

AGES AND TYPES OF HERBICIDE RESIDUES IN WELL
WATERS OF FRESNO AND TULARE COUNTIES, CALIFORNIA

By

F. Spurlock



STATE OF CALIFORNIA
Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch
Environmental Hazards Assessment Program
Sacramento, California 95814-5624

EH 97-04

AGES AND TYPES OF HERBICIDE RESIDUES IN WELL WATERS OF
FRESNO AND TULARE COUNTIES, CALIFORNIA

F. Spurlock

Environmental Hazards Assessment Program
Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulation
Sacramento, California 95814

EH97-04
September 1997

ABSTRACT

A study was conducted in citrus- and grape-growing areas of Fresno and Tulare Counties to (1) estimate the time between application of preemergent herbicides and their subsequent detection in well waters, (2) determine whether herbicide concentrations in 30 wells had changed between 1994 and 1996, and (3) evaluate the concentrations of two *N*-dealkylated simazine degradates [deethyl simazine or DES, and diaminochlorotriazine or DACT] in simazine positive wells. No change in herbicide concentrations (simazine, DES, diuron, and bromacil) of 30 wells was evident between 1994 and 1996 (signed rank $p=0.22$). Simazine herbicide accounted for only 10-20% of the triazine residues determined in the well water samples; concentrations of the triazine degradates DES and DACT were greater than simazine in nearly all wells. More than 2/3 of the well water samples contained detectable levels of diuron and/or bromacil, while 1/3 of the wells contained all five residues (simazine, DES, DACT, diuron, and bromacil). Chlorofluorocarbon (CFC) age-dating combined with one-dimensional vadose zone transport modeling yielded an estimate for the median time between herbicide application and subsequent detection in 18 wells of 7-9 years. These results indicate that any changes in ground water quality arising from mandatory adoption of regulatory herbicide controls or wide-spread voluntary adoption of agricultural management practices to protect ground water will probably not be discernible for at least a decade.

ACKNOWLEDGEMENTS

This study was conducted in cooperation with the United States Geological Survey (USGS). I thank the USGS scientists who participated in discussions on CFC age-dating and ground water hydrology in Fresno and Tulare Counties, including Neil Dubrovsky, Karen Burrows, and Ed Busenberg, and those who assisted with the chlorofluorocarbon sampling, Dave Kremer and Ron Fay. A special thank you to EMPM staff who conducted the first sampling for herbicides in July 1996: Pam Wofford, Clarice Ando, Cindy Garcia, and Dee Dee Jones.

DISCLAIMER

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

TABLE OF CONTENTS

Abstract	ii
Acknowledgements	iii
Table of Contents	iv
List of Tables	v
List of Figures	v
Background	1
Study Objectives.....	5
Materials and Methods	6
Study Design	6
Domestic Well Selection	6
Herbicide Sampling and Analysis	6
CFC Sampling and Analysis	6
Estimating Recharge Age from Aqueous CFC Concentrations	10
Results.....	16
Sampling #1 – herbicides	16
degradate concentrations	
soil type	
comparison of 1994 and 1996 concentrations	
Sampling #2 – CFCs and herbicides	18
monitoring wells	
domestic wells	
Conclusions	23
Literature Cited	24

TABLE OF CONTENTS (CONTINUED)

LIST OF TABLES

Table 1. Well site descriptions	8
Table 2. Ongoing QC herbicide spike recoveries	9
Table 3. Summary of herbicide analytical results.	17

LIST OF FIGURES

Figure 1. Schematic of herbicide transport to well screen.....	2
Figure 2. Triazine degradates.....	4
Figure 3. Study area map.....	7
Figure 4. CFC tracers and their uses.....	11
Figure 5. CFC tropospheric growth curves	12
Figure 6. Schematic of CFC movement in terrestrial/ground water system	14
Figure 7. Summary of triazine degradate data.	17
Figure 8. Comparison of 1996 vs 1994 herbicide concentrations.....	19
Figure 9. Recharge age at various depths below water table	20
Figure 10. Estimated recharge age of domestic wells..	22

APPENDICES

- Appendix 1. North American continental CFC mixing ratios, 1930 – present
- Appendix 2. Herbicide analytical data, 1994 and 1996
- Appendix 3. Aqueous CFC data and calculated recharge dates.

BACKGROUND

Detections of the preemergent herbicides simazine, diuron, and bromacil have been found in several hundred Fresno and Tulare County wells. These herbicides are primarily associated with grape and citrus production. The Environmental Hazards Assessment Program (EHAP) of the Department of Pesticide Regulation is conducting a voluntary program to mitigate ground water contamination in citrus- and grape-producing areas of Fresno and Tulare counties. The objectives of the grape/citrus project are to identify and encourage the adoption of modified farm management practices that reduce or eliminate herbicide movement to ground water. In discussions with growers, commodity groups, and registrants, a number of questions frequently arise. Two of these are:

1. Do current farming practices contribute to ground water contamination, or are the detections a result of historical applications?
2. Are herbicide concentrations in wells increasing or decreasing?

