

**Chlorofluorocarbon Dating of Herbicide-Containing Well Waters  
in Fresno and Tulare Counties, California**

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### ABSTRACT

Simazine, diuron, and bromacil are the most frequently detected currently registered pesticides in California groundwater. These herbicides have been used for several decades in Fresno and Tulare counties, California; however, previous data are inadequate to determine whether the detections are a result of recent or historical applications (i.e., within the last decade, or 20–30 yr ago). Chlorofluorocarbon (CFC) groundwater age-dating was used in conjunction with one-dimensional transport modeling to address this question. The estimated times between herbicide application and subsequent detection in groundwater samples from 18 domestic wells ranged from 3 to 33 yr; the aggregate data indicate that more than half of the detections are associated with applications in the last decade. The data also suggest that changes in groundwater quality arising from modified management practices will probably not be discernible for at least a decade. A secondary objective of this study was to evaluate the contribution of simazine degradates deethylsimazine (DES; 2-amino-4-chloro-6-ethylamino-*s*-triazine) and diaminochlorotriazine (DACT; 2,4-diamino-6-chloro-*s*-triazine) to total triazine concentrations (defined here as simazine + DES + DACT) in 30 domestic wells. The *N*-dealkylated *s*-chlorotriazine degradates DES and DACT substantially contribute to total triazine concentrations in Fresno and Tulare County groundwater, composing 24 to 100% of the total triazines, with a median of 82%. If *s*-chlorotriazines display a common mode of toxicological action, the prevalence of triazine degradates in water samples found in this and other studies indicate that drinking water standards based on total *s*-chlorotriazine concentrations may be most appropriate.

CALIFORNIA is the most productive agricultural state in the nation, with 1994 farm receipts exceeding \$20 billion. Although a portion of these revenues were from meat, egg, and milk production, more than 60% came from production of 53 million Mg of field crops, fruits, nuts, and vegetables on 3.2 million ha (California Agricultural Statistics Service, 1995a). In achieving this

level of productivity, California growers applied 82 million kg of pesticide active ingredient (California Department of Pesticide Regulation, 1996).

During the 1970s, the potential for pesticides to move to groundwater in California was underestimated. In 1979, the soil fumigant dibromochloropropane (DBCP) was first detected in groundwater in Lathrop, CA (Peoples et al., 1980). Subsequent studies showed the relatively widespread presence of DBCP in San Joaquin Valley groundwater, and groundwater sampling studies are now conducted by several agencies and organizations (Bartkowiak et al., 1997).

In addition to conducting groundwater studies, the Environmental Hazards Assessment Program (EHAP) of the California Department of Pesticide Regulation (CDPR) maintains a statewide Well Inventory Database (WIDB; Bartkowiak et al., 1997). The WIDB is a centralized database of California groundwater monitoring results from private firms and local, state, and federal agencies. Confirmed detections of pesticide active ingredients or degradates have been reported in 1,586 California wells since 1986 (Fig. 1). For the purposes of the WIDB, a confirmed detection is defined as the detection of a compound in two discrete samples from a well.

Preemergent herbicides are usually soil-applied, tend to be relatively water-soluble, display low to moderate soil sorption, and possess long soil half-lives. Owing to these characteristics, and their widespread use in a variety of California crop and noncrop sites, preemergent herbicides are the most commonly detected currently registered pesticides in California groundwater. Sima-

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**Abbreviations:** CDPR, California Department of Pesticide Regulation; CFC, chlorofluorocarbon; DACT, diaminochlorotriazine; DBCP, dibromochloropropane; DES, deethylsimazine; EHAP, Environmental Hazards Assessment Program; ET, evapotranspiration; LC, liquid chromatograph; LEACHM, Leaching Estimation and Chemistry Model; LOQ, limit of quantitation; MCL, maximum contaminant level; MDL, method detection limit; NAWQA, National Water-Quality Assessment Program; SCX, strong cation exchange; USEPA, United States Environmental Protection Agency; USGS, United States Geological Survey; WIDB, Well Inventory Database.

zine, diuron, bromacil, and triazine degradates are the most frequently detected herbicide residues in California groundwater (561, 360, 195, and 147 confirmed detections, respectively; Maes et al., 1993).

