

**SURVEY FOR TRIAZINE HERBICIDES IN
WELL WATER, GLENN COUNTY, 1986**

by

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ABSTRACT

In January, 1986, the Agricultural Commissioner of Glenn County reported the presence of atrazine in a sample of domestic well water. Department of Food and Agriculture staff sampled 137 wells in a 37 square mile area surrounding the original well to confirm and delimit the area of contamination. Of the 137 wells sampled, 34 contained atrazine. In addition, simazine was found in 17 wells and prometon was found in 10 wells. Residues ranged in concentration from 0.1 to 5.9 ppb. Forty-four of the wells sampled contained one or more of these triazine herbicides. The presence of these chemicals was confirmed by a second laboratory and two alternate analytical methods. An area of contamination was not determined, since low levels of residues were found in wells throughout the study area. Possible sources of contamination included normal uses of the pesticides for agricultural crops, rights-of-way, and non-crop areas. A pesticide wash area located in the vicinity was probably not the primary source of contamination.

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I. INTRODUCTION

The Agricultural Commissioner of Glenn County reported in January, 1986 the presence of atrazine in a county-owned water well located near the Willows Airport. The California Department of Food and Agriculture's (CDFA) Environmental Hazards Assessment Program (EHAP) confirmed the presence of atrazine in the well and initiated a study to determine the extent of contamination and identify possible sources of contamination.

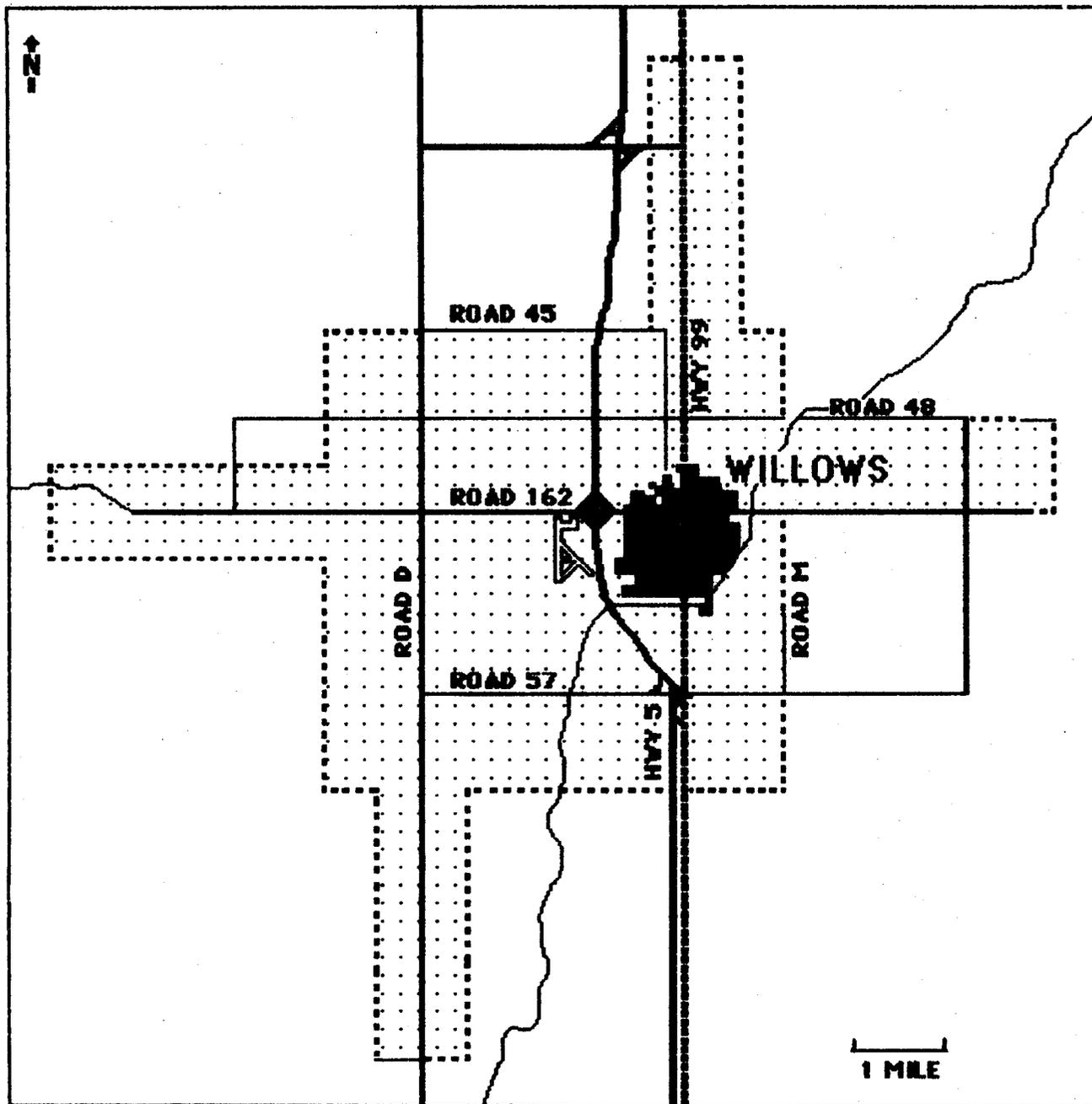
II. MATERIALS AND METHODS

A. Sampling Design

Initially, the area of contamination was thought to be localized at the airport. Therefore, the original positive well and four additional wells located within 300 feet of the original well were sampled. A second positive well found as a result of this sampling, led to additional sampling in an area expanded to a 7,000 foot radius around the original positive well. Of the 32 wells sampled within the 7,000 foot radius, eleven were found to be positive.

Because the region of contamination had not been delimited, a much larger study area was established (Figure 1). This study region consisted of a 5 x 5 mile core area surrounding the original find. Extensions from the core area one mile wide and three miles long were established along a major road in each cardinal (north, south, east, west) direction. The study area was divided into 37 1 x 1 mile sampling cells (25 cells in the core area, plus 12 cells in the four extensions). Five wells within each of the 37 sampling cells were to be sampled. When there

Figure 1. The study area was bordered on the north by Road 45, on the east by an imaginary extension of Road M, on the south by an imaginary line one mile south of Road 57, and on the west by an imaginary line one mile west of Road D. Additional sampling was done in four areas 3 miles long and 1 mile wide (3 sections), extending out from the core area north on Highway 99, west on Road 162, east on Roads 48 and 162, and south on Road D.



were more than five wells in a cell, those with well logs were preferentially sampled.

Soil was also sampled in an attempt to determine the source of contamination. Surface samples were collected along roadsides, in a drainage ditch, and an agricultural field. Soil core samples were also collected at one roadside site.

B. Sampling Methods

Water samples were collected in one-quart amber glass bottles with foil-lined lids. The well pumps were run for a minimum of 10 minutes before sampling. Whenever possible, samples were collected from a port before the storage tank. The samples were immediately cooled with ice and kept refrigerated until analysis. A chain of custody accompanied each sample, on which all pertinent sampling data and all persons handling the sample were recorded. All water samples were collected in February, 1986.

Surface soil samples, 12 inches deep, were collected using a shovel and spade. Samples were placed in one-quart glass jars with foil-lined lids. Soil core samples were collected using a Mobile Drill, Model B-53, with a split barrel sampler (Appendix I). Samples were collected in two to six inch segments from the surface to ground water. All soil samples were cooled immediately with dry ice and kept frozen until analysis. The surface samples were collected in February, and the core samples in April, 1986.

C. Laboratory Methods

The primary chemical analyses were performed by the CDFA Chemistry Laboratory Services Branch. In addition to the atrazine analysis, water samples from one

well in each cell were also analyzed for alachlor and metolachlor as well as for organophosphates, chlorinated hydrocarbons, and carbamates.

The analytical method for atrazine water samples consisted of a dichloromethane extraction. The dichloromethane extracts were evaporated to dryness and redissolved with methanol. The methanol extracts were then analyzed using a Varian 3700 gas chromatograph with a thermionic specific detector and a 10 m x 530 u Hewlett-Packard 50:50 phenyl:methyl megabore column. Positive samples were also analyzed with a Perkin Elmer Series 4 high pressure liquid chromatograph adjusted to 230 nm. A 15 cm x 4.6 mm 5 u ultrasphere ODS column, and 32% acetonitrile:68% water solution were used. Detailed methods for this analysis as well as other pesticides and soil samples are contained in Appendix II.

Extensive laboratory quality control measures were instituted, including spiked sample analyses, replicate sample analyses, replicate extract injections, and split sample analyses. Within the context of this report, spiked samples refer to water samples with a known amount of pesticide added; replicate samples refer to multiple samples collected from the same well at the same time; replicate extract injections refer to multiple measurements of a single extract; and split samples refer to one water sample divided into two portions, one portion analyzed by the CDFA laboratory and the second portion analyzed by California Analytical Laboratories, Inc. (CAL). Spiked samples were analyzed prior to and during the analysis of actual samples. Replicate extract injections were analyzed for one sample. Split samples were analyzed by the two laboratories for 35 wells. As discussed earlier, all positive samples found by the CDFA laboratory were analyzed by two methods, gas chromatography and high pressure liquid chromatography. In addition, mass spectrometry provided qualitative confirmation for several samples.