The first question requires knowledge of the time interval between application and detection in water wells. Movement of a herbicide from the site of application to detection at the well screen can be visualized as occurring in two steps (fig. 1): (1) movement from the point of application to the water table, and (2) movement from the water table to the well screen. The travel time for movement from the ground surface to the water table under leaching conditions can be estimated from one-dimensional vadose zone transport modeling using soil profile, irrigation, and crop water requirement data. Such an estimated leaching travel time would be conservative (i.e., an overestimate) in areas where movement to ground water occurs by a direct transport mechanism such as surface water runoff to dry wells. The transport time for step (2) above is equal to the "effective recharge age" of a sampled water parcel assuming the transport velocity of the herbicide and the water are essentially equal. Scientists with the United States Geological Survey (USGS) have developed a method for estimating the

effective recharge age of shallow ground waters by using chlorofluorocarbon (CFCs) tracers. This method is used to estimate the length of time between entry of a water parcel to the water table and subsequent sampling from the depth of a well's perforated interval (fig. 1). A brief description of CFC dating is given in the *Materials and Methods* section; a detailed analysis of the limitations, assumptions, and applications of CFC age-dating are available in a number of recent studies and reviews (1-10).

The second question of whether there is a temporal ground water concentration trend requires repeat sampling data for positive wells. Such data for currently registered pesticides are sparse; the focus of EHAP's well sampling program has been to identify new areas of contamination and new ground water contaminants.

A third important topic is the extent to which herbicide degradates contribute to total herbicide residue load in positive wells. This question is especially important for s-chlorotriazine herbicides such as simazine. The most common simazine degradates (fig. 2) found in ground water are the stepwise N-dealkylated products deethyl simazine (DES) and diaminochlorotriazine (DACT). DES and DACT are relatively persistent, their toxicological properties have not been fully characterized, and, similar to simazine, they both possess the triazine ring. Their structural similarity to simazine suggests a common toxicological mode of action for simazine, DES, and DACT (11). Based on these characteristics, it has been recommended that health advisory levels set for triazine parents be applied to the total concentration of parent plus degradates [Wisconsin Ground-Water Act 410 (1983), Rule under the Law, Enforcement Standard, Chapter NR, Wisconsin ADM CODE (1991)]. Simazine and both degradates, DES and DACT, have been determined in only one previous California study of 21 wells (12). In that study 9 wells, or 43% of those sampled, exceeded the Maximum Contaminant Level (MCL) of 4 parts per billion (ppb) for simazine as applied to the sum of intact triazine ring residues: simazine, DES, and DACT. Further data are needed to characterize the presence of these degradates in Fresno and Tulare County wells.

OBJECTIVES

The objectives of this study were to

1. estimate the "effective recharge age" of triazine-containing well water samples, that is, the travel time between the water table and the well screen,
2. estimate the time between herbicide application and subsequent detection in ground water using the effective recharge age and the modeled travel time from the surface,
3. measure simazine, DES, diuron, and bromacil concentrations in positive wells that had been previously been sampled in 1994 to evaluate any possible temporal trends in concentration, and
4. determine concentration levels and occurrence of *N*-dealkylated simazine degradates in simazine positive wells.