The largest number of these herbicide detections in groundwater are in Fresno and Tulare counties in the southern San Joaquin Valley; 1 or more of the 3 herbicides (or degradates) have been detected in 509 Fresno and Tulare County wells. The 1994 crop production in these counties included 45 000 ha of citrus and 100 000 ha of fresh market, raisin, and wine grapes (California Agricultural Statistics Service, 1995b). Simazine, diuron, and bromacil are the most common preemergent herbicides used in California citrus production, whereas simazine and diuron are the most common preemergent herbicides applied to grapes. Bromacil is not registered in California for use on grapes. In 1994, grape and citrus applications accounted for 65% of the 300 000 kg active ingredient of simazine, diuron, and bromacil applied in Fresno and Tulare counties (California Department of Pesticide Regulation, 1996).

Several recent studies in the midwestern United States have reported that triazine degradates are frequently present in the surface and groundwaters in areas where atrazine is used (Thurman et al., 1992; Moody and Goolsby, 1993; Kolpin et al., 1995; Kolpin et al., 1996). While little atrazine has been used in Fresno or Tulare counties for at least the last 10 yr, simazine shares two common *N*-dealkylated degradates with atrazine. The two degradates are 2-amino-4-chloro-6-ethylamino-*s*-triazine (DES, also known as deisopropyl atrazine), and the di-dealkylated degradate 2,4-diamino-6-chloro-*s*-triazine (DACT) (Fig. 2). The *N*-dealkylated *s*-chlorotriazine degradates are similar in structure to the parent herbicides, and limited data suggests they may share a common mode of toxicological action (e.g., Babic-Gojmerac et al., 1989). Consequently, the U.S. Environmental Protection Agency (USEPA) is assuming that the total triazine toxic residue of concern in their assessment of dietary risk for the triazine Special Review (U.S. Environmental Protection Agency, 1994) is the parent triazine plus all metabolites with a triazine ring. In addition, although there are no current National Primary or Secondary Drinking Water Standards for total triazines, total triazines are listed on USEPA's Drinking Water Contaminant Candidate list (U.S. Environmental Protection Agency, 1998a). The state of Wisconsin has applied atrazine health advisory levels to the total concentration of atrazine plus select degradates [Wisconsin Ground-Water Act 410 (1983), Rule under the Law, Enforcement Standard, Chapter NR, Wisconsin ADM CODE (1991)]. There has been only limited sampling for the triazine degradates DES and DACT in California wells, and further occurrence data are needed.

In response to the large number of confirmed herbicide detections, EHAP is developing, testing, and promoting management practices to reduce the movement of herbicides to groundwater. In discussions with the public, growers, commodity groups, and pesticide registrants, questions frequently arise about the extent to

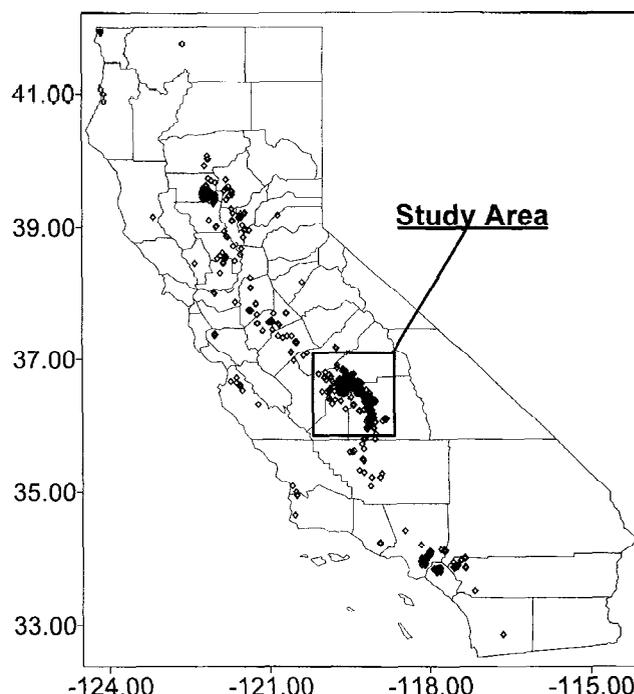


Fig. 1. Location of confirmed pesticide detections in California groundwater reported to EHAP since 1986.

which current farming practices contribute to herbicides in groundwater—as opposed to historical applications from 20–30 yr ago.