III. RESULTS

A. Well Sampling

Results of the chemical analyses in this study are summarized in Table 1. In addition to atrazine, two other triazine herbicides, simazine and prometon, were found. Simazine was found among the first samples collected, and a quantitative analysis was done for all samples. In contrast, prometon was not identified until all analyses had been completed. Therefore, a quantitative reanalysis could be done for very few samples. Most of the analyses for prometon were qualitative only. In other words, actual prometon concentrations could not be determined, only if they were positive or negative. Of the 137 wells sampled, 30 contained one chemical, 11 contained two chemicals, and 3 contained three chemicals, for a total of 44 positive wells. The range of concentrations found was very narrow, and near the detection limit of 0.1 part per billion (ppb). Of the 61 triazine concentrations found, only 5 were above one part per billion. For those wells which contained more than one chemical, the highest concentration sum was 6.0 ppb. All 33 samples which were screened for other pesticides were negative. Complete results are shown in Table 2. An explanation of units, statistical terms and calculations is given in Appendix III.

Table 1. Summary of well sampling, Glenn County, 1986.

<u>Chemical</u>	<u># Positive</u>	<u># Analyzed</u>	<u>Concentration Range (ppb)</u>	<u>Detection Limit (ppb)</u>
Atrazine	34	137	0.1 - 1.4	0.1
Simazine	17	137	0.1 - 1.4	0.1
Prometon	10	132	0.1 - 5.9	0.1
Organophosphate	0	33	None Detected	0.1
Chlorinated hydrocarbons	0	33	None Detected	0.5
Carbamates	0	33	None Detected	0.1
Alachlor/Metolachlor	0	33	None Detected	0.1

Table 2. Results of the well sampling in Glenn County for triazine herbicides. Concentrations are shown by chemical and analyzing laboratory. When replicate samples were analyzed, each replicate is shown separately. Blanks are shown when no analysis was conducted.

Well ^a No.	Atrazine COFA	Atrazine CAL	Simazine COFA	Simazine CAL	Prometon COFA	Screens ^b COFA
1	0.12, 0.15		N.D. ^c			
2	0.70, 0.75 ^d		N.D., N.D.			
3	N.D., N.D.		N.D., N.D.			
4	N.D., N.D.		N.D., N.D.			
5	N.D., N.D.		N.D., N.D.			
6	N.D., N.D.		N.D., N.D.		N.D., N.D.	
7	N.D., N.D.		N.D., N.D.		N.D., N.D.	
8	N.D., N.D.		0.20, 0.30		N.D., N.D.	
9	0.55, 0.55		0.60, 1.4		N.D., N.D.	
10	0.90, 0.70 ^d		0.20, 0.10		Trace ^e	
11	0.70, 0.70		0.55, 0.60			
12	0.60, 0.45		0.10, 0.10		Trace, pos. ^f	
13	N.D.		N.D.		N.D.	
14	N.D., N.D.		N.D., N.D.		N.D., N.D.	
15	N.D.		N.D.		N.D.	
16	N.D.		N.D.		N.D.	
17	N.D.		N.D.		N.D.	
18	0.30, 0.35		0.10, 0.10		N.D., trace	
19	0.20, 0.20		0.20, 0.10		N.D., trace	
20	N.D.		N.D.		N.D.	
21	N.D.		N.D.		N.D.	
22	N.D.		N.D.		N.D.	
23	N.D.		N.D.		N.D.	
24	N.D.		N.D.		N.D.	
25	N.D.		N.D.		N.D.	
26	0.10, 0.10		N.D., N.D.		N.D., N.D.	
27	N.D.		N.D.		N.D.	

Well No.	Atrazine CDFA	Atrazine CAL	Simazine CDFA	Simazine CAL	Prometon CDFA	Screens CDFA
28	0.10, 0.15		N.D., N.D.		N.D., N.D.	
29	N.D.		N.D.		N.D.	
30	0.20, 0.25		0.60, 0.50		pos., pos.	
31	N.D.		N.D.		N.D.	
32	N.D.		N.D.		N.D.	
40	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D.	N.D.
41	N.D., N.D.		N.D., N.D.		1.5, pos.	
42	N.D.		N.D.			
43	N.D.		N.D.			
44	N.D.		N.D.			
45	0.25, 0.20, 0.20	0.3	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
46	N.D.		N.D.			
47	N.D.		N.D.		N.D.	
48	N.D.		N.D.		N.D.	
49	N.D.		N.D.		N.D.	
50	0.20, 0.20, 0.30	0.2	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
55	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
56	N.D.		N.D.		N.D.	
60	N.D.		N.D.			
65	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
66	N.D.		N.D.		N.D.	
70	0.30, 0.30, 0.25	0.3	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
71	N.D.		N.D.		N.D.	
72	N.D.		N.D.		N.D.	
73	N.D.		N.D.		N.D.	
74	0.10		N.D.			
75	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
76	N.D.		N.D.		N.D.	
77	N.D., N.D.		N.D., N.D.		0.10, trace	
78	N.D.		N.D.		N.D.	

Well No.	Atrazine CDFA	Atrazine CAL	Simazine CDFA	Simazine CAL	Prometon CDFA	Screens CDFA
79	N.D.		0.17		N.D.	
80	N.D.		N.D.		N.D.	
81	N.D.		N.D.		N.D.	
82	N.D.		N.D.		N.D.	
83	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
84	N.D.		N.D.		N.D.	
85	N.D.		N.D.		N.D.	
86	N.D.		N.D.		N.D.	
87	N.D., 0.10, 0.15	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
88	N.D.		N.D.		N.D.	
90	0.15		N.D.		N.D.	
91	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
92	N.D.		N.D.		N.D.	
93	N.D.		N.D.		N.D.	
94	N.D.		N.D.		N.D.	
95	N.D., N.D., N.D., N.D.	N.D.	N.D., N.D., N.D., N.D.	N.D.	0.2, 0.20, 0.45, 0.40	N.D.
96	N.D.		N.D.		N.D.	
97	N.D.		N.D.		N.D.	
110	0.10, 0.10, 0.20	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
111	N.D.		N.D.		N.D.	
112	N.D.		N.D.		N.D.	
113	N.D.		N.D.		N.D.	
114	N.D.		N.D.		N.D.	
115	N.D.		N.D.		N.D.	
116	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
117	N.D.		N.D.		N.D.	
118	1.4		0.55			
119	0.10		N.D.		N.D.	
120	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
125	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D.	N.D.

Well No.	Atrazine CDFA	Atrazine CAL	Simazine CDFA	Simazine CAL	Prometon CDFA	Screens CDFA
130	N.D.		N.D.		N.D.	
131	N.D., 0.10, trace	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
135	0.10, N.D., 0.10	0.1	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
136	N.D.		N.D.		N.D.	
137	N.D.		N.D.		N.D.	
138	N.D.		N.D.		N.D.	
139	N.D.		N.D.		N.D.	
145	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D.	N.D.
146	N.D.		N.D.		N.D.	
147	N.D.	N.D.	0.10	0.1	N.D.	
148	0.15	0.1	N.D.	N.D.	N.D.	
149	N.D.		N.D.		N.D.	
150	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
155	N.D.		N.D.		N.D.	
157	0.20		N.D.		N.D.	
158	N.D.		N.D.		N.D.	
159	N.D.		N.D.		N.D.	
160	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	2.0, 1.5, 0.4 ^d	N.D.
161	N.D., N.D.		N.D., 0.1		0.20, pos.	
170	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
171	N.D.		N.D.		N.D.	
175	0.15, 0.10, 0.10	0.1	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
176	N.D.		N.D.		N.D.	
181	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
190	0.10, 0.10, 0.10	N.D.	0.10, 0.10, 0.10	N.D.	N.D., N.D., N.D.	N.D.
191	N.D.		N.D.		N.D.	
192	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
195	N.D.		N.D.		N.D.	
196	0.10, 0.10, 0.20	0.1	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
197	N.D.		N.D.		N.D.	

Well No.	Atrazine CDFA	Atrazine CAL	Simazine CDFA	Simazine CAL	Prometon CDFA	Screens CDFA
200	0.30, 0.30, 0.25 ^d	0.3	N.D., N.D., N.D.	N.D.	N.D., N.D.	N.D.
205	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D.	N.D.
206	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
207	N.D.		N.D.		N.D.	
208	0.10		N.D.		N.D.	
210	0.45, 0.40, 0.50	0.5	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
211	N.D.		N.D.		N.D.	
212	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
213	0.20, 0.10		0.40, 0.8		0.30, pos.	
214	N.D.		N.D.		N.D.	
220	0.70		0.10		N.D.	
221	N.D.		N.D.		N.D.	
222	0.10		N.D.		N.D.	
223	N.D.		N.D.		N.D.	
224	0.35, 0.3		0.30, 0.25		N.D., trace	
225	N.D.		N.D.		N.D.	
226	N.D.		N.D.		N.D.	
231	N.D., N.D., N.D., N.D.	N.D.	N.D., N.D., N.D., N.D.	N.D.	N.D., 0.10, 0.10, trace	N.D.
232	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.	N.D., N.D., N.D.	N.D.
233	N.D., N.D.		0.15, 0.1		5.9, pos.	

a/ Arbitrary number assigned by EHAP.

b/ These samples were screened for organophosphates, chlorinated hydrocarbons, and carbamates.

c/ None Detected, detection limit for all chemicals 0.1 ppb, except chlorinated hydrocarbons MDL 0.5 ppb.

d/ These samples confirmed by mass spectrometry.

e/ Unconfirmed concentration below the detection limit, and considered none detected.

f/ Positive sample. Only a qualitative analysis could be done.