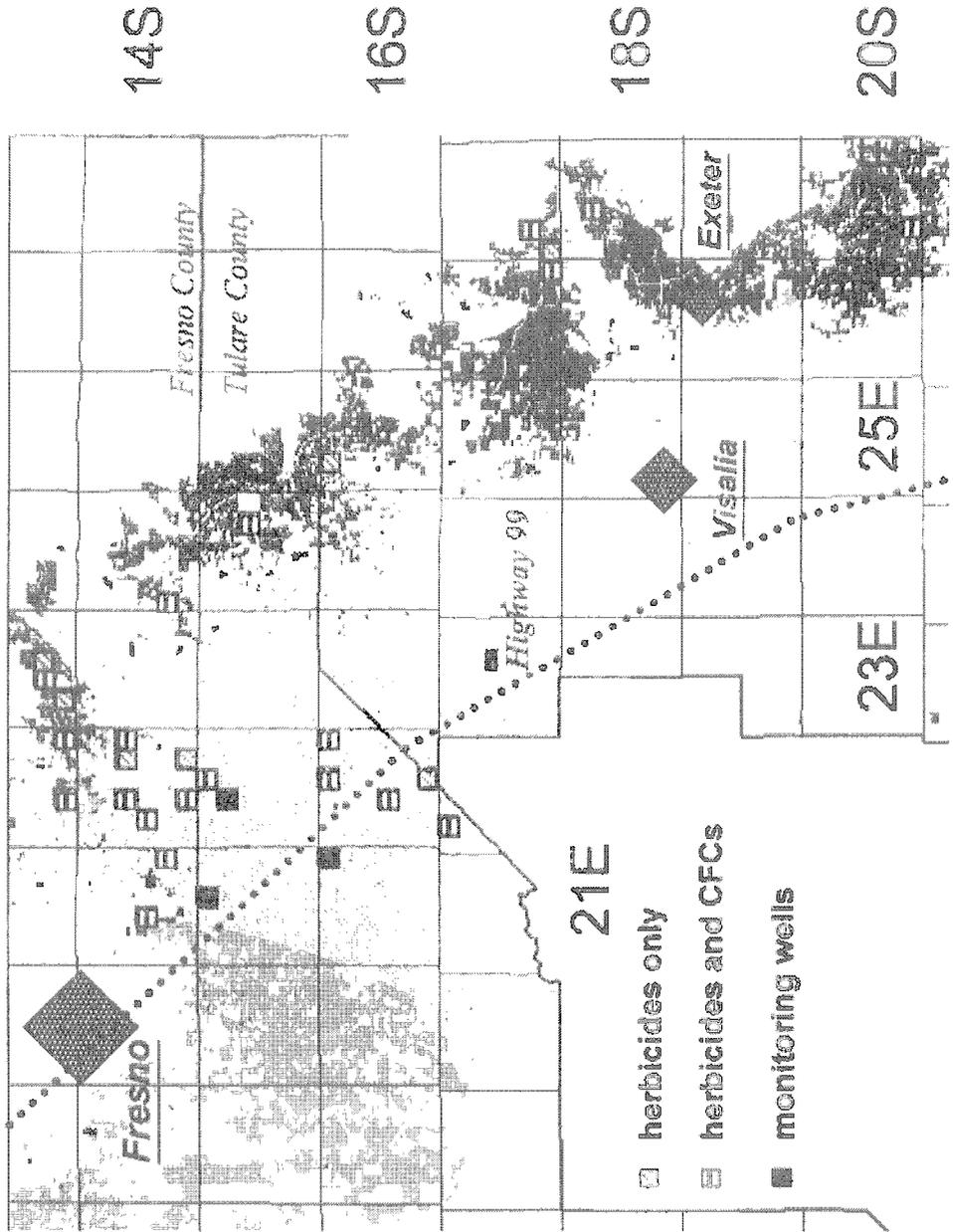


Figure 3. Map of two county study area. Land use colors: dark grey = citrus, light grey = vineyard. The remainder (uncolored) includes mostly deciduous fruits, nuts, alfalfa. Boxes show sections where sampled wells are located. Two samplings: July 1996 for herbicides only - all 30 domestic wells, August sampling a subset of 20 of prior 30 wells, plus 9 USGS wells (3 nested monitoring well pairs plus 3 collocated domestics) sampled for both herbicides and CFCs.

Table 2. Study 146. Continuing QC (%recoveries) for the five triazine extraction sets. All spike levels = 0.20 ppb, reporting limit = 0.05ppb all analytes.

ANALYTE	set #1	set #2	set #3	set #4	set #5	mean	stnd dev	%CV
simazine	96	99	106	101	109	102	5	5
DES ^A	101	107	108	113	115	109	5	5
DACT ^B	65	81	83	92	83	81	10	12
diuron	98	108	101	104	95	101	5	5
bromacil	85	100	87	78	90	88	8	9

^A deethyl simazine

^B diminochlorotriazine

CFC-12: dichlorodifluoromethane -- CCl_2F_2

USES: *small unit and mobil refrigerant*

CFC-11: trichlorofluoromethane -- CCl_3F

USES: *commercial refrigerant, chillers,
foam blowing*

CFC-113: trichlorotrifluoroethane -- $\text{C}_2\text{Cl}_3\text{F}_3$

USES: *solvent, cleaner, foam blowing*

STABILITY: CFC-12 > CFC-11 > CFC-113

SORPTION: CFC-113 > CFC-11 > CFC-12

Figure 4. Chlorofluorocarbon tracers and principal uses.