Chlorofluorocarbons are stable ubiquitous compounds that have been widely used as propellants, refrigerants, foam-blowing agents, and cleaning solvents for several decades. There are no known natural sources of CFCs, and atmospheric concentrations of CFC-11 (trichlorofluoromethane), CFC-12 (dichlorodifluoromethane), and CFC-113 (trichlorotrifluoroethane) have steadily increased over the last several decades (Fig. 11–6, Plummer et al., 1993). CFC-11 and CFC-12 have been regularly used as tracers to follow oceanic circulation and mixing since the 1970s (Lovelock et al., 1973; Hammer et al., 1978; Bullister and Weiss, 1983; Weiss et al., 1985; Wisegarver and Gammon, 1988), whereas their use as tracers of shallow groundwater to estimate recharge ages has been more recent (Busenberg et al., 1993; Busenberg and Plummer, 1992; Cook and Solomon, 1995, 1997; Cook et al., 1995; Dunkle et al., 1993; Ekwurzel et al., 1994; Oster et al., 1996; Szabo et al., 1996; Böhlke and Denver, 1995; Johnston et al., 1998; Modica et al., 1998). The recharge age is defined here as the elapsed time between entry of a water parcel into the water table and subsequent sampling from some location in the aquifer.

A primary objective of this study was to estimate the time between herbicide application and subsequent detection in groundwater using CFC tracers coupled with one-dimensional vadose zone transport modeling. Secondary objectives were to evaluate the presence of triazine degradates in wells where simazine had previously been detected and to determine if herbicide concentrations in wells had changed between 1994 and 1996. In this report, nonparametric statistical methods

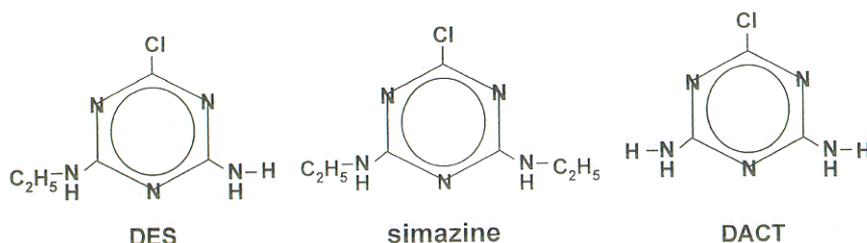


Fig. 2. Simazine and its two *N*-dealkylated degradates DES (2-amino-4-chloro-6-ethylamino-*s*-triazine) and DACT (2,4-diamino-6-chloro-*s*-triazine).

were used to evaluate various hypotheses about detections and herbicide concentrations. An  $\alpha$  value of 0.05 was used for hypothesis testing.

## MATERIALS AND METHODS

### Study Area

Fresno and Tulare counties are located in California's semi-arid southern San Joaquin Valley. Most of the 30 cm annual rainfall in the region occurs during the months of November to February, and summer temperatures often exceed 40°C. Extensive irrigation is used to meet crop water requirements during most of the year.

This study was conducted in the principal grape- and citrus-producing regions of the two counties (Fig. 3). Citrus production occurs primarily in the eastern edge of the San Joaquin Valley, along the base of the Sierra Nevada foothills. Grape

production is more prevalent farther west, toward the center of the valley.

The grape and citrus cropping patterns approximately follow the geographic distribution of soil characteristics. The soils in the citrus-producing areas along the eastern side of the valley are generally coarse to medium-textured soils, but also contain a shallow hard-pan layer (USDA-SCS, 1971, 1982). The most common hard-pan soils are the San Joaquin and Exeter soil series. Both soil series are characterized by a cemented hard-pan layer, typically between 0.3 and 1.2 m in depth. Fresno and Tulare county preemergent herbicide applications to citrus occur primarily in hard-pan soil areas (Table 1). In contrast, much of the grape-producing area south of Fresno is characterized by coarse to very coarse soils with unconsolidated profiles. Typical soils are the Hanford and Delhi series, and the majority of preemergent applications to Fresno and Tulare County grapes occur in coarse soils (Table 1).