The spatial distribution of the sampled wells is shown in Figure 2. Distribution of positive wells was widespread and showed no obvious patterns. Since positive wells were located near all boundaries, the area of contamination was not delimited. While it may appear that more positive wells were located near the original detection (Well #1), this was probably because more wells were sampled in that area.

B. Quality Control

Results of the quality control analyses showed good accuracy and precision as indicated by the spike recoveries and replicate analyses. The spike recoveries ranged between 76 and 96 percent (Tables 3 and 4). The coefficient of variation of replicate injections was between 1.6 and 9.7 percent (Table 5), while the coefficient of variation for replicate sample analyses averaged 18.5 percent for atrazine and 23.9 percent for simazine. An explanation of units, statistical terms, and calculations is given in Appendix III. The results of the samples split between laboratories showed very good agreement. Of the 35 split samples, 23 negatives agreed, 9 positives were within 0.05 ppb of each other, 4 positives agreed at the detection limit, and 3 positives reported at the detection limit by the primary laboratory were reported negative by the quality control laboratory.

Figure 2. Locations of wells tested for triazine herbicides, Glenn County, 1986. Well number identification is given only for positive wells.

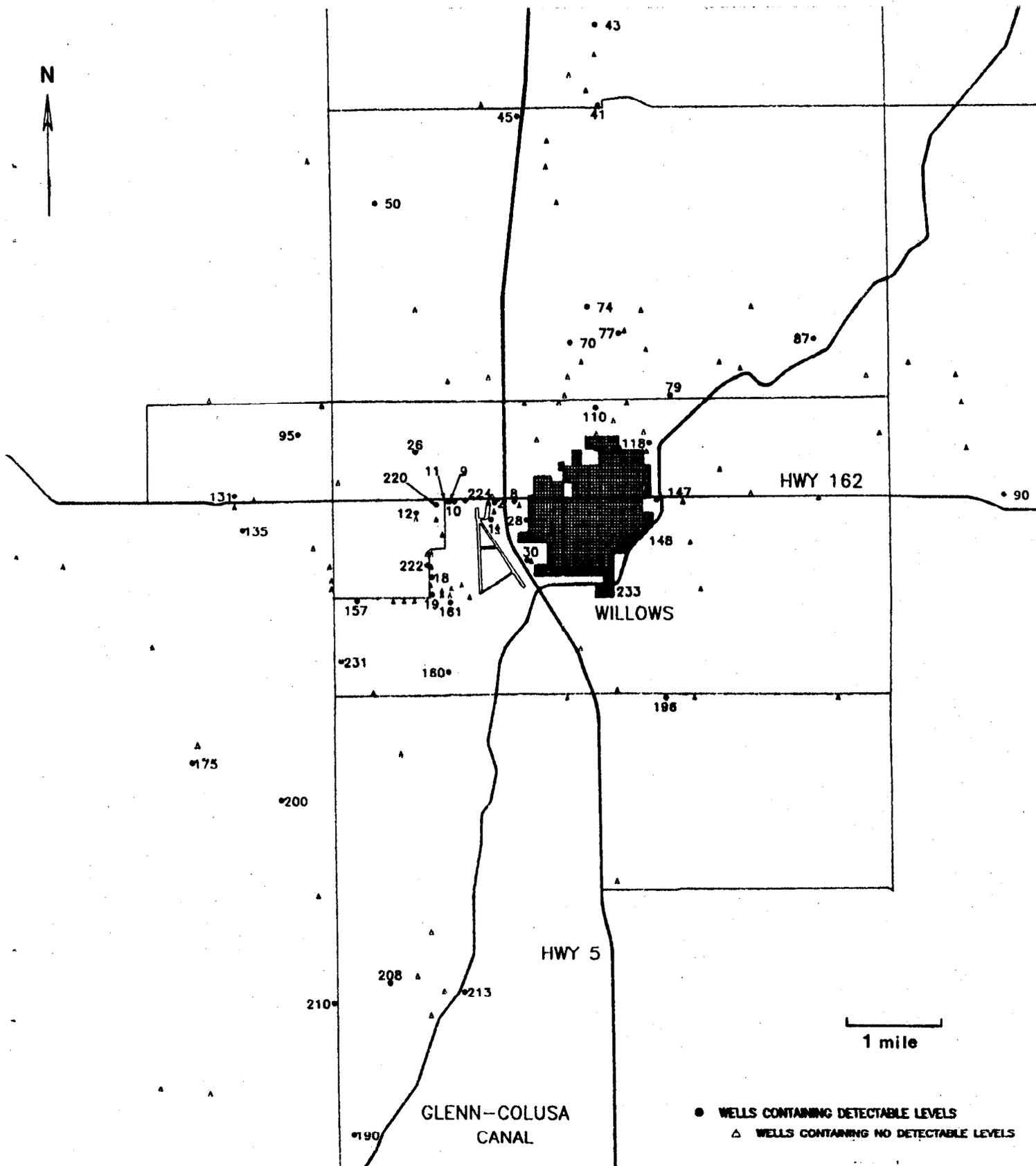


Table 3. Results of initial spiked water sample analyses by gas chromatography.^a

	Atrazine		Simazine		Prometon
Number of replicates	5	5	5	5	3
Spike Level (ppb)	0.31	2.5	0.25	2.5	0.5
Average Recovery (ppb)	0.30	2.3	0.19	2.0	0.43
Standard Deviation	0.02	0.28	0.02	0.09	0.07
% Recovery	97	93	76	82	87
Coefficient of Variation	13	12	11	4.4	16

- a. Spiked sample refers to a known amount of pesticide added to a water sample. An explanation of units, statistical terms, and calculations is given in Appendix III.

Table 4. Results of the continuing spiked water sample analyses by gas chromatography^a.

Date	Atrazine		Simazine ^b	
	Spike Level(ppb)	% Recovery	Spike Level (ppb)	% Recovery
1/7	0.25	84		
1/10	0.25	112		
1/17	0.10	100		
1/17	0.10	100		
1/27	0.13	77		
1/28	0.31	103		
1/28	0.31	110		
2/6	0.31	97	0.31	103
2/7	0.31	94	0.31	90
2/7	0.31	81	0.31	90
2/11	0.62	97	0.62	94
2/11	0.62	89	0.62	87
2/18	0.31	71	0.31	90
2/18	0.31	90	0.31	97
2/18	0.31	110	0.31	81
2/18	0.62	98	0.62	73
Avg. % Recovery		95		89
Standard Deviation		12		8.7

a. Spiked sample refers to a known amount of pesticide added to a water sample. An explanation of units, statistical terms, and calculations is given in Appendix III.

b. Simazine spikes were not analyzed until it was identified on 2/6/86.

Table 5. Results of replicate injections of one water sample by high pressure liquid chromatography (HPLC) and gas chromatography (GC).^a

	<u>Atrazine</u>		<u>Simazine</u>	
	<u>HPLC</u>	<u>GC</u>	<u>HPLC</u>	<u>GC</u>
N	5	5	5	5
Avg. (ppb)	0.70	0.62	0.69	0.59
S.D.	0.01	0.06	0.02	0.03
C.V.	1.6	9.7	2.8	5.4

a. Replicate injections refer to multiple measurements of a single sample extract. An explanation of units, statistical terms, and calculations is given in Appendix III.

C. Soil Sampling

Surface soil site locations are shown in Figure 3, and the results are shown in Table 6. Simazine was found along roadsides and in the drainage ditch, and atrazine was found in the drainage ditch. No prometon was detected, and none of the chemicals were found in the fallow agricultural field.

One deep soil core was drilled along the shoulder of Highway 162 (Figure 3). These results are shown in Table 7. Samples were collected to ground water, which was 10 feet deep. Simazine was found to a depth of one foot, and no other chemicals were found. However, simazine and atrazine were found in water samples collected from the bottom of the core.

Laboratory quality control measurements for soil showed spiked sample recoveries of 89, 91, and 95 percent for atrazine, simazine, and prometon, respectively. The coefficient of variation for replicate injections of a single sample was 1.9 percent. All positive samples were analyzed by GC and HPLC, and one sample was confirmed by mass spectrometry. An explanation of units, statistical terms, and calculations is given in Appendix III.

Figure 3. Locations of surface soil sites (numbered) and soil core sites (labeled) sampled for triazine herbicides, Glenn County, 1986.

