa	3	0	0	3	0	0
	Fresno	38	1	11	11	6	9
	Kern ^{b/}	32	0	0	3	14	14
	Kings	11	2	2	3	0	4
	Madera	10	0	1	7	2	0
	Merced	20	1	10	9	0	0
	San Joaquin	19	0	8	11	0	0
	Stanislaus	11	0	8	3	0	0
	Tulare	22	1	8	7	3	3
TOTAL	166	5	48	57	25	30	

^{a/} Excludes additional wells from two 10 well cells

^{b/} No depth record for one well

2. SANTA MARIA GROUNDWATER BASIN

None of the seven wells that were sampled contained detectable concentrations of the four pesticides under consideration (Table 2). The types of use for the sampled wells were nearly evenly distributed among domestic, municipal and agricultural (Table 3). However, when the wells were characterized by depth, more than 57% were over 300 feet deep and the remainder were between 100 and 300 feet in depth (Table 4).

3. UPPER SANTA ANA GROUNDWATER BASIN

A total of 23 wells were sampled in this groundwater basin and nine of the wells were found to be contaminated by pesticides (Table 2).

DBCP, at concentrations ranging from 0.1 to 8.1 ppb, was found in six different wells (Fig. 2) five of which were municipal and one domestic (Table 5). Four of the six wells that contained DBCP were over 300 feet deep and two were from 51 to 100 feet deep (Table 6).

Samples from two wells, one domestic and one municipal, each contained simazine at concentrations of 0.8 and 1.0 ppb (Fig. 3). Water from both wells also contained DBCP. One of the wells was between 51 and 100 feet deep and the other was over 300 feet deep. Water from one agricultural well contained 0.5 ppb of carbofuran; none of the samples contained EDB.

TABLE 5. Characterization of wells contaminated by four pesticides as determined by analysis of water samples collected in Summer, 1982

Pesticide	County	Number of wells contaminated ^{a/}			
		Total	Domestic	Municipal	Agricultural
Carbofuran	Riverside	1	0	0	1 (0.5) ^{b/}
DBCP	Fresno	9	8 (0.1-10.5)	0	1 (5.7)
	Kern	3	3 (0.3-6.7)	0	0
	Madera	1	1 (1.3)	0	0
	Merced	1	1 (1.1)	0	0
	Riverside	4	1 (0.1)	3 (0.1-8.1)	0
	San Bernardino	2	0	2 (0.2-0.4)	0
	San Joaquin	3	3 (0.3-0.7)	0	0
	Stanislaus	1	1 (3.9)	0	0
	Tulare	3	3 (0.3-0.4)	0	0
	TOTAL	33	26 (0.1-10.5)	5 (0.1-8.1)	2 (0.5-5.7)
EDB	Fresno	2	2 (0.1-0.2)	0	0
Simazine	Fresno	2	1 (0.5)	0	1 (0.5)
	Riverside	2	1 (1.0)	1 (0.8)	0
	Tulare	2	2 (2.0-3.5)	0	0
	TOTAL	6	4 (0.5-3.5)	1 (0.8)	1 (0.5)

a/ Results for additional wells in two 10 well **cells** are not included.

b/ Values enclosed in parentheses represent the range of pesticide contamination in ppb.

TABLE 6. Characterization of wells contaminated by four pesticides as determined by analysis of water samples collected in Summer, 1982.

Pesticide	County	Total	Number of contaminated wells in various depth (ft) ranges ^{a/}				
			20-50	51-100	101-200	201-300	>300 ^{b/}
Carbofuran	Riverside	1	0	1 (0.5)	0	0	0
	Total	1	0	1	0	0	0
DBCP	Fresno	9	0	2 (0.3-1.0)	5 (0.3-8.3)	2 (0.1)	0
	Kern	3	0	0	0	1 (1.0)	2 (0.3-6.7)
	Madera	1	0	0	1 (1.3)	0	0
	Merced	1	0	1 (1.1)	0	0	0
	Riverside	4	0	2 (1.4-8.1)	0	0	2 (0.1)
	San Bernardino	2	0	0	0	0	2 (0.2-0.4)
	San Joaquin	3	0	1 (0.7)	2 (0.3-0.6)	0	0
	Stanislaus	1	0	1 (3.9)	0	0	0
	Tulare	3	0	0	1 (0.3)	1 (0.2)	1 (0.4)
	Total	27	0	7	9	4	7
EDB	Fresno	2	0	0	1 (0.1)	1 (0.2)	0
	Total	2	0	0	1	1	0
Simazine	Fresno	2	0	2 (0.5)	0	0	0
	Riverside	2	0	1 (0.8)	0	0	1 (1.0)
	Tulare	2	1 (2.0)	1 (3.5)	0	0	0
	Total	6	1	4	0	0	1

^{a/} Results for additional wells in 10 well cells are not included.

^{b/} Values enclosed in parentheses represent the range of pesticide contamination in ppb.

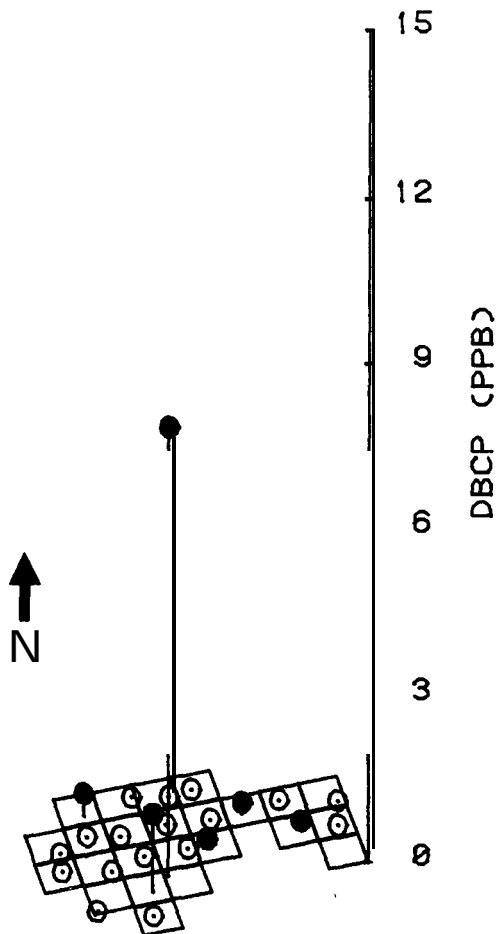


Figure 2. Arrangement of 6 x 6 mile cells in the Upper Santa Ana groundwater basin and locations of sampled wells that did (●) or did not (○) contain DBCP.