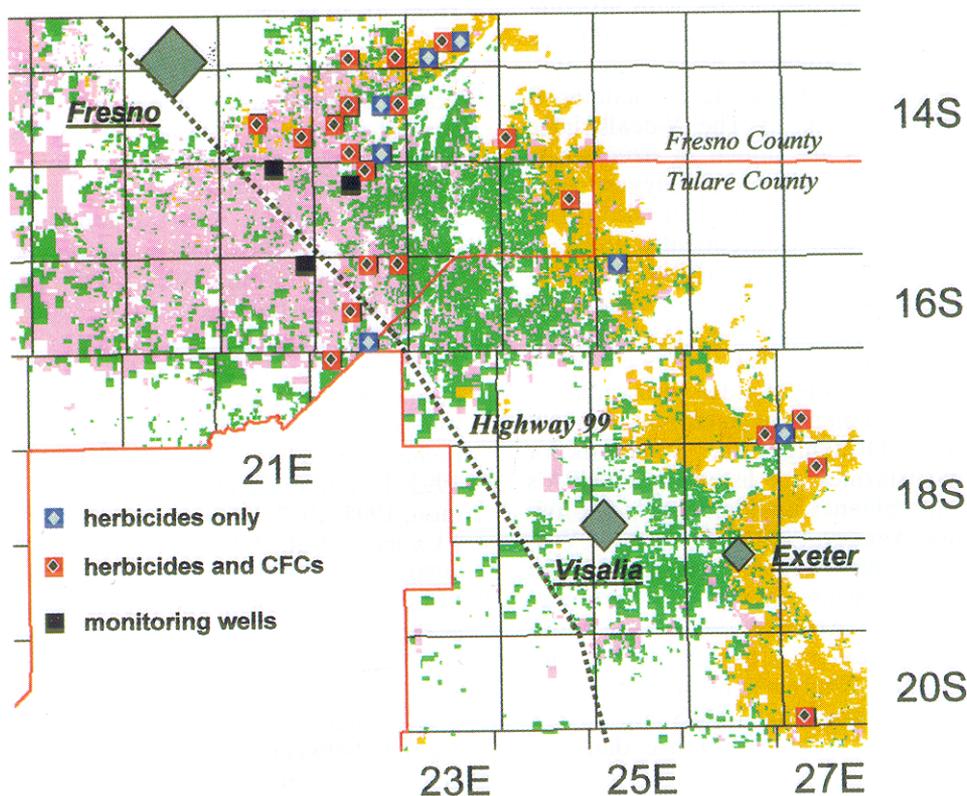


Fig. 3. Two-county study area. Land use colors: yellow = citrus, pink = vineyard, green = deciduous stonefruit and nuts. The remainder (uncolored) includes alfalfa, corn, grain, cotton, and dairy. Boxes show sections where sampled wells are located. Two samplings: Sampling 1, 30 domestic wells for herbicides only; sampling 2, a subset of 20 of the 30 domestic wells from sampling 1, and an additional three USGS well triplets. Each triplet consists of a nested monitoring well pair and a collocated domestic well. All wells in sampling 2 were sampled for both herbicides and CFCs.

**Table 1. Mass (kg) active ingredient of (simazine + diuron) applied to crops† in Fresno and Tulare counties in calendar year 1994 (California Dep. of Pesticide Regulation, 1996).**

Soil‡	Crop			Total by soil
	Citrus	Grapes	All others§	
Coarse	7 360	40 750	7 890	56 000
Hard pan	92 560	14 750	21 040	128 350
Other	31 800	3 810	17 410	53 020
Total by crop	131 720	59 310	46 340	
			<b>Grand total</b>	<b>237 370</b>

† Does not include applications to noncrop areas, e.g., rights-of-ways, roadsides, ditches, etc.