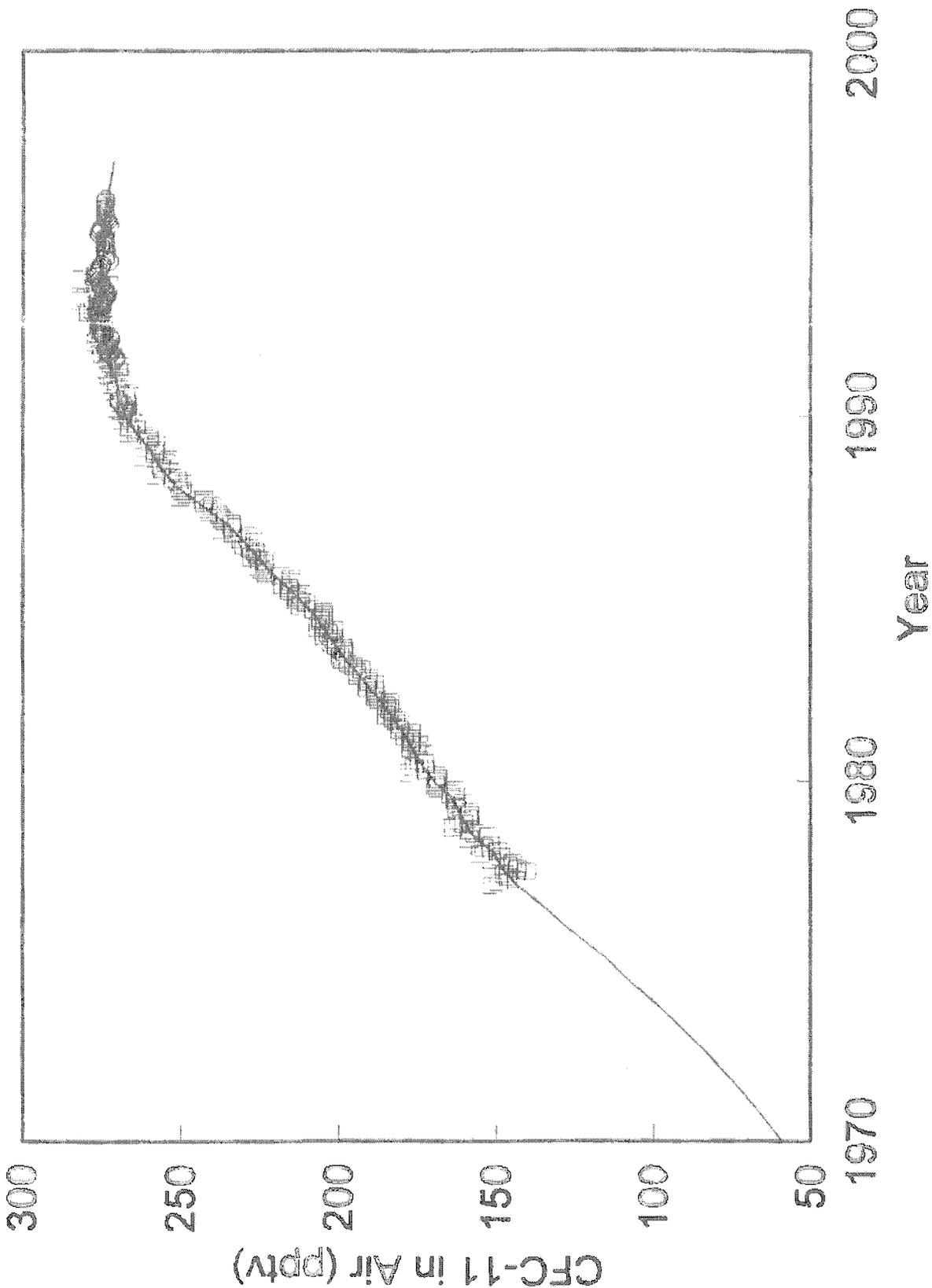


Figure 5b. North American continental tropospheric CFC-11 growth curve based on data collected by National Oceanic and Atmospheric Administration at Niwot Ridge, CO, and United States Geological Survey Data. Data courtesy Ed Busenberg, USGS, Reston, VA.

that water becomes isolated from the vadose atmosphere, i.e., when that water enters the saturated zone (aquifer). The CFC air/water equilibrium is described by the respective Henry's law constant for each CFC. These constants have been accurately determined as a function of temperature (14, 15). Thus, provided the recharge temperature is known, aqueous CFC concentrations in a well water sample can be used to determine vadose atmosphere CFC concentrations at the time a water parcel enters an aquifer at the capillary fringe of the saturated zone, and the year that the water entered the aquifer can subsequently be determined from the atmospheric growth curves (fig. 5).

Many ground water CFC age-dating studies have used dissolved gas concentrations (nitrogen and argon) to estimate ground water recharge temperature (8, 16). While the procedure has been useful for non-agricultural areas, it is also known that the use of dissolved gases to estimate recharge temperature is problematic in areas where recharge is dominated by irrigation water applications, and where nitrogen fertilizer use is significant (E. Busenberg, U.S. Geological Survey, personal communication). As an alternate approach, seasonal soil temperature variations decrease with depth, approaching a constant value near the mean annual air temperature at depths below a few meters. In this study, a mean recharge temperature of 17°C – that is, the mean temperature at the base of the unsaturated zone (~ 10m below ground surface) - was assigned based on 10 year mean air temperature data from Fresno, Orange Cove, Lindsay, and Visalia. The mean annual air temperature is expected to closely approximate the mean recharge temperature at depths greater than a few meters in the absence of significant geologic heating (8, 16).

Table 3. Summary of herbicide analytical results for the July 1996 (first) sampling of 30 domestic wells.

	simazine ppb	DES ^A ppb	DACT ^A ppb	sum triazine ppb	diuron ppb	bromasil ppb
% positive	97	100	87	100	63	47
median conc.	0.16	0.60	0.19	0.91	0.13	-- ^c
mean	0.17	0.65	0.24	1.1	0.30	0.32
standard dev.	0.08	0.62	0.20	0.79	0.40	0.66
maximum	0.41	3.0	0.85	3.8	1.5	3.2
minimum	ND ^B	0.07	ND ^B	0.15	ND ^B	ND ^B

^A DES = deethyl simazine, DACT = diaminochlorotriazine

^B ND = nondetect; median and mean concentrations calculated assuming ND = 0.