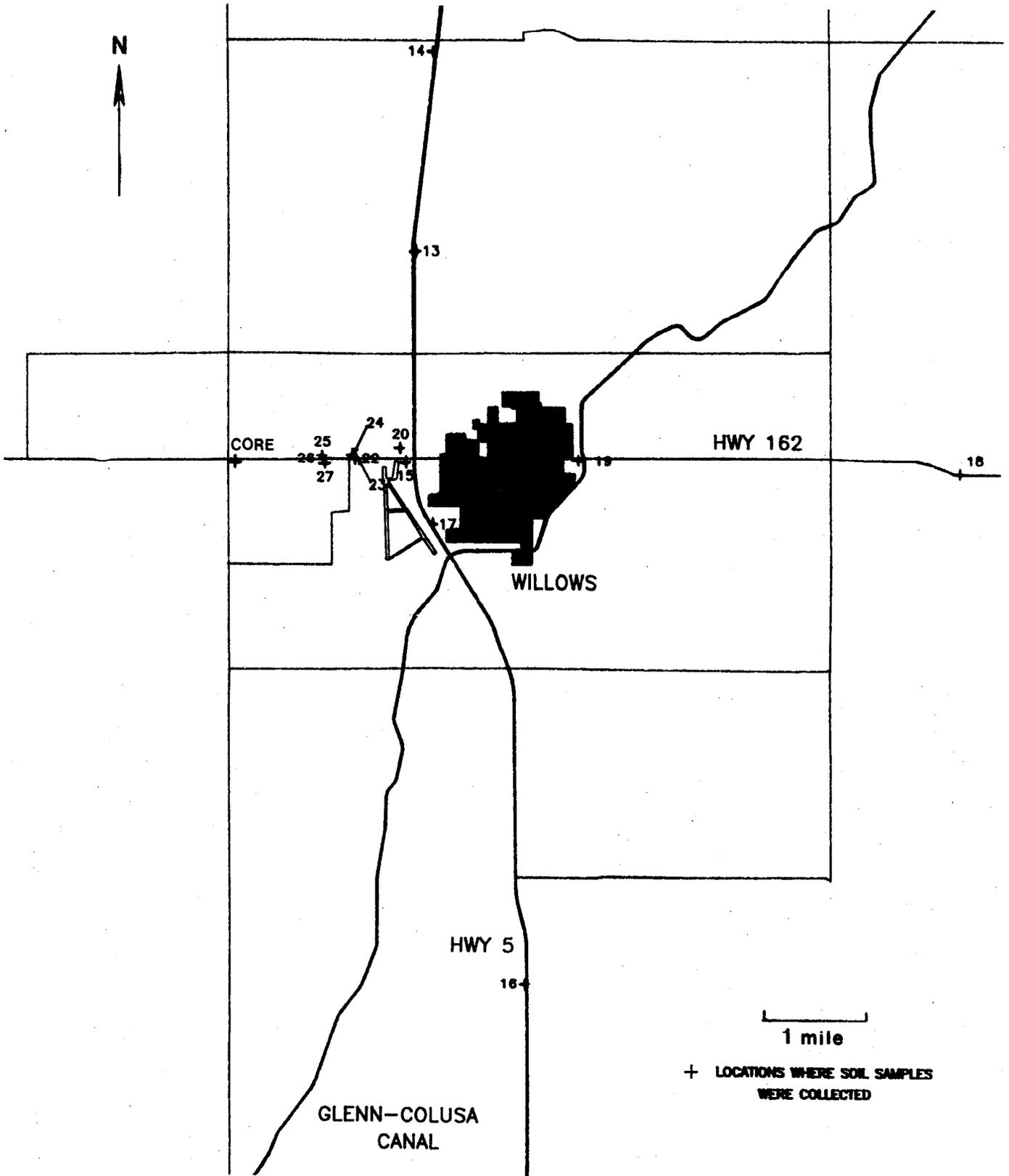


Table 6. Results of the surface soil sampling.

Location ^a	Concentration (ppb, dry weight basis)		
	Atrazine	Simazine	Prometon
Roadside			
13	N.D. ^b	4.0	N.D.
14	N.D.	2.5	N.D.
15	N.D.	61	N.D.
16	N.D.	2.0	N.D.
17	N.D.	4.5	N.D.
18	N.D.	N.D.	N.D.
19	N.D.	120	N.D.
22	N.D.	2.0	N.D.
26	N.D.	176	N.D.
Drainage Ditch			
23	3.5	14	N.D.
27	N.D.	23	N.D.
Ag Field			
20	N.D.	N.D.	N.D.
24	N.D.	N.D.	N.D.
25	N.D.	N.D.	N.D.

a. Locations are shown in Figure 3.

b. None detected. Detection limit 2.0 ppb.

Table 7. Results of the soil core sampling.^a

Segment Depth (inches)	Concentrations (ppb, dry weight basis)		
	Atrazine	Simazine	Prometon
0-6	N.D. ^b	16	N.D.
6-12	N.D.	11	N.D.
12-18	N.D.	N.D.	N.D.
20-22	N.D.	N.D.	N.D.
22-28	N.D.	N.D.	N.D.
28-31	N.D.	N.D.	N.D.
42-48	N.D.	N.D.	N.D.
48-54	N.D.	N.D.	N.D.
54-58	N.D.	N.D.	N.D.
58-60	N.D.	N.D.	N.D.
60-62	N.D.	N.D.	N.D.
62-68	N.D.	N.D.	N.D.
68-74	N.D.	N.D.	N.D.
74-76	N.D.	N.D.	N.D.
76-80	N.D.	N.D.	N.D.
80-86	N.D.	N.D.	N.D.
86-92	N.D.	N.D.	N.D.
92-98	N.D.	N.D.	N.D.
98-100	N.D.	N.D.	N.D.
100-106	N.D.	N.D.	N.D.
106-112	N.D.	N.D.	N.D.
112-118	N.D.	N.D.	N.D.
118-120	N.D.	N.D.	N.D.
120 Water	0.4	0.3	N.D.
120 Water	0.5	0.3	N.D.

a. Location of the soil core is shown in Figure 3.

b. None detected. Detection limit 2.0 ppb.

IV. WELL DATA

Well data were obtained for 35 of the wells (Table 8), and 12 of these contained pesticides. No correlation was found between incidence of positive wells and well characteristics. The well depths of positive samples ranged between 100 and 320 feet, and 85 to 732 feet for negative samples. Four of the 12 positive wells, and 7 of the 23 negative wells had cement annular seals. The positive wells were installed between 1964 and 1982, and the negative wells were installed between 1950 and 1982.

V. PESTICIDE USE HISTORY

Atrazine, prometon and simazine are not California restricted use pesticides, therefore application of these materials must be reported only by licensed Pest Control Operators. Table 9 shows the amount of pesticides that have been reported for the last three years. These data indicate that non-crop applications constitute a significant portion of total use for atrazine and simazine. Since there are no agricultural crop registrations for prometon, all use is non-crop¹. These observations have been confirmed by the County Agricultural Commissioner. The data also indicate a large increase in the use of these chemicals in 1984. This may not actually be true, and the data may only indicate increased reporting of applications.

VI. DISCUSSION

Atrazine, simazine and prometon belong to the class of chemicals called triazine herbicides. Triazine herbicides have several chemical and use characteristics which may promote their mobility through soil. Their soil half-lives are long

1. "Crop" use within the context of this report refers to applications on produce or commodities. This term should not be confused with "agricultural use" as define in the Food and Agricultural Code (Section 11408).

Table 8. Available well data for sampled wells.

Well Number ^a	Results of Chemical Analysis	Well Depth	Seal Type	Year Installed
2	Positive	230	Grout	76
8	Positive	155	Cement	67
10	Positive	100	Unknown	Unknown
13	None detected	140	Cement	76
16	None detected	238	Cement	79
29	None detected	675	Unknown	50
40	None detected	140	Unsealed	72
42	None detected	170	Cement	69
43	None detected	245	Unknown	66
44	None detected	140	Unsealed	74
45	Positive	124	Unsealed	67
46	None detected	196	Cement	63
47	None detected	172	Unsealed	65
60	None detected	140	Unknown	68
70	Positive	245	Cement	82
71	None detected	320	Bentonite	81
72	None detected	170	Unknown	80
74	Positive	165	Unknown	78
75	None detected	145	Unknown	Unknown
76	None detected	276	Unsealed	77
87	None detected	85	Unsealed	77
110	Positive	116	Unsealed	64
111	None detected	104	Unsealed	68
112	None detected	200	Unsealed	75
114	None detected	170	Cement	74
116	None detected	88	Unsealed	75
117	None detected	152	Unsealed	78
135	Positive	162	Unknown	64
145	None detected	92	Unsealed	78
147	Positive	281	Unsealed	71
196	Positive	320	Cement	77
205	None detected	156	Cement	82
221	None detected	227	Cement	81
222	Positive	175	Unknown	71
232	None detected	732	Unknown	Unknown

a. For well numbers and results refer to Table 2.