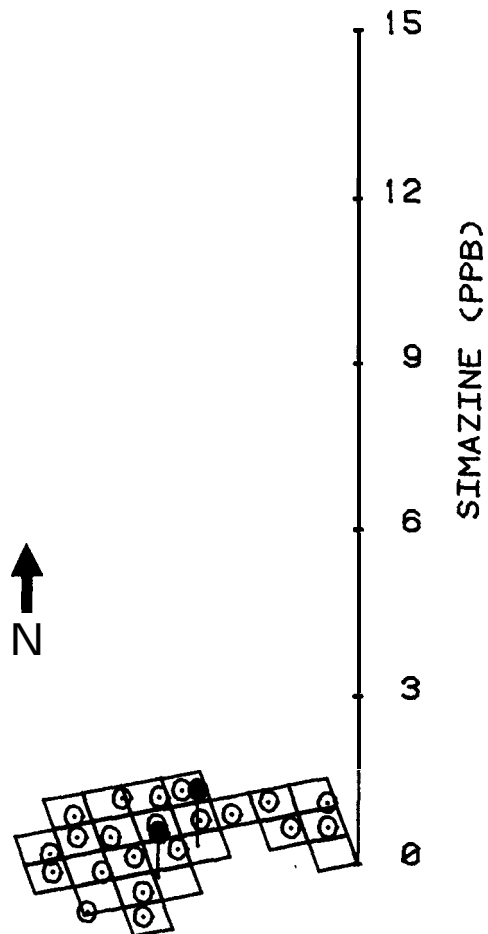


Figure 3. Arrangement of 6 x 6 mile cells in the Upper Santa Ana groundwater basin and locations of sampled wells that did (●) or did not (○) contain simazine.

4. SAN JOAQUIN VALLEY GROUNDWATER BASIN

A total of 166 wells were sampled in the San Joaquin Valley and 24 (14.5%) of the wells contained at least one of the pesticides under consideration.

Twenty-one (12.6%) wells contained DBCP at concentrations ranging from 0.1 to 10.5 ppb (Fig. 4, Tables 2,5,6). Over 95% of these wells were domestic, the remainder being agricultural. Many (42.8%) of the wells containing DBCP were in the 101 to 200 foot depth range but several (23.8%) ranged from 51 to 100 feet and one third were 201 feet or deeper. Correlations between well characteristics and concentration of DBCP in the water proved to be statistically insignificant.

Samples from two wells, both domestic and in the depth range of 101-300 feet, contained EDB at concentrations of 0.1 and 0.2 ppb, respectively. One of these wells also contained DBCP. Simazine at concentrations ranging from 0.5 to 3.5 ppb was found in four wells (Figure 5), three of which were domestic and one municipal. One of the wells was less than 50 feet deep and the remaining three were between 51 and 100 feet deep.

B. RESULTS- TEN WELL CELLS

1. SALINAS VALLEY- None of the 10 wells sampled in one 6 x 6 mile cell contained any of the pesticides under consideration (Table 7). Five

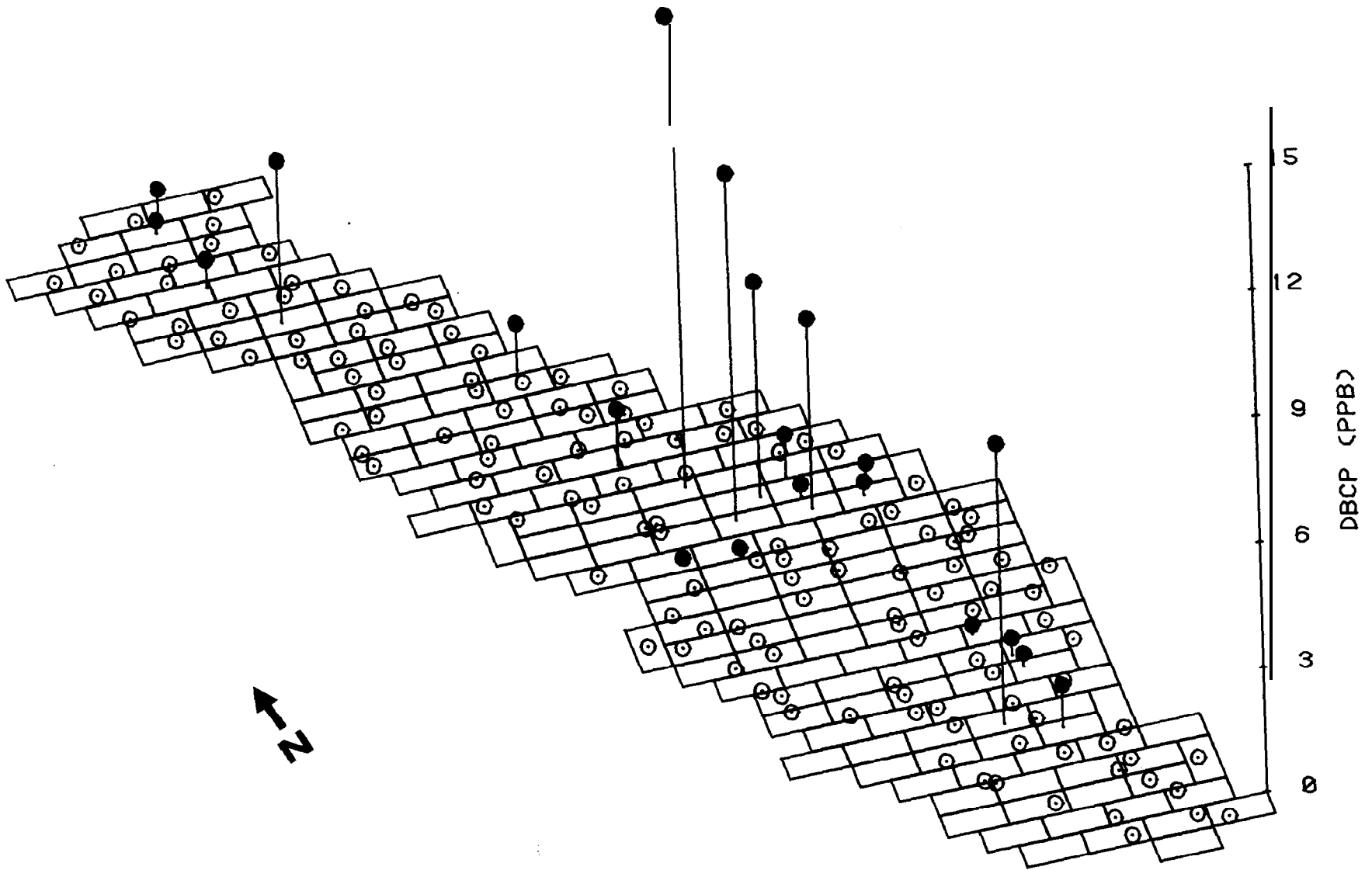


Figure 4. Arrangement of 6 x 12 mile cells in the San Joaquin Valley
 and locations of sampled wells that did (●) or did
 not (○) contain DBCP.