^C More than 50% of bromacil analyses were nondetects

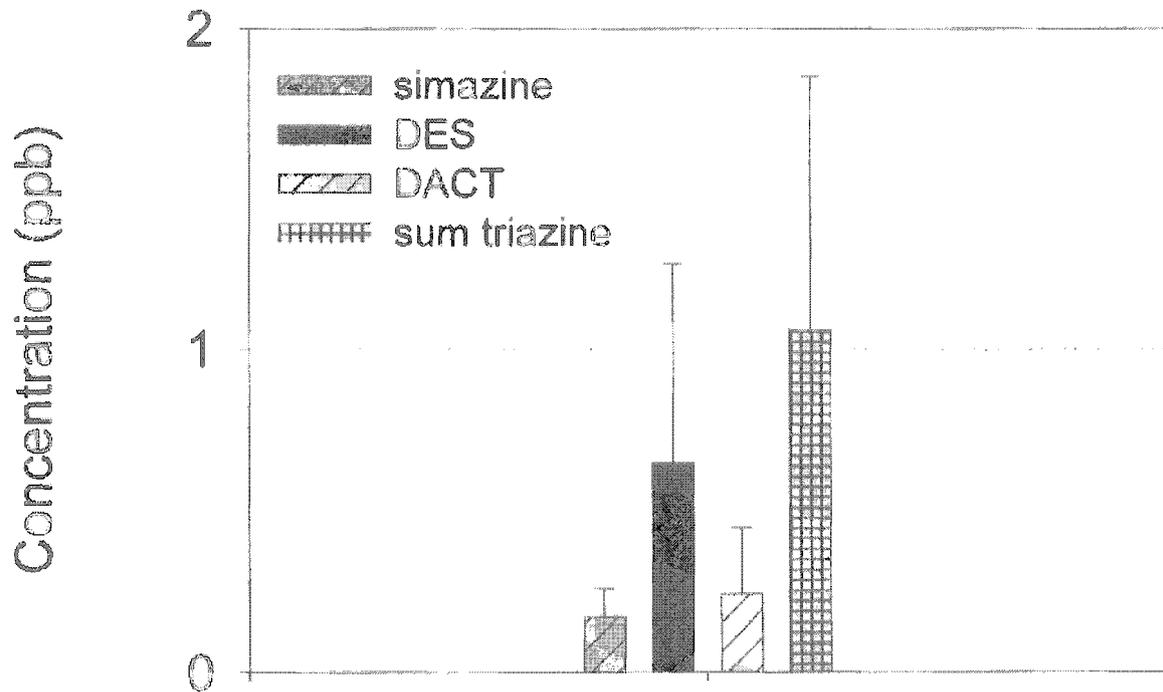


Figure 7. Mean and standard deviation of triazine concentrations in 30 domestic wells sampled in July 1996