‡ Soil classifications from Troiano et al., 1994.

§ Includes deciduous orchards, olive, alfalfa, cotton, etc.

### Study Design

Samples were collected twice in this study. The first sampling consisted of 30 domestic wells in which simazine and/or DES had been detected in 1994. This sampling occurred for herbicide residues (simazine, diuron, bromacil, DES, and DACT) in July 1996. The purpose of this sampling was to confirm that herbicide residues were still present in the domestic wells, to compare the 1996 and 1994 concentrations, and to determine the relative contribution of DES and DACT to the total triazine concentrations (defined here as simazine + DES + DACT) in the 30 wells. The second sampling consisted of a subset of 20 of the 30 domestic wells and also a set of three well triplets, where each triplet consisted of a monitoring well pair and a collocated domestic well. All wells in the second sampling were analyzed for herbicides and CFCs as described below. The purpose of the second sampling was to estimate the recharge ages of samples from the domestic wells, and to evaluate the vertical distribution of recharge ages below the water table using the monitoring wells.

### Sampling 1

The 30 domestic wells sampled during the first sampling (Table 2) were regularly used domestic wells located in shallow groundwater areas (<14 m 1990 spring depth to groundwater; U.S. Bureau of Reclamation, 1990). Simazine or DES had been detected previously in all 30 wells in the summer of 1994. Prior to sampling, each well was checked to verify that the well pad and cover were in good condition, no pesticides were stored in the vicinity of the well, and that the site was not a mixer or loader site for pesticides.

Fifteen of the 30 wells were in coarse soil sections, and 15 wells were in hard-pan soil sections (Table 2). Sections are approximately 2.59-km<sup>2</sup> (1-mi<sup>2</sup>) areas, as described by the U.S. Public Land Survey. The soil classifications (coarse and hard-pan) were developed for an empirical California vulnerability model (Troiano et al., 1994, 1997), and are based on soil survey data (USDA-SCS 1971, 1982). In general, coarse soil sections are land survey sections where the majority of soils range from coarse to very coarse in texture and have no hard-pan within the first 1.5 m in depth. In contrast, hard-pan soil sections are dominated by coarse- to medium-textured soils that contain a cemented hard-pan layer, usually between the 0.3 and 1.2 m depth.

Simazine and diuron use in proximity of the 30 domestic wells is similar to regional simazine and diuron use patterns (Table 1), with applications to grapes dominating coarse-soil areas and applications to citrus occurring primarily in hard-pan soil areas (Table 1). This pattern of use was reflected in

**Table 2. General characteristics of 2.59-km<sup>2</sup> (1 mi<sup>2</sup>) sections of land surrounding the wells. Wells 1 to 30 were sampled for herbicides only in Sampling 1; wells 1 to 20, and 31a to 33c were sampled for herbicides and CFCs during Sampling 2.**

Well	Well type	Dominant surrounding land use	Depth to ground water†	Soil classification‡
			m	
1	Domestic	Citrus	11	Coarse
2	Domestic	Citrus	9	Pan
3	Domestic	Citrus	6	Pan
4	Domestic	Deciduous	12	Pan
5	Domestic	Vineyard	11	Coarse
6	Domestic	Deciduous	9	Coarse
7	Domestic	Vineyard	11	Pan
8	Domestic	Vineyard	11	Pan
9	Domestic	Vineyard	11	Coarse
10	Domestic	Citrus	14	Coarse
11	Domestic	Vineyard	11	Coarse
12	Domestic	Citrus	11	Pan
13	Domestic	Deciduous	14	Coarse
14	Domestic	Vineyard	12	Coarse
15	Domestic	Vineyard	11	Coarse
16	Domestic	Vineyard	14	Coarse
17	Domestic	Citrus	9	Pan
18	Domestic	Citrus	9	Pan
19	Domestic	Citrus	9	Pan
20	Domestic	Citrus	8	Pan
21	Domestic	Citrus	11	Coarse
22	Domestic	Citrus	11	Coarse
23	Domestic	Citrus	6	Pan
24	Domestic	Citrus	6	Pan
25	Domestic	Vineyard	11	Pan
26	Domestic	Vineyard	11	Pan
27	Domestic	Vineyard	11	Coarse
28	Domestic	Vineyard	11	Coarse
29	Domestic	Citrus	11	Coarse
30	Domestic	Citrus	9	Pan
31a	Domestic	Vineyard	11	Coarse
31b	Monitoring	Vineyard	11	Coarse
31c	Monitoring	Vineyard	11	Coarse
32a	Domestic	Vineyard	11	Coarse
32b	Monitoring	Vineyard	11	Coarse
32c	Monitoring	Vineyard	11	Coarse
33a	Domestic	Vineyard	12	Coarse
33b	Monitoring	Vineyard	12	Coarse
33c	Monitoring	Vineyard	12	Coarse