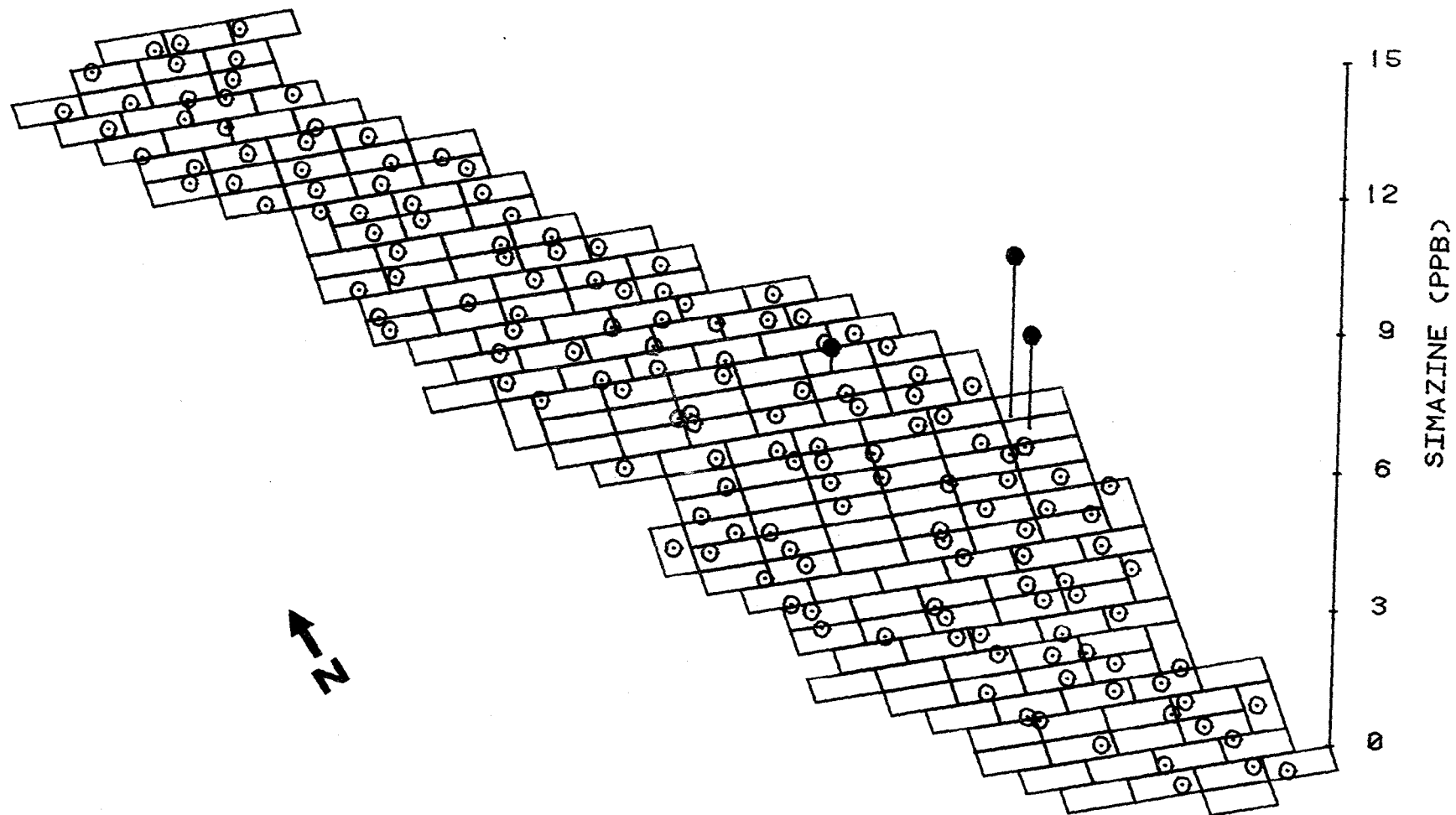


Figure 5. Arrangement of 6 x 12 mile cells in the San Joaquin Valley groundwater basin and locations of sampled wells that did (●) or did not (○) contain simazine.

wells were domestic and the remainder were divided among municipal, agricultural and industrial wells (Table 8). Nine out of ten of the wells were between 101 and 200 feet deep (Table 9).

2. SAN JOAQUIN VALLEY- DBCP, at concentrations ranging from 0.3 to 7.2 ppb, was found in seven of the ten wells sampled in this 6 x 12 mile (72 square miles) cell, located in Fresno County (Fig. 6, Table 7). The ten wells produced a mean concentration of 1.2 ppb, with a standard deviation of 1.1 ppb. All of the wells were less than 200 feet deep with 70% being between 51 and 100 feet deep (Table 8). Nine of the ten wells were for domestic use, one was an agricultural well (Table 9). Statistical comparisons made between DBCP concentration and certain well characteristics (well depth, depth to top of perforation and perforation length) showed no significant correlations. Further, the results of an unpaired students t test were not significant indicating that the values obtained by sampling eight wells were no better than values obtained by sampling two wells. However, due to limited manpower and resources we were only able to sample one well per cell.

EDB (0.1 ppb) was also found in one of the wells containing DBCP; simazine at 0.5 ppb was found in another. None of the sampled wells contained carbofuran.

TABLE 7. Pesticide contamination of wells sampled in each of two 10 well cells

10 Well Cell. Location	Total no. of wells containing:			
	Carbofuran	DBCP	EDB	Simazine
Salinas Valley	0	0	0	0
San Joaquin Valley	0	7 (0.3-7.2) ^{a/}	1 (0.1)	1 (0.5)

a/ Values enclosed in parentheses represent the range of pesticide contamination in ppb.

TABLE 8. Characterization by well depth of wells sampled in each of two 10 well cells

10 Well Cell. Location	Number of wells in various depth (ft) ranges				
	20-50	51-100	101-200	201-300	>300
Salinas Valley	0	1	9 ^{a/}	0	0
San Joaquin Valley	0	7	3 ^{a/}	0	0

a/ Includes one well that represented the cell in the overall study.

TABLE 9. Characterization by type of use of wells sampled in each of two 10 well cells

10 Well Cell Location	Number of wells by type of use			
	Domestic	Municipal	Agricultural	Industrial
Salinas Valley	5	2	2 ^{a/}	1
San Joaquin Valley	9 ^{a/}	0	1	0

a/ Includes one well that represented the cell in the overall study.