1996 vs 1994 herbicide concentrations

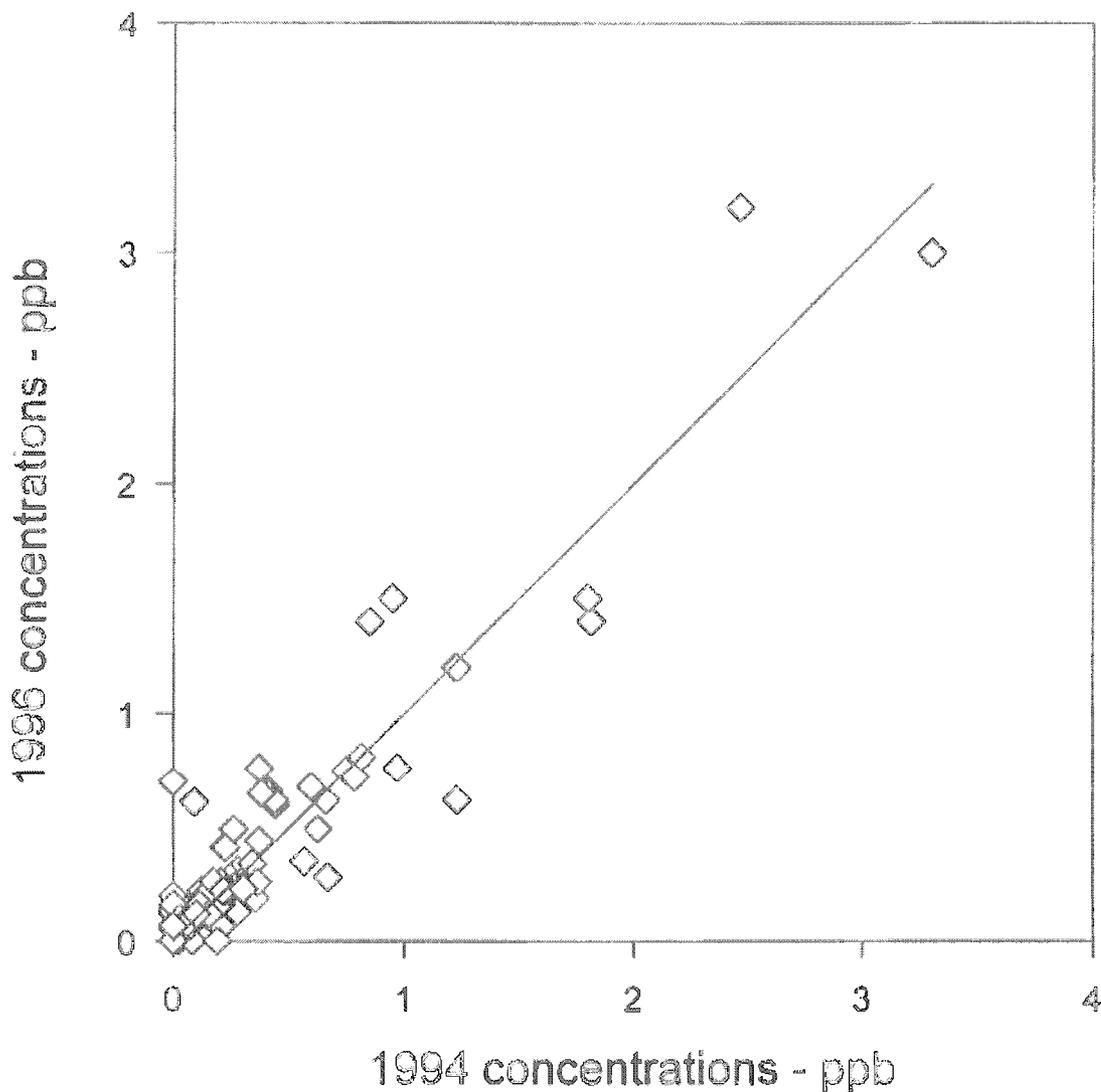


Figure 8. Comparison of all analyses conducted in both 1994 and July 1996. Line shows where all data would fall if 1996 concentrations were *exactly* equal to 1994 concentrations. Includes analysis for simazine, DES, bromacil and diuron. A signed rank test indicates that the difference between 1994 and 1996 concentrations is not different than zero ($p= 0.22$).

Domestic wells. Five of the 23 domestic wells sampled yielded calculated CFC concentrations that exceeded the continental mixing ratio (appendix 3). The estimated recharge ages of the remaining 17 domestic wells ranged from 1 to 31 years, with a median age of 6 years (fig. 10). Elevated levels of CFCs in the 5 wells may have been a result of contamination. Sewage is known to often contain very high levels of CFCs (e.g., 2); local atmospheric CFC excesses of the magnitude required to explain most of the elevated CFC levels in the wells are unlikely. It is evident that CFC-113 contamination is present in many of the wells, limiting its usefulness as a ground water dating tracer. This result is consistent with its widespread use as a solvent, and its high miscibility in oils and greases (15). As noted previously, few if any ground water studies have reported using CFC-113; its application in this study was experimental. CFC-12 and CFC-11 appear to be superior age-dating tracers.

The effective recharge ages in figure 10 represent the time between arrival at the water table of the water sampled and the actual sampling event (August, 1996). To estimate the time between application and detection of the herbicides, the travel time from the ground surface to the water table must also be accounted for. One-dimensional vadose zone modeling of pesticide leaching to ground water yielded an estimate for the surface to water table travel time of 1–3 years. These data indicate that the detections in the 17 domestic wells are associated with herbicide applications ranging from 3-33 years ago, with more than half of the detections associated with applications made in the last 8 years.

Finally, there was no apparent relationship between estimated recharge ages and herbicide concentrations, soil type (pan vs coarse), or fraction of triazine degradates ($= \frac{[DES + DACT]}{[DES + DACT + simazine]}$).

CONCLUSIONS

1. In Fresno and Tulare County wells that are positive for simazine, simazine residues constitute only a fraction of the total triazine residues present, in this study around 10-20%. While no well water samples in this study contained "total" triazine residue concentrations (simazine + DES + DACT) that exceeded the simazine MCL of 4 ppb, several wells approached this level; the maximum total triazine residues observed in this study was 3.8 ppb, or 95% of the simazine MCL.
2. More than 2/3 of the wells also contained detectable levels of diuron and/or bromacil, while 1/3 of the wells contained detectable levels of all five residues bromacil, diuron, simazine, DES, and DACT (reporting limit of 0.05 ppb).
3. There was no detectable change in herbicide concentrations in the 30 domestic wells over the 2 year time period between 1994 and 1996.
4. Estimated times between herbicide application and subsequent detection in well water ranged from 2 -- 33 years, with more than half of the detections associated with applications made within the last 7-9 years. The data indicate that any changes in ground water quality arising from mandatory adoption of regulatory controls or wide-spread voluntary adoption of agricultural management practices will probably not be discernible for at least a decade.

11. Barret, M. 1996. Impact of triazine degradates in groundwater in relation to relevant regulatory endpoints. Presented at 211th American Chemical Society National Meeting, Agrochemical Division, Special Symposium on "The Triazine Herbicides". March 1996. New Orleans, LA.
12. Ciba-Giegy Corporation. 1996. Unpublished well monitoring data from Fresno and Tulare Counties, California.
13. Sava, R. 1994. Guide to Sampling Air, Water, Soil, and Vegetation for Chemical Analysis.
14. Warner, M.J. and R.F. Weiss. 1985. Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep Sea Research* 32:1485-1497.
15. Bu, X., and M.J. Warner. 1995. Solubility of chlorofluorocarbon 113 in water and seawater. *Deep Sea Research* 42:1151-1161.
16. Heaton, T.H.E. and J.C. Vogel. 1981. "Excess air" in groundwater. *Journal of Hydrology*. 50:201-216.
17. Troiano, J., B.R. Johnson, S. Powell, and S. Schoenig. 1994. Use of cluster and principal component analysis to profile areas in California where ground water has been contaminated by pesticides. *Environmental Monitoring and Assessment* 32:269-288.

Appendix 1. CFC-11, CFC-12, and CFC-113 North American Continental mixing ratios (parts per trillion v/v) 1930 – present. Data courtesy USGS.

Busenberg and Plummer, 1998

CFC's - 1/13/97 - Continental U.S. mixing ratio

CFC-113 data completely revised.

CFC-11 and CFC-12 revised after 1993.