Table 9. Amount of reported pesticides applied, Glenn County, 1982-84.^a

Chemical	Commodity	Amount Applied (lbs active ingredient)		
		1982	1983	1984
<u>Atrazine</u>				
	Hemp	147	6	328
	Landscape maintenance ^b	-	1	662
	Non-ag areas ^c	9	-	-
	Rights-of-way ^d	-	-	585
	Sorghum	44	1	43
	Turf	-	-	214
<u>Prometon</u>				
	Industrial areas ^e	-	-	39
	Landscape maintenance	-	-	1
	Non-ag areas	-	1	-
	Rights-of-way	-	1	-
<u>Simazine</u>				
	Landscape maintenance	-	-	195
	Non-ag areas	1	1	82
	Rights-of-way	21	22	2214

- a. These materials are not restricted-use materials and the reports probably do not reflect the actual amounts applied.
- b. For example, nurseries, parks, golf courses.
- c. For example, refuse pits, airstrips, ditches, roadways, fence lines.
- d. For example, power lines, ditch banks.
- e. For example, parking lots, sidewalk, pavement, water tower, school exterior, sub-asphalt.

enough to permit movement from the microbially-active root zone to lower soil depths. Additionally, their adsorption to soil constituents may be low enough to also permit movement (1). These chemicals can be applied to soil at high rates, as much as 60 pounds per acre for some uses. Because they are applied directly to the soil, a higher proportion of the amount applied is available for migration through soil compared to foliar-applied pesticides. The most crucial factor leading to ground water contamination in this area may be the shallow depth of ground water which was at ten feet when this study was conducted.

The concentrations found were very low, with the great majority less than one part per billion. The atrazine and simazine concentrations were similar to those found previously (2), and subsequently (3) in other areas of the state. Prometon had not been found previously in California. Atrazine concentrations were below the National Academy of Science's (NAS) suggested no adverse health effects level of 150 ppb, as well as the California Department of Health Services' (CDHS) action level of 15 ppb. Simazine concentrations were also below the NAS suggested no adverse health effects level of 1505 ppb and the CDHS action level of 150 ppb. No similar tolerances have been established for prometon.

Several possible sources of contamination were identified. The soil sampling and pesticide use reports showed that rights-of-way use was probably a contributing factor. It is also possible that other non-crop uses of the pesticides also contributed to the contamination. This is especially true for prometon since there are no agricultural crop registrations for this chemical. Agricultural crop applications were another possible source for atrazine and simazine contamination. Pesticide use reports indicated only a limited amount was applied

to agricultural crops; however, triazines are not restricted pesticides and the reports probably did not reflect the actual amounts applied.

Other possible, but less likely sources of contamination included a pesticide wash area located at the northeast corner of the Willows Airport. Wells sampled in the vicinity of the airport did not show a higher incidence of contamination or higher pesticide concentrations than other areas. In addition, soil samples collected by county personnel from the wash area contained atrazine, but no simazine or prometon. This evidence indicates the wash area was probably not a major source of contamination. Other less likely sources of contamination were wells themselves. The well itself or the annular space between the drilled hole and the well casing can act as conduits for surface contamination to ground water. Under normal circumstances this can only occur if the well or annular space is not sufficiently sealed. Poorly sealed wells are more common in older wells. However, no correlation was found between the incidence of contaminated wells and well characteristics.

LITERATURE CITED

1. Rao, P.S.C., A.G. Hornsby, and R.E. Jessup. Indices for Ranking the Potential for Pesticide Contamination of Groundwater. Proceedings of the Soil and Crop Science of Florida, Vol. 44, 1985, pp. 1-24.
2. Weaver, D.J., et al. 1983. Pesticide Movement to Groundwater, Volume I: Survey of Groundwater Basins for DBCP, EDB, Simazine and Carbofuran. California Department of Food and Agriculture.
3. Segawa, R. Memo to Designated State and County Personnel, dated August 20, 1986. California Department of Food and Agriculture.

APPENDIX I

Soil Core Drilling, Sample Collection and Processing

Soil Core Drilling, Sample Collection and Processing

The drilling and sampling were accomplished using a truck-mounted hydraulically driven drill. The equipment consisted of a 1982 Mobile Drill, Model B-53, mounted on a 1982 International Harvester S1800, 4x4 cab and chassis. Hollow stem augers (5 ft. long, 3 3/8 inches inside diameter [i.d.], 8 inches outside diameter [o.d.]) in conjunction with the Mobile Drill's Moss Wireline Sampling System were utilized in the drilling operation (Figure 1). The soil core segments were brought to the surface in a split barrel sampler (20 inches long, 2.5 inches i.d.). The split barrel sampler (Figure 2) contained three stainless steel liners that served as the actual collection tubes for the soil. Each liner was 6 inches long, 2.5 inches o.d. and 2.37 inches i.d. An additional 2 inches of soil was lodged in the cutter shoe.

The selected equipment allows core sampling to take place concurrently with the drilling process. The Moss sampling apparatus, which included a split barrel sampler, was loaded inside the augers and lowered until it mated with the latch body on the lead auger (Figure 1). The Moss System positioned the cutting edge of the sampler ahead of the auger cutter flights for undisturbed sampling. The winch cable, Moss sampling apparatus and split barrel sampler remained in the hole while drilling the distance required to fill the sampler. The sampler did not rotate during drilling, but was pressed through the soil as the auger rotated and advanced downward. This method was designed to produce undisturbed soil samples.

Each time the sampling apparatus was placed in the ground, it advanced in increments equal to the length of the sampler used, 20 inches. In some highly expansive or hard soils (clay hardpan or calcareous soils), significant wall friction between the sampler and soil prevented the soil from completely filling the sampler. In these instances, the sample recovered was the upper portion of the production depth that was collected prior to the critical buildup of friction. The rest of the production (the lower portion) was lost. The lost soil was presumed to have been pushed aside and removed by the auger cutter head.

When water saturated soil was reached, drilling was stopped, and the Moss sampling apparatus was replaced with a teflon bailer (2 ft long, 1 11/16 inches