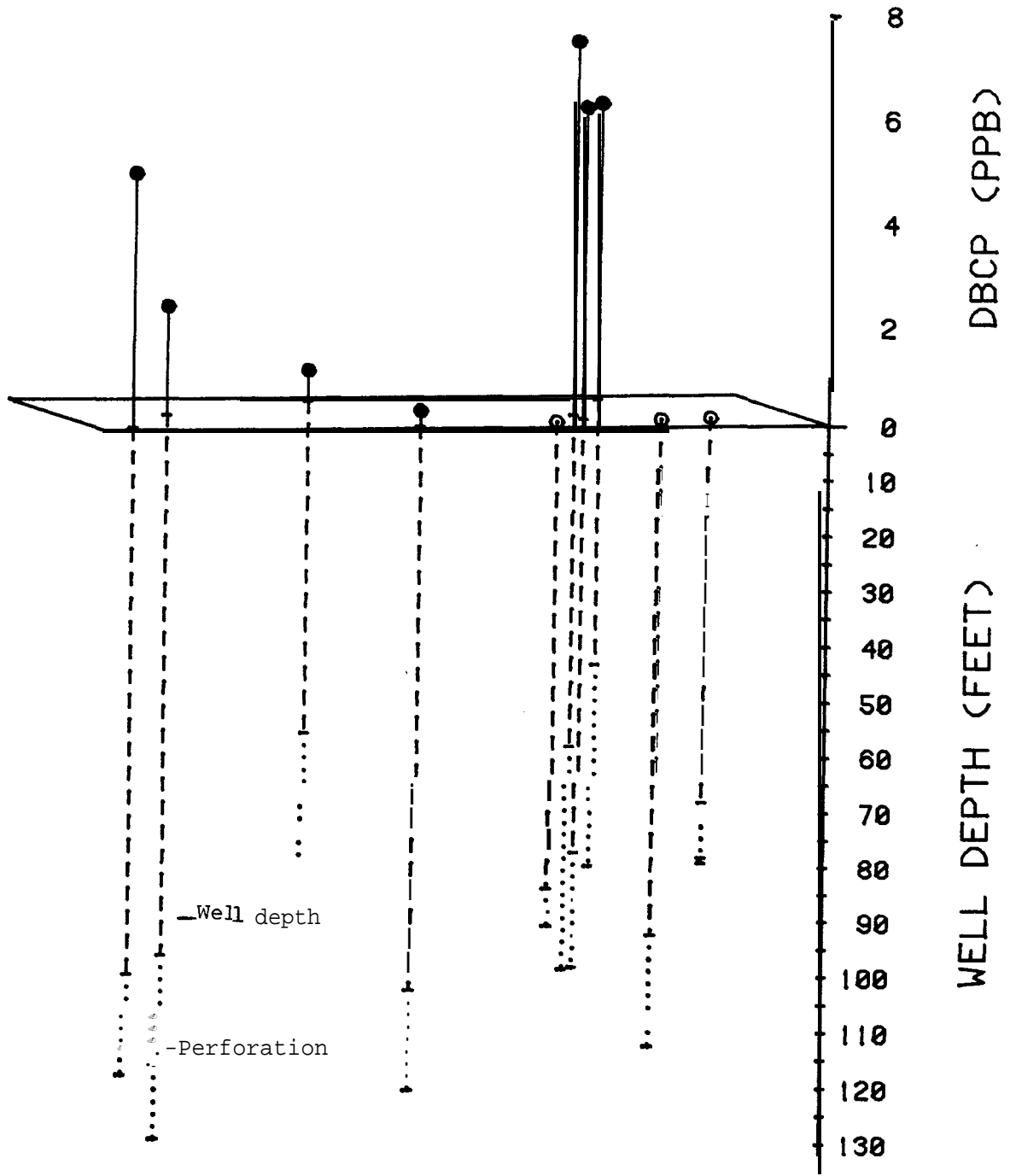


Figure 6. Locations in a 6 x 12 mile cell in Fresno County of 10 wells that did (●) or did not (○) contain DBCP.

C. RESULTS- COMPARATIVE ANALYSES OF DUPLICATE SAMPLES

The results of DBCP analyses of selected water samples, performed by California Analytical Laboratories and by the Department of Health Services Laboratory, were generally very close to results obtained by the Department of Food and Agriculture Laboratory (Table 10). Only two positive findings by the CDFA laboratory, one at 0.6 ppb and one at 0.1 ppb, were not confirmed by the outside laboratories. In all but one case, when a positive DBCP was confirmed by one of the outside laboratories, their reported concentrations were higher than those found by the CDFA Laboratory.

The results of a two-tailed paired t test of duplicate samples analyzed by both the CDFA and California Analytical Laboratories showed that differences were significant at the 0.05 level **but** not at the 0.01 level of confidence. Consideration must also be given to the fact that these results were not for duplicate analyses of a split sample, but rather for comparative analyses of samples taken consecutively from the same well.

D. RESULTS- EFFECT OF STORAGE ON PESTICIDE CONCENTRATIONS IN SPIKED SAMPLES

Concentrations of DBCP and EDB remained at nearly constant levels (2.0 to 2.4 ppb) after being added to well water samples and stored for 0, 7, 8 or 9 days at 4°C (Table 11). For **DBCP**, values greater than the

TABLE 10. Comparison of analyses of well water samples for DBCP by three different laboratories.

DBCP concentrations (ppb) in water samples analyzed by:			
Sampled from Cell No.	Dept. of Food & Agriculture Lab	Dept of Health Services Lab	California Analytical Lab
22	0.0	0.0	<u>a/</u>
23	0.6	0.0	-
25	0.0	0.0	-
46	3.9	5.8	-
57	0.0	0.0	-
65	0.0	0.0	-
237	0.0	0.0	-
239	0.0	0.0	-
240	0.0	0.0	-
241	0.0	0.0	-
87	1.3		1.5
89	0.0	-	0.0
97	0.0	-	0.0
101	10.5	-	11.0
108	5.1	-	5.4
109 <u>b/</u>	0.6	-	4.2
	5.7	-	6.9
	7.2	-	7.3
114	8.3	-	9.1
115	4.5	-	4.9
116	0.3	-	0.4
119	0.1	-	0.0
165	0.0	-	0.0
170	0.0	-	0.0
181	6.7	-	7.9
182	0.0	-	0.0

a/ Water sample was not analyzed

b/ Three separate wells were sampled in cell 109.

TABLE 11 Effect of storage at 4°C on concentrations of four pesticides in well water samples.

Pesticide ^{a/}	Sample No.	No. of days stored before analysis	Concentration (ppb) after storage
Atrazine	1	0	3.8
	2	7	3.5
	3	9	3c.4
	4	9	2.6
Carbofuran	1	0	3.9
	2	7	2.5
	3	8	1.0
	4	9	2.3
DBCP	1	0	2.2
	2	7	2.2
	3	8	2.4
	4	9	N. D. ^{b/}
EDB	1	0	2.0
	2	7	2.0
	3	9	2.1
	4	9	2.0

a/ A quantity of pesticide was added to 1 liter bottles of well water to give a final concentration of 2 ppb.

b/ None detected; initial spiking of sample is suspect.

original spiked concentrations were due to an interference peak that resulted from the solvent that was used to spike the samples.

Initial concentrations of atrazine and carbofuran were at the desired level of 4 ppb. Within the error limits of the analytical method used for atrazine, there was no apparent loss after 9 days. Samples containing carbofuran held for 7 days or more under the conditions of this study, lost an average of 52% of their original concentration.

DISCUSSION

This study was conducted to quantify the **spacial** distribution of shallow groundwater contamination by certain pesticides in four major California agricultural production regions. The intent was to use groundwater as the sampling medium to determine if the pesticides had moved downward through the soil after application.

The groundwater basins that were sampled in the course of this study included the Santa Maria, Upper Santa **Ana**, Salinas Valley and San Joaquin Valley. Sizable quantities of carbofuran, DBCP, EDB and simazine were applied in all of these areas during the past ten years. However, the pesticides were found in water samples from only two of the groundwater basins. No pesticides were detected in water samples from the Salinas Valley or Santa Maria groundwater basins where one well was sampled in each 36 square mile area that made up a sample cell. Even when an addititonal nine wells were sampled from one of the cells in the Salinas Valley (ten well cell), no pesticides were detected. Other studies have also shown a lack of groundwater contamination by pesticides in these two groundwater basins.