† 1990 Spring depth to ground water (U.S. Bureau of Reclamation, 1990).

‡ Based on soil classifications of Troiano et al., 1994 (see text).

the 1994 simazine and diuron use data for the 23.31-km<sup>2</sup> (9-mi<sup>2</sup>) area consisting of nine sections, including the well in the center section. The median percent of total kg herbicide applied to grapes was 64% in the vicinity of the wells in the coarse-soil sections and only 2% around the wells in the hard-pan soil sections ( $p = 0.022$ , Wilcoxon rank sum test). In contrast, herbicide applications in proximity of the wells in the hard-pan sections were primarily to citrus. The median percent of total kg herbicide applied to citrus was 75% in proximity of the wells in the hard-pan sections and 1% in proximity of the wells in the coarse sections ( $p = 0.005$ , Wilcoxon rank sum test).

### Sampling 2

Samples were collected from two groups of wells and analyzed for both herbicide residues and CFCs (CFC-11, CFC-12, and CFC-113) in the second sampling (August 1996). One group of wells in the second sampling were the domestic wells 1 to 20, a subset of the 30 wells in the first sampling (Table 2). The second group of wells in the second sampling consisted of three well triplets, wells 31a to c, 32a to c, and 33a to c, each triplet consisting of a nested monitoring well pair and a collocated domestic well (Table 2). The well triplets are part

of a larger network installed as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment Program (NAWQA) (Leahy et al., 1990; Burow et al., 1998).

The CFC data from the second sampling were used to estimate the recharge ages of the water sampled from the wells. The domestic well recharge ages were combined with one-dimensional transport modeling to estimate mean times between herbicide application and subsequent detection in domestic wells. The monitoring well recharge ages were used to evaluate the vertical distribution of recharge ages below the water table. One reason for examining the vertical distribution of ages in the aquifer was to verify that older, deeper waters were distinguishable from shallower, younger waters.

## Sampling and Analytical Procedures

### Herbicides

The domestic wells were sampled as close as possible to the wellhead; in all cases samples were taken before the storage tank. The wells sampled were allowed to operate continuously for at least 15 min prior to drawing the samples for herbicide analysis. The monitoring wells were sampled using an air-driven, low-discharge, submersible portable stainless steel pump. Each well was purged of a minimum of three casing volumes, and sampling initiated after the electrical conductivity of the water stabilized.

The extraction procedure consisted of acidifying 100 mL of sample by addition of 0.2 mL 3N HCl and passing the solution through piggybacked octadecyl ( $C_{18}$ ) and strong cation exchange (SCX) disposable solid phase extraction columns (VWR JT7020-03 and J.T. Baker 7090-03, respectively). The  $C_{18}$  column was preconditioned by rinsing with one column volume methanol followed by one column volume distilled water. The SCX column was preconditioned by rinsing with one column volume 75/20/5 methanol/water/ammonium hydroxide, followed by one column volume methanol, followed by one column volume distilled water. After passing the sample through the columns, the piggybacked columns were rinsed with one column volume of distilled water. The columns were then separated and eluted with one column volume of either methanol ( $C_{18}$  column) or 75/20/5 methanol/water/ammonium hydroxide (SCX column). The eluants were combined and evaporated to dryness under a stream of nitrogen in a 35°C water bath. The samples were reconstituted in 1.0 mL (95/5 10mM ammonium formate/methanol) 0.1% formic acid and filtered through a 0.45- $\mu$  filter into an autoinjector vial. The analytes were separated using gradient elution on a Shimadzu LC10-AD liquid chromatograph (LC) equipped with a Waters Nova-Pak column (Waters 11670) with a flow rate of 0.8 mL  $\text{min}^{-1}$ . The injection volume was 50  $\mu$ L. Mobile phase A consisted of (95/5 10 mM ammonium formate/methanol) 0.1% formic acid, whereas mobile phase B consisted of (90/10 methanol/0.1 M ammonium formate). The mobile phase composition was steadily modified from 100/0 A/B to 15/85 A/B in 6 min, maintained constant for 7 min and returned to 100/0 A/B.