YEAR	CFC-11	CFC-12	CFC-113
1930.0	0	0	0
1930.5	0	0	0
1931.0	0	0.0027	0
1931.5	0	0.0055	0
1932.0	0	0.0082	0
1932.5	0	0.0109	0
1933.0	0	0.0136	0
1933.5	0	0.0163	0
1934.0	0	0.0217	0
1934.5	0	0.0271	0
1935.0	0	0.0352	0
1935.5	0	0.0433	0
1936.0	0	0.0568	0
1936.5	0	0.0703	0
1937.0	0	0.0919	0
1937.5	0	0.1135	0
1938.0	0.0024	0.1459	0
1938.5	0.0048	0.1783	0
1939.0	0.0072	0.2241	0
1939.5	0.0095	0.2699	0
1940.0	0.0118	0.332	0
1940.5	0.0141	0.394	0
1941.0	0.0164	0.474	0
1941.5	0.0186	0.554	0
1942.0	0.0208	0.653	0
1942.5	0.0231	0.752	0
1943.0	0.0276	0.872	0
1943.5	0.0322	0.992	0.007
1944.0	0.0367	1.155	0.013
1944.5	0.0412	1.318	0.028
1945.0	0.0479	1.531	0.043
1945.5	0.0547	1.745	0.059
1946.0	0.0686	2.118	0.075
1946.5	0.0824	2.491	0.093
1947.0	0.1128	3.063	0.110
1947.5	0.1432	3.636	0.131
1948.0	0.1970	4.299	0.152
1948.5	0.2507	4.963	0.174
1949.0	0.3394	5.670	0.196
1949.5	0.4281	6.377	0.222
1950.0	0.5559	7.157	0.249
1950.5	0.6836	7.937	0.279
1951.0	0.8592	8.790	0.308
1951.5	1.035	9.643	0.343
1952.0	1.288	10.52	0.377
1952.5	1.542	11.41	0.415
1953.0	1.807	12.39	0.454
1953.5	2.231	13.38	0.497
1954.0	2.655	14.50	0.540
1954.5	3.079	15.62	0.591

	CFC-11	CFC-12	CFC-113
1980.0	169.67	306.19	23.00
1980.5	173.92	312.30	24.59
1981.0	177.13	317.53	26.19
1981.5	180.89	323.41	27.84
1982.0	185.03	338.06	29.49
1982.5	189.56	347.03	31.32
1983.0	194.54	355.76	33.14
1983.5	199.29	366.23	35.43
1984.0	203.24	372.48	37.71
1984.5	207.35	380.00	40.42
1985.0	212.59	389.00	43.12
1985.5	218.66	396.75	46.00
1986.0	224.42	407.93	48.89
1986.5	229.38	416.63	52.06
1987.0	234.97	426.59	55.23
1987.5	242.60	442.06	58.79
1988.0	250.25	452.06	62.34
1988.5	255.60	461.52	66.05
1989.0	259.10	468.98	69.77
1989.5	263.67	476.22	72.82
1990.0	267.64	484.97	75.87
1990.5	269.04	491.52	78.03
1991.0	270.59	495.59	80.19
1991.5	272.78	501.13	81.75
1992.0	273.50	510.52	83.10
1992.5	274.80	512.50	84.50
1993.0	275.10	517.00	85.00
1993.5	275.15	521.30	85.30
1994.0	275.10	526.30	85.40
1994.5	274.10	531.10	85.30
1995.0	274.08	533.50	85.20
1995.5	273.90	535.30	84.80
1996.0	273.00	537.30	84.50
1996.5	272.00	541.00	84.20
1997.0	271.00	543.00	83.70

**Appendix 2. Herbicide data for 30 domestic wells,
1994 sampling and 1996 sampling,
simazine, DES, DACT, diuron, bromacil**

Herbicide Concentrations in 1994 and 1996 - parts per billion (ppb)

WELL	MTRS	simazine		DFS		DACT	sum		percent simazine (sim/sum)
		1994	1996	1994	1996		1994	1996	
1	M13S22E33	0.09	0.09	0.30	0.28	N/A	0.34	0.71	13
2	M13S22E33	0.03	0.10	ND	0.15	N/A	0.14	0.40	25
3	M13S22E33	0.15	0.16	0.28	0.31	N/A	0.25	0.72	22
4	M13S22E35	0.06	0.11	0.41	0.65	N/A	0.27	1.03	11
5	M13S23E27	0.18	0.17	N/A	0.60	N/A	0.58	1.35	13
6	M13S23E28	0.16	0.14	N/A	0.68	N/A	0.60	1.42	10
7	M13S23E32	0.22	0.23	0.66	0.62	N/A	0.37	1.22	19
8	M14S21E21	0.30	0.26	N/A	1.20	N/A	0.16	1.62	15
9	M14S21E25	0.09	0.12	N/A	0.41	N/A	0.16	0.69	17
10	M14S22E13	0.06	0.08	N/A	0.07	N/A	ND	0.15	51
11	M14S22E14	0.21	0.16	N/A	0.43	N/A	0.20	0.79	20
12	M14S22E14	0.17	0.15	N/A	0.60	N/A	0.13	0.88	17
13	M14S22E16	ND	0.07	0.25	0.28	N/A	0.20	0.55	12
14	M14S22E20	0.27	0.24	0.15	0.11	N/A	ND	0.35	69
15	M14S22E33	0.19	0.15	0.05	0.08	N/A	ND	0.23	65
16	M14S22E35	0.21	0.26	0.44	0.62	N/A	0.10	0.98	27
17	M14S24E30	0.13	0.19	0.38	0.65	N/A	0.09	0.93	20
18	M15S22E03	0.23	0.22	0.82	0.81	N/A	0.85	1.88	12
19	M15S24E14	0.11	0.11	1.23	1.20	N/A	0.34	1.65	7
20	M16S22E01	0.36	0.26	0.79	0.72	N/A	0.06	1.04	25
21	M16S22E03	0.12	0.16	0.30	0.23	N/A	0.18	0.57	28
22	M16S22E21	ND	0.07	0.34	0.34	N/A	0.14	0.55	12
23	M16S22E34	0.16	0.12	0.08	0.12	N/A	0.10	0.34	36
24	M16S25E05	0.18	0.26	1.80	1.50	N/A	0.27	2.03	13
25	M17S22E05	0.10	0.12	0.06	0.10	N/A	0.08	0.30	40
26	M17S26E36	0.23	0.41	3.30	3.00	N/A	0.43	3.84	11
27	M17S27E29	0.19	ND	0.60	0.68	N/A	0.26	0.94	0
28	M17S27E31	0.22	0.22	ND	0.07	N/A	ND	0.29	76
29	M18S27E09	0.30	0.23	N/A	1.60	N/A	0.43	2.26	10
30	M20S27E32	0.67	0.26	N/A	1.30	N/A	0.51	2.09	13