The presence of DBCP in wells in the Uppper Santa **Ana** and San Joaquin Valley groundwater basins has been previously documented (3). Our findings confirm those results and demonstrate that the sample cell size that was used gives a reliable estimation of the **spacial**

distribution of groundwater contamination by DBCP. We sampled one well in each 36 square mile cell in the Upper Santa Ana and in each 72 square mile cell in the San Joaquin Valley and found DBCP contamination in areas previously reported to be contaminated as well as in other areas. One of the 72 square mile cells in Fresno County that was known to have widespread contamination of DBCP in wells was also sampled as a 10 well cell. Seven out of the 10 wells contained DBCP; a statistical analysis of the DBCP concentration data showed that the results obtained by sampling ten wells in the cell were no better than if two wells had been sampled.

The results of our study also showed the presence of EDB in two wells in Fresno County, carbofuran in one well in Riverside County, and simazine in certain wells in **Fresno**, Tulare and Riverside Counties. This is the first report of groundwater contamination by these chemicals in California. Studies conducted as recently as 1981 (1,2) failed to show the presence of carbofuran or atrazine, a herbicide closely related to simazine and one not detected in any of our water samples, in groundwater samples taken from counties in the San Joaquin Valley. Atrazine has been detected in groundwater in Nebraska (4) where the herbicide is extensively used in corn production.

This study has established the contamination of shallow groundwater by certain pesticides in some but not all areas where they were applied. In Volume II of this report, information on the downward movement of the pesticides through soil to groundwater depth will be presented.

Then, in Volume III numerous factors including cropping practices, application of water, soil types and soil physical factors will be analyzed for possible correlations that may explain why the pesticides have contaminated groundwater in one location and not another.

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A P P E N D I X I

Water Sample Chain of Custody

Study #	Sample #	Well Number				Cell #	Date Collected				Sample Location			Collector	Minutes Pumped	Pump type	Remarks																						
		TWN	RNG	SEC			MO	DAY	YR	TIME	Tank	Pump	Other																										
1	6																																						
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40

Companion #1	Companion #2	CONDUCTIVITY	Atrazine	Carbofuran		DBCP	EDB	Chemist																															
				Units	Units																																		
41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80

Partner:
Owner:
Address:

Lab Results: SAVE EXTRACTS
Atrazine:
Carbofuran:
DBCP:
EDB:

Sampling methods (Schrader valve, faucet, etc. and location), observations, remarks, etc.

CHEMIST: _____ DATE: _____

Relinquished by: (Signature)	Date/Time	
Received by: (Signature)	Relinquished by: (Signature)	Date/Time
Received by: (Signature)	Relinquished by: (Signature)	Date/Time

KEY
Col 32: water from storage tank
Col 33: water from pump
Col 39: s=submersible
t=turbine
Col 60: M=PPM
B=PPB
T=PPT

Received by: (Signature)	Relinquished by: (Signature)	Date/Time
Received by (Signature)	Relinquished by (Signature)	Date/Time
Received by (Signature)	Relinquished by (Signature)	Date/Time

Received for Laboratory by: (Signature)	Date/Time	Lab #
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A P P E N D I X I I

Well Identification Chain of Custody

During the period of May 1982 to August 1982, the Department of Food and Agriculture's Environmental Monitoring and Pest Management Unit will sample well water throughout the State. The results will determine if certain agrichemicals are present in groundwater on an area-wide basis. We request your permission to collect a water sample for the following well:

Well No. _____ Address: _____

The exact date and time will be arranged with you prior to obtaining the sample.

Owner Name _____

Signature of Property Owner Granting Permission _____ Date _____

Owner Address _____

Contact Person _____ Phone () _____

If any problems should arise, please contact:

Ron Oshima
916-322-2395

Scott Simpson
714-787-4684

Study	County	Basin	Well Number	Depth from Surface																																			
				Aq	Well	Perf	Cas																																
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Casing S/P Seal Y/N Use DIMO	Phone																		Name, Address																				
41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80

A P P E N D I X I I I

Determination of DBCP In Crops, Soil, Water, Bark
and Leaves

DETERMINATION OF DBCP
(1,2-Dibromo-3-chloropropane)
IN CROPS, SOIL, WATER, BARK AND LEAVES

Principle:

Crop samples are prepared by chopping in a frozen state. Other samples are thoroughly mixed and sampled directly. Leaf punches are stripped and prepared by the Sur-ten strip method. A suitable size sample is codistilled with ethyl acetate from an aqueous mixture of sample, ethyl acetate, and water. The recovered ethyl acetate (plus any DBCP from sample) is dried with sodium sulfate and determined quantitatively through the use of gas-liquid chromatography with electron capture detector.

Scope:

This method has been checked for the quantitative recovery of DBCP (1,2-dibromo-3-chloropropane) from crops, soil, water, peeling, leaves, and bark samples. It is suspected that this method would also apply to assays of many similar materials such as ethylene dibromide and possibly compounds such as DDVP and Dibrom.

Equipment:

1. Hobart food chopper, Model 8181D or equivalent.
2. One-pint, wide mouth, tapered fruit jars with rings, lids and solvent washed foil liners. Mason, Bull, Kerr, or equivalent.
3. Nalgene scoop **or** similar device to remove sample from Hobart. Homemade or stainless steel restaurant supply.
0. Balance, sensitive to 10 mg.
5. Distillation Receiver - Barrett trap 25 ml capacity **with 24/40** joints.
6. Heating Mantle controlled by variable transformer, 500 boiling flask capacity.
7. 500 ml flat or round bottomed boiling flask with **24/40** joint. (If many bark or leaf samples are to be run, it may be desirable to substitute a larger joint such as **45/50** with adapters to **24/40**).
8. Condenser, Allihn type: 250 to 300 mm jacket with **24/40** lower joint and drip tip.
9. Gas Chromatograph with electron capture detector.
Temperatures: °C
Column: 90
Injector: 125

Detector: 280 or 220*
*Nickel or Tritium respectively
Flows: Nitrogen carrier gas, 20-30 ml/min
Columns: Glass, 6' x 2 mm i.d.
10% OV 101 or 50/50 mix of 6% OV 101 and
4% OV 210 or 10% **Tenax**, or
4% OV 275 on Chromosorb WHP
or Gas Chrom Q 80/100 mesh
solid support.

10. Glass stoppered test tubes or auto sampler vials fitted with **Teflon** faced septa for holding samples.
11. Pipette, 10 ml. T.D. or 10 ml repipet.
12. Graduate, 250 ml capacity.
13. Syringes, assorted microliter syringes for injection on gas **chromatograph**. Suggested sized 1, 5, and 10 microliter.