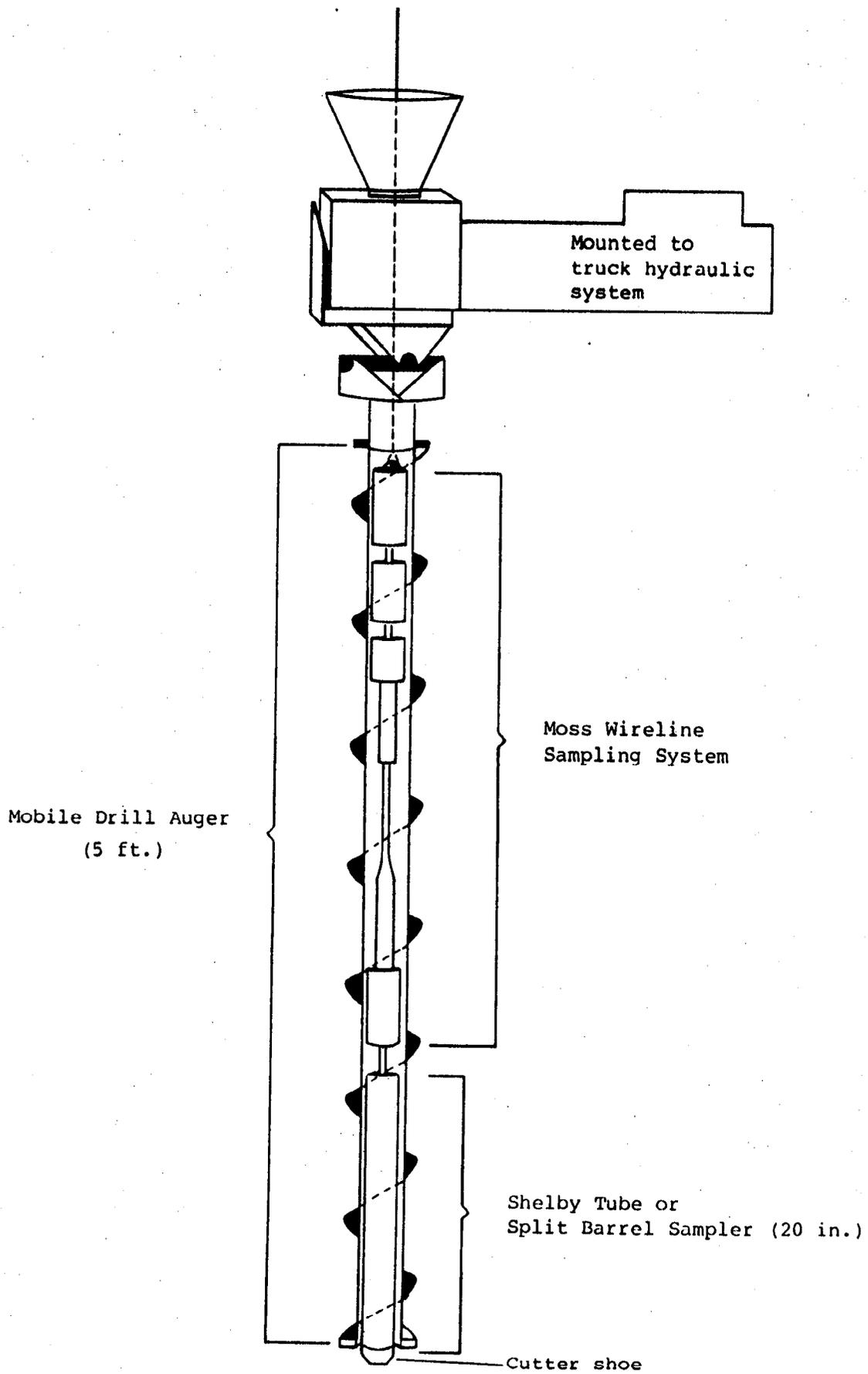


Figure 1. Mobile Drill/Moss Wireline Sampling Schematic

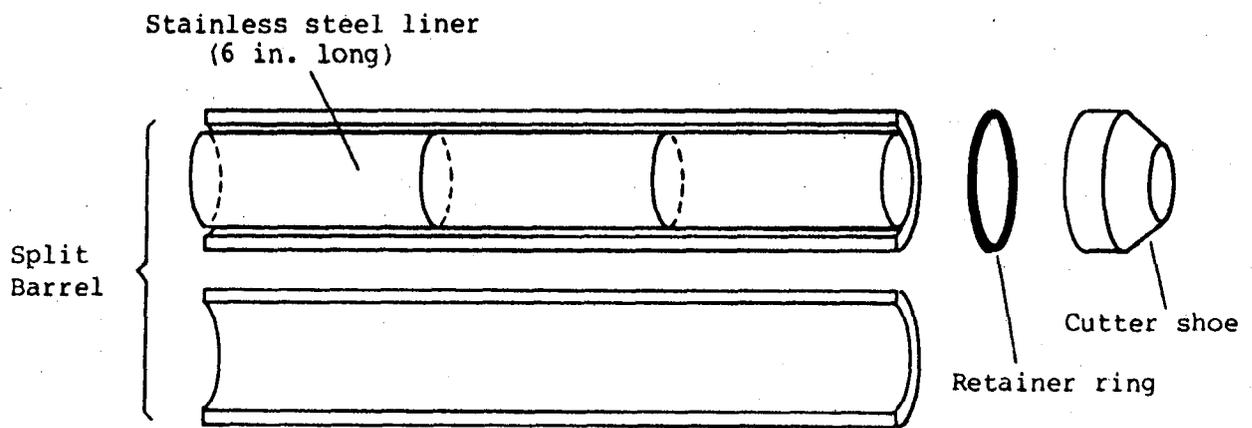


Figure 2. Split Barrel Sampler (soil)

o.d., 1 1/2 inches i.d.) to collect a ground water sample. The bailer consisted of a hollow teflon tube with a teflon ball check valve at one end. The bailer was lowered through the hollow stem augers into the saturated soil. The check valve allowed water into the tube and retained it in the tube while the bailer was retrieved. Water from the bailer was poured into a glass bottle for storage.

Two people were required to operate the drill and handle the sampler tooling. Once the sampler was brought out of the ground and disconnected from the Moss sampling apparatus, it was handed over to three people who processed the samples and cleaned the sampler tooling. The split barrel samplers were cleaned between uses on site and recycled into the drilling operation. They were washed in a detergent mix, and rinsed in water. Soil samples collected using the split barrel sampler were kept in their original 6 inch stainless steel liners. The liners were removed from the sampler and the ends sealed with aluminum foil and plastic caps. The two inch segments in the cutter head were removed and kept in glass jars for analysis. All soil samples were placed immediately on dry ice and kept frozen until splitting for analysis.

To prepare the samples for analysis, the soil was extruded and split out of the steel liners using a hydraulic press. The samples were first thawed slightly in the steel liners, then placed in the hydraulic press. The press was constructed with two blades to divide the soil sample into three longitudinal portions while being extruded out of the liner. One portion was used for the pesticide analysis, one portion was used for soil moisture determination, and the third portion for the rest of the analyses.

APPENDIX II

Laboratory Analytical Methods

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CHEMISTRY LABORATORY SERVICES
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Original Date: 1/4/86
Supercedes: 1/4/86
Current Date: 3/6/86
Method #: 115

ATRAZINE & SIMAZINE IN WATER

SCOPE:

This method is for the extraction and analysis of Simazine and Atrazine in water.

PRINCIPLE:

The water is extracted with Dichloromethane. The solvent is evaporated to dryness on a rotary evaporator. The residue is brought to volume with Methanol and analyzed by GLC (TSD Detector) and HPLC (UV Detection 230nm).

REAGENTS AND EQUIPMENT:

Dichloromethane (Pesticide Quality)
Methanol (U.V. Grade)
Sodium Sulfate anhydrous
1000ml Separatory funnels
15cm Column Funnels
500ml Round Bottom Evaporating Flasks
Rotary Evaporator
P.E.C. (Perkin Elmer Series 4, U.V. detector, Autosampler)
B.C. (Varian 3700, TSD Detector, Autosampler)

ANALYSIS:

- 1) 800 grams of water sample is poured into a 1000ml separatory funnel.
- 2) 100 ml of Dichloromethane is added and sample shaken for 1 minute.
- 3) The organic layer is drained through filter with 20grams anhydrous Sodium Sulfate into a 500ml Round bottom flask.
- 4) Steps 2 & 3 are repeated once more.
- 5) The Sulfate is rinsed with 50 ml dichloromethane.
- 6) The dichloromethane is evaporated to dryness on a Rotary vacuum evaporator with 35 degree centigrade water bath.
- 7) The extract is transferred to a graduated test tube with 5ml of methanol.
- 8) The extract is concentrated to 2mls final volume on a water bath (40 Cent) under nitrogen.
- 9) The extract is analyzed by HPLC and GLC (see equipment and conditions).

EQUIPMENT CONDITIONS:

HPLC CONDITIONS

Perkin Elmer Series 4 HPLC With Kratos variable wavelength
UV detector : P.E. ISS100 Autosampler (30ul injection)
15cm X 4.6mm 5um Ultrasphere ODS Column (Beckman Labs);
32% Acetonitrile; 68% water : flow= 2.0mls/minute
Absorbance= 230nm
Atrazine R.T. = 4.10min Simazine R.T. = 2.53min

GAS CHROMATOGRAPH CONDITIONS

Varian 3700 Gas Chromatograph with Thermionic Specific Detector
Hewlett Packard 7672A Autosampler (2ul injection splitless)
Injector= 210 Cent : Detector= 230 Cent : Oven= 165 Cent
He Flow= 15mls/min : H2 =25psi : Bead= 6.05
10 meter x 530u Hewlett Packard 50:50 Phenyl:Methyl Megabore
Atrazine RT= 5.12 minutes Simazine RT= 5.47 minutes

CALCULATIONS:

(Area Sample) (NG Std) (Final Volume ml) (1000)
PPB Herbicide=-----
(Area Standard) (UL Sample injected) (Weight H2O)

DISCUSSION:

Recoveries and Sensitivities
(Sensitivities may vary with sample interferences)

ATRAZINE

Chromatographic M.D.L. (3x noise)
GLC 0.04ngs injected HPLC 0.65ngs injected

Recoveries

0.32PPB Spikes- x= 99.2% Sx%= 6.7% n=5
2.5 PPB Spikes- x= 93% Sx%= 12% n=5

SIMAZINE

Chromatographic M.D.L. (3x noise)
GLC 0.04ngs injected HPLC 0.15ngs injected

Recoveries

0.25PPB Spikes- x= 76% Sx%= 12% n=5
2.5PPB Spikes- x= 82% Sx%= 5.5% n=5

REFERENCES:

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TITLE: Agricultural Chemist II

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TITLE:

APPROVED BY: David Conrad

TITLE: Agricultural Chemist III

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Original Date: 3-5-86
Supercedes: New
Current Date: March 5, 1986
Method #: 117

CARBAMATE SCREENING USING HPLC

SCOPE:

This method was used to screen water samples for Carbamates at 0.1 ppb level.

PRINCIPLE:

Water samples were saturated with Anhydrous Sodium Sulfate, extracted with Dichloromethane, evaporated to dryness, made to volume in water and analysed using a post column derivitization technique.