N/D = not detected reporting limit = 0.05 ppb

N/A = analysis not performed

Appendix 3. aqueous CFC analytical data, calculated CFC vadose zone
atmosphere concentrations at time of water entry into water table,
and estimated recharge age

CFC DATING RESULTS 7/27/97

ASSIGNED RECHARGE TEMP: 17

Township/ Range/ Section	well type	MEASURED			CALCULATED			CFC MODEL				est. recharge date	est. travel time (y)	
		aqueous concentrations		atmospheric mixing ratio - pptv	cfc-113		RECHARGE DATES		cfc-113	cfc-113	cfc-113			cfc-113
		pg kg-1	cfc-12		cfc-11	cfc-12	cfc-11	cfc-12						
13S22E33	domestic	519	402	76	260	850	93	1988	XXXX	1994	1991	5		
13S22E36	domestic	539	715	59	270	513	73	1991	XXXXXX	1990	1991	6		
13S23E28	domestic	499	263	90	251	567	12	1988	XXXXXX	XXXXXX	1992	4		
14S21E21	domestic	504	451	48	253	874	60	1988	XXXXXX	1988	1988	8		
14S21E25	domestic	614	547	18	209	1157	23	XXXXXX	XXXXXX	1979	XXXXXX	XXXXXX		
14S22E13	domestic	659	330	101	331	697	124	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX		
14S22E16	domestic	578	264	126	290	558	56	1994	XXXXXX	XXXXXX	1995	1		
14S22E20	domestic	819	25138	108	11	5348	13	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX		
14S22E33	domestic	234	199	38	117	420	48	1975	1987	1986	1983	13		
14S24E30	domestic	192	155	23	96	328	28	1973	1981	1982	1979	17		
15S22E03	domestic	509	241	76	255	510	94	1989	1992	1994	1992	4		
15S24E14	domestic	295	214	28	148	453	35	1978	1986	1984	1983	13		
16S22E01	domestic	471	248	46	236	524	57	1987	1994	1987	1989	7		
16S22E03	domestic	403	242	36	202	511	44	1984	1992	1985	1987	9		
16S22E21	domestic	533	273	58	268	588	72	1990	1995	1990	1992	4		
17S26E36	domestic	464	282	129	233	596	60	1987	1996	XXXXXX	1992	5		
17S27E29	domestic	472	310	62377	237	656	72	1987	XXXXXX	XXXXXX	XXXXXX	XXXXXX		
18S27E09	domestic	426	217	47	214	460	58	1985	1988	1987	1987	9		
20S27E32	domestic	381	206	37	191	439	46	1983	1967	1986	1985	11		
15S21E03	domestic	477	258	78	240	545	96	1987	1996	XXXXXX	1992	5		
15S22E09	domestic	590	231	41	296	407	51	1994	1990	1986	1990	6		
16S21E01	domestic	29	868	4	15	896	5	1962	XXXXXX	1969	1966	31		
15S21E03	monitoring	7	12	154	4	25	190	1955	1958	XXXXXX	1957	40		
15S21E03	monitoring	111	107	131	56	226	62	1970	1975	XXXXXX	1973	24		
15S22E09	monitoring	511	196	185	256	414	25	1989	1986	XXXXXX	1988	9		
15S22E09	monitoring	755	322	178	339	680	240	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX		
16S21E01	monitoring	42	71	156	21	151	53	1964	1972	XXXX	1968	28		
16S21E01	monitoring	482	272	186	242	575	236	1988	1996	XXXXXX	1992	4		
MAX. CONTINENTAL U.S. MIXING RATIO														
					275	543	85.4	XXXXXX	= not dated; calculated atmospheric CFC					
					1993	1997	1994		mixing ratio exceeds continental mixing					
					303	597	94		ratio by more than 10%					