Reagents:

1. Analytical Standard or DBCP.
Contact Dr. E. Feichtmeir, Shell Development **Company**,
P.O. Box 4248, Modesto, CA 95352.
 - a. Stock Standard - Prepare 1 mg/ml in ethyl acetate,
 - b. Working Standards - Dilute stock standard to several working standards covering the linear range of specific e.c. detector used. **Typically** in the range of 0.02 - 1.0 nanogram/microliter.
 - c. Ethyl Acetate - nanograde or better. Test for interferences before use.
 - d. Acetone - nanograde or better for prerinsing and drying equipment.
 - e. Anhydrous Sodium Sulfate, Granular. Suggest **Mallinkrodt**. Pretest for interferences. Ethyl Acetate wash or heat in muffle furnace if interferences are found. If interferences are not removed, use sulfate from a different **source**.
 - f. **Antifoam** - Silicone **antifoam** agent for organics or mixed aqueous and organics.
Note: Use only if absolutely necessary, Will depress recovery of DBCP.
 - g. Distilled Water - Good quality distilled water stored in glass. Test water with a reagent blank for extraneous peaks and large solvent front.

Procedure:

- A. Sample Preparation.
 1. Crops,

- a. Place crop sample and broken chunks of dry ice into Hobart bowl. Add both in small quantities at a time to quickly freeze the macerated crop tissue. (1)
- b. Add up to 60% by weight of dry ice to sample (this varies with the moisture content and nature of sample) until sample in chopper forms a homogeneous friable mixture.
- c. Place subsample into the wide mouthed fruit jar. Cover jar with solvent washed aluminum foil and a ring, An inverted lid may also be used but do not secure lid tight as an explosion of the jar will result.

Place jars in freezer overnight to allow the CO₂ from the dry ice to evaporate.

- d. If samples are to be run immediately after chopping, take an aliquot of sample and weigh until sample weight is constant. Agitation helps speed CO₂ removal.

2. Leaf Punches

- a. For total residue, weigh directly into boiling flask.
- b. For penetrated and dislodgeable, use the modified Sur-ten stripping procedure for foliage samples (2) to wash leaves. Run aqueous washings and the washed leaves.

B. Sample Distillation

1. Weigh sample into boiling flask. (10 to 50 grams or more, depending on interferences. For example, 25 grams of citrus, 50 grams of soil, 100-150 ml of water sample).
2. Add several prewashed glass beads, approximately 160 ml of distilled water, and exactly 10.0 ml of ethyl acetate, If experience has indicated that sample will foam uncontrollably, add 1 drop of antifoam. If **antifoam** is used the recoveries must be rechecked with **antifoam** in fortified samples.
3. Place the boiling flask into the heating mantle and assemble the Barrett trap and condenser (with flowing water) in place.
4. Apply full voltage to heating mantle until mixture starts to boil (approximately 5 to 7 minutes), then reduce voltage to $\frac{1}{4}$ to $\frac{1}{2}$ and allow to reflux for 15 minutes,
5. Check graduations on Barrett trap to determine if all of the ethyl acetate has been distilled over. If it hasn't, continue refluxing in 5 minute intervals, otherwise, remove heat from flask and wash down condenser and trap neck with a few mls of distilled water. Leave cool (approximately 5 minutes).

6. Drain off lower aqueous layer from trap and discard.
7. Drain Ethyl Acetate layer into glass stoppered test tube for analysis.

C. Sample Clean-up and Analysis

1. Add a small amount of Sodium Sulfate to the test tube and shake well to remove entrapped water.
2. The sample is ready for injection on the gas **chromatograph**. It has normally been considered that this extract cannot be concentrated without loss of **DBCP**. However, verbal communication with EPA labs in Beltsville, Maryland, has indicated the possible concentration by means of a gentle flowing stream of nitrogen at room temperature,
 Note: We normally attempt to match standards in peak height and area to the peak height and area of DBCP peak in samples.
3. It has been reported that further sample clean-up may be obtained by adding **0.25** grams of Merk Silica gel 60 per ml of extract and shaking. (We have not currently checked this step out).

Calculations:

Due to the levels of DBCP currently found , results are calculated on a ppb basis. Soils are calculated on a dry weight basis, Dislodgeable leaf punches are calculated on a surface area and weight of punch basis.

$$\text{ppb} = \frac{\text{Area or (Height of Sample Peak) (Nanogram Std) } (10^3)}{\text{Area or (Height of Standard Peak) } \left(\frac{\text{grams sample}}{\text{mls extract}} \right) (\text{ injected}) \left(\frac{\text{Recovery}}{\text{Factor}} \right)}$$

References:

1. Personal Discussions with Dr. W. Winterland of University of California-Davis; Dr. J. T. Leffingwell of University of California-Berkeley; Dr. J. Knaak, California Department of Food and Agriculture; and others regarding preparation of samples by macerating with dry ice.
2. Iwata, V., et. al., "Procedure for the Determination of Dislodgeable Pesticide Residues on Foliage", Bulletin of Environmental Contamination and Toxicology, Vol. 18, No. 6 (1977)
3. A Method for the Estimation of **1,2-Dibromo-ethane** in Vegetables, Hargreaves, et. al., Pesticide Science **5:22S** (1974)
4. "Residue Determination of Dibromo-chloropropane in crops, soil, and water", Shell Development Co., Biological Sciences Research Center, Modesto, California, Method #MMS-R-272-3 (September 1976)
5. "Final Report - Development of a Method for the Specific Determination of Low Level Residues of Ethylene Dibromide", Bionetics Division of Litton Industries (October 1976)
6. Malone, B., "Analysis of Grains for Multiple Residues of Organic Fumigants", Journal of Association of Official Analytical Chemists, Vol. 52, No. 4, pp 800-805 (1969)

A P P E N D I X I V

Analysis of Simazine/Atrazine in Water

Analysis of Simazine/Atrazine in Water

SCOPE: This method is for the determination of Simazine/Atrazine in water.

PRINCIPLE: Water was extracted with dichloromethane using a separatory funnel. The dichloromethane extracts were run through anhydrous sodium sulfate, and then rotary evaporated to dryness. They were then brought up to 5 milliliters volume in ethyl acetate, and gas chromatographed using TSD and hall conductivity detectors.

Reagents and equipment:

- 1) Dichloromethane, MCB omnisolve
- 2) Ethyl acetate, MCB omnisolve
- 3) Sodium sulfate, anhydrous, Mallinckrodt **#8024**
- 4) Mettler PC4400 top loading balance
- 5) **Kimble #29048F-2L** separatory funnel with Corning **#7650-38** barrel head glass stopper
- 6) 50 ML lab industries repipet
- 7) Column, glass, custom made, approximately 19 mm diameter, 10 cm long, with reservoir
- 8) Kimble **#28017A-5** volumetric flask
- 9) Kimble **#25055-500** flat bottomed boiling flask with a **24/40** standard taper joint.
- 10) Buchi RE-120 rotaryevaporator with duraire **#PV-200** diaphragm vacuum pump and neslab CFT-75 refregerated recirculator.
- II) Varian 3700 GLC with hall conductivity detector in chloride mode: column: 6 ft long 10% **SP2100** on **100/120** supelcoport; 190 degree centigrade column: 210 degree injector; attenuation: 10 x 10, **CDS111=** x 8; nitrogen carrier = 25 **cc/min**; approximately 4 minutes retention time.
- 12) Varian 3700 GLC with TSD detector; column: 2 ft long 10% **SP2250** on **100/120** supelcoport; 170 degrees **centrigrade** column; 200 degree injector; 210 degree detector; nitrogen carrier = 20 **cc/min**; TSD bead heat setting = 400; approximately 4 minutes retention time.