The LC was interfaced to a Perkin-Elmer SCIEX API III triple-stage mass spectrometer with a heated nebulizer. The curtain, nebulizer, and auxiliary gas was nitrogen, and argon was employed as the collision gas. The herbicides were analyzed by positive ion tandem mass spectrometry using the protonated molecular ion as the precursor ion. The precursor ions were used to generate additional fragment ions by collision-induced dissociation; these product ions were then analyzed. The principal precursor to product ion transitions used for identification and quantitation were simazine, 202 to 132; DES, 174 to 132; DACT, 146 to 104; bromacil, 261 to 132; and diuron, 233 to 72.

The method detection limit (MDL) was determined by the analysis of seven samples fortified at a concentration level of 0.05 ppb for all analytes. The MDL for each analyte was determined as 3.143 [ $= t_{0.01, 6}$ ] multiplied by the SD of the respective results. The MDLs ranged from 0.007 to 0.014 ppb. The limit of quantitation (LOQ) was determined as  $10 \times \text{SD}$ , ranging from 0.01 to 0.04. These results were used to support the practical reporting limit of 0.05 ppb for all analytes. A method validation study was subsequently conducted using 15 fortified samples (5 samples at each of 3 concentration levels—0.05, 0.2, and 0.5 ppb). Overall mean percent recoveries  $\pm$  SD were  $100 \pm 4$ ,  $75 \pm 11$ ,  $107 \pm 3$ ,  $102 \pm 11$ , and  $102 \pm 4$  for simazine, DES, DACT, diuron, and bromacil, respectively. Five quality-control blind spikes were also submitted to the laboratory; these samples were spiked at the 0.20  $\mu\text{g L}^{-1}$  level for all analytes. The mean recoveries for the spikes were 102% (simazine), 109% (DES), 81% (DACT), 101% (diuron), and 88% (bromacil). Field blanks were prepared at each sampling site and transported and analyzed with the samples. No herbicides were detected in the blank samples.

### Chlorofluorocarbons

Triplicate water samples for CFC analysis were collected from each well using a custom CFC sampling apparatus developed by the USGS that prevents sample-atmosphere contact during the sampling process (Busenberg and Plummer, 1992). The samples were collected and flame-sealed in 62 mL borosilicate ampules. The triplicate CFC samples were analyzed by USGS laboratories using purge and trap gas chromatography with electron capture detection. Further details on analytical procedures and preparation of blanks and standards are given by Busenberg and Plummer (1992).

### Estimation of Effective Recharge Age using Chlorofluorocarbons

The conditions that are most suitable for CFC age-dating of groundwater are rural areas where groundwater is shallow ( $< \sim 10$  m) and oxic, and soils are low in organic carbon content (Plummer et al., 1993). Such conditions closely match the study area (Burow et al., 1998).

CFC-11 and CFC-12 atmospheric mixing ratios vary somewhat with latitude (Cunnold et al., 1994). For the present study conducted in California's agricultural San Joaquin Valley (study area latitude  $\sim 36.6^\circ\text{N}$ ), reference historical North American atmospheric CFC growth curves (CFC atmospheric concentrations vs. time) were developed from data collected at Niwot Ridge, Colorado ( $40^\circ\text{N}$ ), augmented by recent data obtained at Shenandoah National Park, Virginia ( $38^\circ\text{N}$ ) (E. Busenberg, 1997, personal communication). These CFC-11 and CFC-12 data sets are updated versions of data used in other recent groundwater studies (Busenberg et al., 1993; Busenberg and Plummer, 1992; Cook and Solomon, 1995; Cook et al., 1995; Dunkle et al., 1993; Ekwurzel et al., 1994; Szabo et al., 1996).