REAGENTS AND EQUIPMENT:

Balance Analytical
Flasks 500ml flat bottom
Fluorescent detector (Spectra/glo filter Fluorometer)
High Performance Liquid Chromatograph (Perkin Elmer Series 4)
equipped with ISS-100 Auto-Sampler.
Rainin 0.2u x 25mm sample filter (Catalog # 38-151)
Rotary evaporator
Separatory Funnels (1000ml)
Solvent Filtration Unit
Test tubes
Water bath

Acetonitrile
Dichloromethane
Sodium hydroxide
Sodium sulfate (Anhydrous)
Mercaptoethanol
Methanol
O-Pthaldehyde crystals
Potassium borate buffer 1.0 M pH 10.4

POST COLUMN SET

Heating Jacket
Rabbit pump

ANALYSIS:

Pour 800ml water sample into 1L separatory funnel. Add 160g sodium sulfate (anhydrous). Shake it real well for 1 min. to dissolve as much of sodium sulfate in water as possible. Add 100ml Dichloromethane (DCM). Shake vigorously for 2 min. Let

the two solvents layer separate out. Drain DCM into a 500ml flat bottom flask through a funnel containing a bed of anhydrous sodium sulfate. Repeat the extraction two more times with DCM each time draining into the flask. Rinse the top of sodium sulfate with app. 25ml DCM. Evaporate DCM using a rotary evaporator at 35 C to 2-3 ml. Evaporate the last 2-3 ml of DCM under a current of Nitrogen. Rinse the flask a few times with Methanol and quantitatively transfer the aliquot into test tubes. Evaporate to dryness under a current of Nitrogen. Bring to 2ml final volume with filtered water. Sonicate for a few minutes, filter through 0.2u Rainin filter into an Autosampler vial and analyse by HPLC.

RECOVERY:

COMPOUND	LEVEL SPIKED	RECOVERED %	LEVEL SPIKED	RECOVERED %
Aldicarb Sulfoxide	0.25ppb	62	1.25ppb	65
Aldicarb Sulfone	0.25ppb	103	1.25ppb	106
3-Hydroxy Carbofuran	0.25ppb	90	1.25ppb	105
Carbofuran	0.25ppb	52	1.25ppb	61
3-Keto Carbofuran	0.25ppb	74	1.25ppb	86

EQUIPMENT CONDITIONS:

COLUMN- Sepralyte CH 5u x 25cm Analytichem International

SOLVENTS FLOW PARAMETERS

SECTOR	TIME	FLOW (ml/min)	ACN	WATER	CURVE
Equil.	7	1.5	18	82	
1	4	1.5	18	82	
2	4	1.5	40	60	1
3	3	1.5	40	60	
4	4	1.5	80	20	1
5	10	1.5	80	20	

POST COLUMN DERIVITIZATION

Solution A, 0.05N sodium Hydroxide (2g/1000ml) was added to the post column eluent before it enters the heating coil.

Add derivitizing reagent solution B (0.5g o-pthaldehyde+ 1ml mercaptoethanol + 10ml methanol + 50ml buffer and make to 1L in water) to the basic eluent coming out of the heating coil and detect carbamates using Fluorescent detector.

Use 0.8mm I.D. tubing for post column setup.

Attn. 2 ^ 2 Peak Width = 0.6 Peak Threshold = 2

RETENTION TIMES:

Aldicarb Sulfoxide	4.5 min
Aldicarb Sulfone	6.2 min
3-Hydroxy Carbofuran	11.25min
Carbofuran	17.0 min
3-Keto Carbofuran	18.0 min

DISCUSSION:

Aldicarb Sulfoxide is very difficult to extract because of its being highly soluble in water. It is very important therefore to saturate water samples with Sodium Sulfate. Sodium Chloride was tried in place of Sodium Sulfate but it gave poor recoveries. The minimum amount of each of the standards shot was 20ng which gave about 30% F.S.D.

REFERENCES:

Cochrane, W.P.; Lanouette, M and Trudeau, S. J. of Chromatography 243 (1982) 307-314
Krause, R.T. J. A.O.A.C. V.63, No 5, 1980 1114-1124

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Original Date: 3/6/86
Supercedes: 2/1/84
Current Date: 3/6/86
Method #: ?? 118

Glenn County-Well Water Screen for Lasso, Metolachlor, and other
Chlorinated Hydrocarbons

SCOPE:

This method has been developed and used to screen Glenn County well water for Lasso, Metolachlor, and other chlorinated hydrocarbon pesticides.

PRINCIPLE:

Well waters from Glenn County were extracted for chlorinated hydrocarbons with dichloromethane. The dichloromethane was rotary evaporated to dryness and brought to volume in hexane for GLC analysis.

REAGENTS AND EQUIPMENT:

1. Dichloromethane, pesticide grade
2. Hexane, pesticide grade
3. Sodium sulfate (anhydrous), Mallinkrodt #8024
4. Separatory funnel-1000 ml
5. Funnels, 60 degree short stem, 3-4 inch diameter
6. Flask, flat-bottomed boiling-250 ml
7. Graduated conical centrifuge tube-15 ml
8. Rotary evaporator-Buchi
9. Meyers N-EVAP - Organomation Associates Incorporated
Northborough, Ma.

ANALYSIS:

1. 800 grams (+/- 1g) of the water sample was weighed out into a 1 liter separatory funnel after being well shaken.
2. Approximately 50 ml dichloromethane was added to the water in the separatory funnel, and the mixture gently shaken.
3. After the two liquid phases had satisfactorily separated, the bottom (dichloromethane) layer was drained into a funnel containing a bed of anhydrous sodium sulfate. The dried dichloromethane extract was collected in a 250 ml flat bottomed boiling flask.
4. The remaining aqueous phase in the separatory funnel was extracted twice again as in steps 2 and 3 using 50 ml of dichloromethane each time.
5. The sodium sulfate in the funnel was rinsed out with 25 ml of dichloromethane.

6. The dichloromethane was rotary evaporated to just dryness at 35 degrees centigrade under approximately 17 inches of Hg vacuum.
7. The flask was then placed under a stream of Nitrogen for approximately one minute to evaporate any remaining dichloromethane.
8. The sample residue was rinsed with hexane and quantitatively transferred to a conical graduated centrifuge tube, placed in the N-EVAP at 40 degree centigrade under a stream of Nitrogen, evaporated to 1 ml volume in hexane and saved for GC analysis.

EQUIPMENT CONDITIONS:

GC CONDITIONS:

CHLORINATED HYDROCARBON ANALYSIS:

HP 5880 equipped with a Electron Capture detector
 Column/s: HP X-Linked Capillary 0.2mm I.D. X 12m
 fused silica with a Helium (99.99%) carrier,
 pressure 15 psig.

Injector: Splitless; 225 degree C
 Detector: 350 degree C
 Temperature Program: 180 C initial temperature
 5 C/minute program rate
 220 C/12 minutes final temperature
 Make-up Gas: Argon-Methane (5%/95%)
 Flow 30ml/minute

Varian 3700 equipped with a Hall electroconductivity detector
 Injector: Splitless; 210 C
 Detector: 250 C
 Temperature Program: 155 C/3 minutes initial temperature
 5 C/minute program rate
 240 C/5 minutes final temperature
 Column: 50% Phenylmethyl X-linked Capillary
 0.20mm I.D. X 25m fused silica column
 column pressure 30psig (helium)
 Make-up Gas: Argon-Methane (5%/95%)
 Flow 20 ml/minute

CALCULATIONS:

$$PPB = \frac{(Peak\ Ht\ Sample)(NG\ Std\ inj)(1\ ml)(1000)}{(peak\ Ht\ Std)(UL\ inj)(Sample\ Weight)}$$

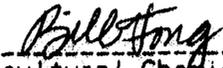
DISCUSSION:

Recoveries for Lindane, Heptachlor, Aldrin, Hept. Epoxide, Thiodan I & II, Dieldrin, Endrin, pp DDT ranged from 80 to 100% at 0.5 ppb level. Recoveries for Laeso and Metolachlor were 100% each at 1.0 ppb level. MDL for the ECD was 0.1 ppb; for Hal1, 0.5 ppb.

REFERENCES:

EPA MANUAL OF ANALYTICAL METHODS FOR THE ANALYSIS OF PESTICIDES IN HUMANS AND ENVIRONMENTAL SAMPLES.

REVISED BY: Bill Fong



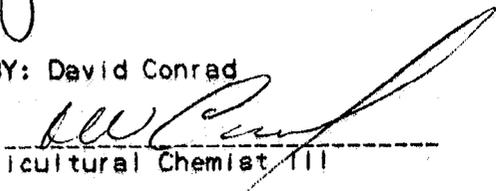
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Original Date: 3/20/86
Supercedes: NEW
Current Date: 3/20/86
Method #: ?? 119

**Glenn County-Well Water Screen for Organophosphate Pesticides
and other Miscellaneous Herbicides**

SCOPE:

This method has been developed and used to screen Glenn County well water for organophosphate pesticides and miscellaneous herbicides, specifically Bolero and its metabolite, and Ordram and its metabolite. Prometone, Atrazine, and Simazine were also screened for in conjunction with the main study.

PRINCIPLE:

Well waters from Glenn County were extracted for organophosphate pesticide residues, the herbicides Bolero and Bolero Sulfoxide, Ordram and Ordram Sulfoxide, Prometone, Simazine and Atrazine with dichloromethane. The dichloromethane was rotary evaporated to dryness and brought to volume in hexane for GLC analysis.

REAGENTS AND EQUIPMENT:

1. Dichloromethane, pesticide grade
2. Hexane, pesticide grade
3. Sodium sulfate (anhydrous), Mallinkrodt #8024
4. Separatory funnel-1000 ml
5. Funnels, 60 degree short stem, 3-4 inch diameter
6. Flask, flat-bottomed boiling-250 ml
7. Graduated conical centrifuge tube-15 ml
8. Rotary evaporator-Buchi
9. Meyers N-EVAP - Organomation Associates Incorporated
Northborough, Ma.