Determination of Atrazine/Simazine:

- 1) The sample bottle holding approx 1 liter of water was weighed and then poured out into a 2 liter separatory funnel. The bottle was shaken after it was partly empty to include all sediments in the sample,

- 2) The sample bottle was then reweighed , the difference being the sample weight.
- 3) Using a 50 ML repipet, 70 ML of dichloromethane was added to the sample bottle. The bottle was swirled to remove all possible residues,
- 4) The dichloromethane was then poured into the sample bottle's corresponding separatory funnel,
- 5) The water/dichloromethane mixture was vigorously shaken for 30 seconds,
- 6) After allowing time for the aqueous and dichloromethane layers to separate, the lower layer (dichloromethane) was drawn off and run through a short column of anhydrous sodium sulfate , into a 500 ML flat bottomed boiling flask.
- 7) Another 70 ML of dichloromethane was added to the aqueous layer in the separatory funnel. The mixture was shaken vigorously for 30 seconds.
- 8) Step #6; Step #7, Step #6, Step #9.
- 9) The dichloromethane was rotary evaporated to dryness using approx 35 degrees centigrade at about 18 inches of HG vacuum.
- 10) The sample was transferred to a 5.0 milliliter volumetric flask, and brought to volume, with ethyl acetate.
- 11) Gas chromatography was performed upon the sample extract.

Recoveries:

Recoveries are approximately 90+% at the 5 ppb level.

Calculations:

PPM Simazine or Atrazine= Nanograms Simazine or Atrazine / milligrams sample represented by injection

A P P E N D I X V

Analysis of Carbofuran in Water

ANALYSIS OF CARBOFURAN IN WATER

SCOPE: This method is for the determination of Carbofuran in water.

PRINCIPLE: Water was extracted with dichloromethane using a separatory funnel. The dichloromethane extracts were run through anhydrous sodium sulfate, and then rotary evaporated to dryness. They were then brought up to 5 milliliters volume in ethyl acetate, and gas chromatographed using TSD and hall conductivity detectors.

REAGENTS AND EQUIPMENT:

- 1) Dichloromethane, MCB omnisolve
- 2) Ethyl acetate, MCB omnisolve
- 3) Sodium sulfate, anhydrous, Mallinckrodt #8024
- 4) Mettler PC4400 top loading balance
- 5) Kimble #29048F-2L separatory funnel with Corning #7650-38 barrel head glass stopper
- 6) 50 mL lab industries repipet
- 7) Column, glass, custom made, approximately 19 mm diameter, 10 cm long, with reservoir
- 8) Kimble #28017A-5 volumetric flask
- 9) Kimble #25055-500 flat bottomed boiling flask with a 24/40 standard taper joint
- 10) Buchi RE-120 rotary evaporator with duraire #PV-200 diaphragm vacuum pump and neslab CFT-75 refrigerated recirculator.
- 11) Varian 3700 GLC with hall conductivity detector in nitrogen mode; column: 2 ft. long 10% SP2250 on 100/120 supelcoport; 180 degree centigrade column: 210 degree injector; helium carrier = 25 cc/min; approximately 4 minutes retention time.
- 12) Varian 3700 GLC with TSD detector; column: 2 ft. long 10% SP2250 on 100/120 supelcoport; 180 degrees centigrade column; 200 degree injector; 210 degree detector; nitrogen carrier = 20 cc/min; TSD bead heat setting = 400; approximately 4 minutes retention time.

ANALYSIS:

DETERMINATION OF CARBOFURAN:

- 1) The sample bottle holding approx 1 liter of water was weighed and then poured out into a 2 liter separatory funnel. The bottle was shaken after it was partly emptied to include all sediments in the sample.
- 2) The sample bottle was then reweighed, the difference being the sample weight.
- 3) Using a 50 ml repipet, 70 ml of dichloromethane was added to the sample bottle. The bottle was swirled to remove all possible residues.
- 4) The dichloromethane was then poured into the sample bottle's corresponding separatory funnel.
- 5) The water/dichloromethane mixture was vigorously shaken for 30 seconds.
- 6) After allowing time for the aqueous and dichloromethane layers to separate, the lower layer (dichloromethane) was drawn off and run through a short column of anhydrous sodium sulfate, into a 500 ml flat bottomed boiling flask.
- 7) Another 70 ml of dichloromethane was added to the aqueous layer in the separatory funnel. The mixture was shaken vigorously for 30 seconds.
- 8) Step #6; step #7; step #6, step #9.
- 9) The dichloromethane was rotary evaporated to dryness using approx 35 degrees centigrade at about 18 inches of GH vacuum.
- 10) The sample was transferred to a 5.0 milliliter volumetric flask, and brought to volume, with ethyl acetate.
- 11) Gas chromatography was performed upon the sample extract.

DESORPTION COEFFICIENT:

Recoveries were approximately 90+% at the 5 PPB level.

CALCULATIONS:

PPM carbofuran = nanograms carbofuran/milligrams sample represented by injection.

A P P E N D I X V I

Determination of EDB In Crops, Soil, Water,
Bark, and Leaves

DETERMINATION OF EDB
(1,2-Dibromoethane)
IN CROPS, SOIL, WATER, BARK, AND LEAVES

Principle:

Crop samples are prepared by chopping in a frozen state. Other samples are thoroughly mixed and sampled directly. Leaf punches are stripped and prepared by the Sur-ten strip method. A suitable size sample is codistilled with ethyl acetate from an aqueous mixture of sample, ethyl acetate, and water. The recovered ethyl acetate (plus any EDB from sample) is dried with sodium sulfate and determined quantitatively through the use of gas-liquid chromatography with electron capture detector.

Scope:

This method has been checked for the quantitative recovery of EDB (1,2-Dibromoethane) from crops, soil, water, and fruit peelings. It is suspected that this method would also apply to the assay of other materials such as leaves and other plant parts.

Equipment:

1. Hobart food chopper, Model **8181D** or equivalent.
2. One-pint, wide mouth, tapered fruit jars with rings, lids and solvent washed foil liners. Mason, Ball, Kerr, or equivalent.
3. Nalgene scoop or similar device to remove sample from Hobart. Cut from 500 ml Nalgene squirt bottle.
4. Balance, sensitive to **10 mg**.
5. Distillation Receiver - Barrett trap 25 ml capacity with **24/40** joints.
6. Heating Mantle controlled by variable transformer, 500 boiling flask capacity.
7. 500 ml flat or round bottomed boiling flask with **24/40** joint. (**IF** many bark or leaf samples are to be run, it may be desirable to substitute a larger joint such as **45/50** with adapters to **24/40**.)
8. Condenser, Allihn type: 250 to 300 mm jacket with **24/40** lower joint and drip tip.

Equipment (continued)

9. Gas chromatograph with Ni⁶³ electron capture detector.

Note: At this time, it is believed H³ detectors cannot be substituted. The different emission frequency detects an interference peak at the EDB elution time on the suggested columns.

Temperatures ~ Injector: 125
 Detector: 280

Column: 20' x 1/8" O.D. nickel tubing
 10% SP-2100 on 100/120 chromosorb W-BP
 58 C, 10 cc/min N₂
 EDB retention time approximately 10 minutes

column : 20' x 1/8" O.D. nickel tubing
 10% FFRP on 100/120 Supelcoport
 130 C, 30 cc/min N₂
 EDB retention time approximately 6.2 minutes

Note: Several other columns have been tried without success. The problem is that Ethyl Acetate has an interference peak that is very difficult to separate from EDB. These columns include 10% FFAP, 3% OV-275, 4% OV¹⁰¹/6% OV-210, and 6% OV-210.

10. Glass stoppered test tubes or auto sampler vials fitted with Teflon faced septa for holding samples,
11. Pipette" 10 ml T.D. or 10 ml repipet.
12. Graduate, 250 ml capacity.
13. Syringes, assorted microliter syringes for injection on gas chromatograph. Suggested sized 1, 5, and 10 microliter.

Reagents:

1. Analytical Standard of EDB.
- a. Stock Standard ~ Prepare 1 mg/ml in ethyl acetate.
 - b. Working Standards ~ Dilute stock standard to several working standards covering the linear range of specific e.c. detector used. Typically in the range of 0.02 - 1.0 nanogram/microliter.
 - c. Ethyl. Acetate ~ nanograde or better. Test for interferences before use.
 - d. Acetone - nanograde or better for prerinsing and drying equipment.
 - e. Anhydrous Sodium Sulfate, Granular. Suggest Mallinkrodt. Pretest for interferences. Ethyl Acetate wash or heat in muffle furnace if interferences are found. If interferences are not removed, use sulfate from a different source-
 - f. Antifoam ~ Silicone antifoam agent for organics or mixed aqueous and organics.
Note : Use only if absolutely necessary. Will depress recovery of EDB.

Reagents (continued)

- g. Distilled Water - **Good** quality distilled water stored in glass. Test water with a reagent blank for extraneous peaks and large solvent front.

Note: It has been necessary to pre-extract water using the outlined co-distillation method in order to remove materials interfering with the GLC analysis.

Procedure:

A. Sample Preparation

1. Crops.

- a. Place crop sample and broken chunks of **dry** ice into Hobart bowl. Add both in small quantities at a time to quickly freeze the macerated crop tissue. **(1)**
- b. Add up to 60% by weight of dry ice to sample (this varies with the moisture content and nature of sample) until sample in chopper forms a homogenous friable mixture,
- c. Place subsample into the wide mouthed fruit jar. Cover jar with solvent washed aluminum foil and a ring. An inverted lid may also be used but do not secure lid tight as an explosion of the jar will result.

Place jars in freezer overnight to allow the CO₂ from the dry ice to evaporate.

- d. If samples are to be run immediately after chopping, take an aliquot of sample and weigh until sample weight is constant. Agitation helps speed CO₂ removal.

2. Leaf Punches.

- a. For total residue, weigh directly into boiling flask.
- b. For penetrated and dislodgeable, use the modified Sur-ten stripping procedure for foliage samples **(2)** to wash leaves. Run aqueous washings and the washed leaves.

3. Bark. Sliver bark into thin strips.

4. Soil and similar samples. Mix well, sieve if necessary to remove stones, twigs or clumps, and weigh directly into boiling flask. Run a duplicate soil sample for moisture determination. Calculate soil results on dry weight basis.

B. Sample Distillation.

1. Weigh sample into boiling flask. (10 to 50 grams or more, depending on interferences. For example, 25 grams of citrus, 50 grams of soil, 100-150 ml of water sample.)

2. Add several prewashed glass beads, approximately 160 ml of distilled water, and exactly 10.0 ml of ethyl acetate. If experience has indicated that sample will foam uncontrollably, add 1 drop of antifoam. If **antifoam** is used the recoveries must be rechecked withantifoam in the fortified samples.
3. Place the boiling flask into the heating mantle and assemble the Barrett trap and condenser (with flowing water) in place.
4. Apply full voltage to heating mantle until mixture starts to boil (approximately 5 to 7 minutes) , then reduce voltage to **1/4** to **1/2** and allow to reflux for 15 minutes.
5. Check graduations on Barrett trap to determine if all of the ethyl acetate has been distilled over. If it hasn't, continue refluxing in 5 minute intervals, otherwise, remove heat from flask and wash down condenser and trap neck with a few **mls** of distilled water. Let cool (approximately 5 minutes).
6. Drain off lower aqueous layer from trap and discard.
7. Drain Ethyl Acetate layer into glass stoppered test tube for analysis.

C. Sample Clean-up and Analysis.

1. Add a small amount of Sodium Sulfate to the test tube and shake well to remove entrapped water.
2. **The** sample is ready for injection on the gas **chromatograph**. It has normally been considered that this extract cannot be concentrated without loss of **EDB**. However, verbal communication with EPA labs in **Beltsville**, Maryland, has indicated the possible concentration by means of a gentle flowing stream of nitrogen at room temperature.
Note : We normally attempt to match standards in peak height and area to the peak height and area of EDB peak in samples.
3. It has been reported that further sample clean-up may be obtained by adding 0.25 grams of Merk Silica gel 60 per ml of extract and shaking. (**We** have not currently checked this step out.)

Calculations:

Due to the levels of EDB currently found, results are calculated on a ppb basis. Soils are calculated on a dry weight basis. Dislodgeable leaf punches are calculated on a surface area and weight of punch basis.

$$\text{ppb} = \frac{\text{(Area or Height Sample Peak)} \text{ (Nanogram Std)} (10^3)}{\text{(Area of Height Standard Peak)} \left(\frac{\text{grams sample}}{\text{mls extract}} \right) (\lambda \text{ injected}) \text{ (Recovery Factor)}}$$

References:

1. Personal discussions with Dr. W. Winterland of University of California-Davis; Dr. J. T. Leffingwell of University of California-Berkeley; Dr. **J. Knaak**, California Department of Food and Agriculture; and others regarding preparation of samples by macerating with dry ice.
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3. A Method for the Estimation of **1,2-Dibromoethane** in Vegetables, Hargreaves, et. al., Pesticide Science **5:22S** (1974)
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5. "Final Report - Development of a Method for the Specific Determination of **Low** Level Residues of Ethylene Dibromide," Bionetics Division of Litton Industries (October 1972)
6. Malone, **B.**, "Analysis of Grains for Multiple Residues of Organic Fumigants," Journal of Association of Official Analytical Chemists, Vol. 52, No. 4, pp 800-805 (1969)
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8. Heuser, et. al., "Selective Determination of Ionized Bromide and Organic Bromides in Foodstuffs by Gas-Liquid Chromatography with Special Reference to Fumigant Residues," Pesticide Science, Vol. 1, pp 244-249, November-December (1970)

A. Scott Fredrickson
Agricultural Chemist II