ANALYSIS:

1. 800 grams (+/- 1g) of the water sample was weighed out into a 1 liter separatory funnel after being well shaken.
2. Approximately 50 ml dichloromethane was added to the water in the separatory funnel, and the mixture gently shaken.
3. After the two liquid phases had satisfactorily separated, the bottom (dichloromethane) layer was drained into a funnel containing a bed of anhydrous sodium sulfate. The dried dichloromethane extract was collected in a 250 ml flat bottomed boiling flask.
4. The remaining aqueous phase in the separatory funnel was extracted twice again as in steps 2 and 3 using 50 ml of dichloromethane each time.

5. The sodium sulfate in the funnel was rinsed out with 25 ml of dichloromethane.
6. The dichloromethane was rotary evaporated to just dryness at 35 degrees centigrade under approximately 17 inches of Hg vacuum.
7. The flask was then placed under a stream of Nitrogen for approximately one minute to evaporate any remaining dichloromethane.
8. The sample residue was rinsed with hexane and quantitatively transferred to a conical graduated centrifuge tube, placed in the N-EVAP at 40 degree centigrade under a stream of Nitrogen, evaporated to 1 ml volume in hexane and saved for GC analysis.

EQUIPMENT CONDITIONS:

GC CONDITIONS:

ORGANOPHOSPHATE ANALYSIS:

HP 5880 equipped with a Nitrogen/Phosphorus detector
 Column/s: HP X-Linked Capillary 0.2mm I.D. X 12m
 fused silica with a Helium (99.99%) carrier,
 pressure 15 psig.

Injector: Splitless; 225 degree C
 Detector: 300 degree C
 Temperature Program: 180 C initial temperature
 5 C/minute program rate
 220 C/12 minutes final temperature
 Make-up Gas: Argon-Methane (5%/95%)
 Flow 24ml/minute

PROMETONE/ATRAZINE/SIMAZINE ANALYSIS:

Varian 3700 equipped with a Thermionic Specific Detector
 Injector: Splitless, 210 C
 Detector: 250 C Bead: 630 Hydrogen: 25psig
 Isothermal: 165 C
 Column: 50% Phenylmethyl Megabore Capillary
 0.53mm I.D. X 12m fused silica column
 column flow 8psig

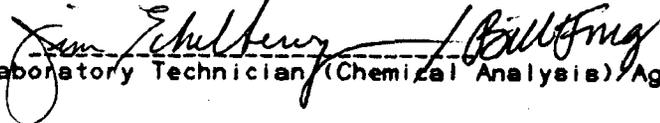
CALCULATIONS:

$$PPB = \frac{(\text{Peak Ht Sample})(\text{NG Std inj})(1\text{ml})(1000)}{(\text{peak Ht Std})(\text{UL inj})(\text{Sample Weight})}$$

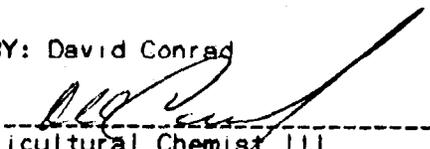
DISCUSSION:

Recoveries for DDVP, Dlayston, Phosdrin, Cygon, Diazinon, Ethyl Parathion, Methyl Parathion, Malathion, Dursban, Supracide, Ethion, Trithion, Imidan, Guthion, and Torak ranged from 85 to 100% at 0.2 ppb level. Recoveries for Bolero and Ordram were 100% each at 1.0 ppb level. MDL for the NPD was 0.1 ppb; for the TSD, 0.1 ppb.

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TITLE: Laboratory Technician (Chemical Analysis) Agricultural Chemist
I

APPROVED BY: David Conrad


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Original Date: 02/27/86
Supersedes: NEW
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Method #: *Tentative*

SIMAZINE AND DIURON IN WELL CORE SOILS

SCOPE:

This method is for the determination of Simazine And Diuron in well core soil samples.

PRINCIPLE:

A representative sample is extracted with Ethyl Acetate using an ultrasonic bath. The extract is filtered and a 50ml aliquot is evaporated to near dryness under N₂. This is brought to 3.0ml final volume with methanol. The extract is analyzed by Gas Chromatography using a nitrogen specific detector (Simazine) and by H.P.L.C. (UV Detection at 246nm) for Diuron.

REAGENTS AND EQUIPMENT:

- 1) Methanol (Pesticide residue grade)
- 2) Ethyl Acetate (Pesticide residue grade)
- 3) Sodium Sulfate, Anhydrous
- 4) Top loading balance
- 5) Ultrasonic Bath (ambient Temperature)
- 6) Filter Paper, Whatman #1 ; 9.0cm
- 7) 500ml amber wide mouth jars
- 8) 15ml conical glass stoppered test tubes
- 9) 1.5 ml Autosampler vials
- 10) Evaporator (Organomation Model #112)
- 11) H.P.L.C. with UV Detector
- 12) Gas Chromatograph with Thermionic Specific Detector

ANALYSIS:

- 1) The frozen well core samples were removed from -20 degree Centigrade storage and thawed at room temperature.
- 2) Each sample was mixed to obtain a relatively uniform mixture.

(DETERMINATION OF MOISTURE CONTENT)

- 3) Approximately 10 grams of soil was weighed into a preweighed aluminium weighing dish. The pan with soil was dried for 16 hours at 105 degrees Centigrade and then cooled in a dessicator before reweighing.

(EXTRACTION OF SOIL)

- 4) A 50 gram portion of the non-dried soil sample was placed into a 500 milliliter bottle and 100 milliliters of Ethyl Acetate was added.
- 5) After sealing with aluminium foil and screwcap the jar was placed into an ultrasonic bath for 1 hour.
- 6) The sample was removed from the ultrasonic bath and then allowed to settle for 30 minutes.
- 7) The extract was decanted through filter paper and sodium sulfate into 100 ml beaker.
- 8) The extract was evaporated to near dryness under nitrogen.

9) The residue was transferred to a volumetric test tube with methanol and brought to a final volume of 3mls.

EQUIPMENT CONDITIONS:

Varian 3700 Gas Chromatograph with Thermionic Specific Detector
10meter x 530um Hewlett Packard 50:50 Phenyl:methyl Megabore
He flow = 15mls/minute H2 = 20 PSI OVEN = 165 Centigrade
INJECTOR: 210 Centigrade DETECTOR: 220 Centigrade

2) Perkin Elmer Series 4 HPLC : ISS 100 Autosampler (30ul inj)
35:65 Acetonitrile:Water : Flow = 2.0 ml/min
15cm X 4.6mm 5um Ultrasphere ODS Column (Beckman Labs)
Kratos variable wavelength UV Detector
Absorbance = 230 nm (Simazine) and 246nm (Diuron)

CALCULATIONS:

% MOISTURE =
((weight undried sample+pan)-(weight dried sample+pan))
100X-----
((weight undried sample+pan)-(weight of pan))

PPB HERBICIDE =

(100%-Xmoisture) x (peak height sample) x (NG Std) x (final volume)

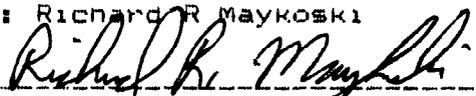
(peak height standard) x (UL sample injected) x (sample weight)

DISCUSSION:

RECOVERY AND SENSITIVITY

(Sensitivity may vary with sample interferences)

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APPENDIX III

Units, Statistical Terms, and Calculations

Units, Statistical Terms, and Calculations

Parts Per Billion (ppb) - Concentrations were expressed on a parts per billion (ppb) basis, that is, one part pesticide for every one billion parts water or soil. For water samples, concentrations expressed in ppb are equivalent to concentrations expressed as micrograms per liter (ug/l), that is, micrograms of pesticide in a liter of water. For soil samples, concentrations expressed in ppb are equivalent to concentrations expressed as nanograms per gram (ng/g) or micrograms per kilogram (ug/kg). Laboratory calculations are shown in Appendix II.

Spike Recoveries - Spike recoveries are expressed in percent of the amount added (spike level).

$$\% \text{ Recovery} = \frac{\text{Amount recovered}}{\text{Spike level}} \times 100\%$$

Standard Deviation (S.D.) - Standard deviation is a measure of the dispersion or spread of all values around the average. Under normal circumstances, the values within the range of (average - S.D.) to (average + S.D.) represent 68% of all the values. For example, the average concentration of five samples collected from a well was 10 ppb, with a standard deviation of 3 ppb. If additional samples from the same well were analyzed, 68% would have concentrations between 7 and 13.

$$\text{Standard Deviation} = \sqrt{\frac{\text{sum of (individual measurements - average)}^2}{\text{Number of measurements} - 1}}$$

Coefficient of Variation (C.V.) - The coefficient of variation is the standard deviation expressed in percent of the average.

$$\text{Coefficient of Variation} = \frac{\text{Standard deviation}}{\text{average}} \times 100\%$$