Short-term fluctuations in local tropospheric CFC concentrations are damped at the base of the vadose zone, so that CFC concentrations at depths greater than approximately 4 m reflect long-term (e.g., annual) trends in atmospheric CFC concentrations (Oster et al., 1996). Vadose-zone gas monitoring and vadose-zone gas transport modeling studies indicate that in shallow coarse-textured soil profiles ( $\sim 10$  m depth to groundwater), the concentration time lag between increasing atmospheric CFC concentrations and CFC concentrations at the base of the vadose zone is about 1 yr (Cook and Solomon, 1995; Weeks et al., 1982). In the present study, where the

mean depth to groundwater of wells 1 to 30 is 10 m (Table 2), we assume that the shallow vadose-atmosphere CFC concentrations at the water table are equal to the reference North American continental atmospheric CFC concentrations.

The CFC Henry's law constants were determined from the data of Warner and Weiss (1985) and Bu and Warner (1995). Seasonal soil temperature variations decrease markedly with depth, so temperatures in the unsaturated zone approach a constant value at depths greater than a few meters (Hillel, 1980; Heaton and Vogel, 1981; Plummer et al., 1993). In the absence of geologic heating, this constant temperature is closely approximated by the mean annual air temperature. In this study, a mean recharge temperature of 17°C—that is, the mean soil temperature at the base of the unsaturated zone 10 m below ground surface—was assigned based on the mean of 10 yr of daily air temperature data from four weather stations located in the study area. This mean recharge temperature was used to determine the appropriate value for the CFC Henry's law constants which, in turn, allowed the calculation of CFC vadose-zone gas phase concentrations at the time of recharge from measured CFC groundwater concentrations. The error in CFC-estimated recharge age attributable to inaccuracies in recharge temperature is about 1 to 2 yr °C<sup>-1</sup> for groundwater recharged in the last 5 yr, but is much less for older waters (Busenberg and Plummer, 1992).

The estimated recharge ages were determined as the average of the individual results for all three CFCs when possible, but always using at least two. As discussed later, selected groundwater samples contained levels of a particular CFC that were too high to be explained by atmospheric equilibration.

#### Vadose Zone Transport Modeling

The Leaching Estimation and Chemistry Model (LEACHM, v. 3; Hutson and Wagenet, 1992) was used to estimate simazine travel time from the land surface to the

water table. LEACHM input data sources included crop ET data for the southern San Joaquin Valley (Dep. of Water Resources, 1993), precipitation and temperature data (Univ. of California, 1997), and soil texture and organic carbon data from 10-m-depth soil cores from Fresno County obtained in a previous EHAP study (Zalkin et al., 1984). The simulated irrigation applications were based on crop water requirements calculated from ET (Goldhamer and Snyder, 1984), and irrigation water efficiencies (crop water requirements/water applied) of 65% (Snyder et al., 1986; Hanson, 1994).

## RESULTS

### Sampling 1: Herbicides

Two or three triazines were detected in samples from each of the 30 wells (Table 3). In addition to simazine, DES and DACT, 70% of the wells also contained detectable levels of diuron and/or bromacil, while 33% of the wells had detectable levels of all five residues (Table 4).

The degradates DES and DACT composed the greatest fraction of total triazines in the well samples, with the median total triazine concentration (simazine + DES + DACT) more than 5 times greater than the median concentration of simazine alone (Table 4). Among the three triazine species, DES was generally present at the highest concentrations, followed by DACT and simazine (Table 4). The highest total triazine concentration of 3.8 µg L<sup>-1</sup> approached the simazine maximum contaminant level (MCL) of 4 µg L<sup>-1</sup> (U.S. Environmental Protection Agency, 1998b).

There was a modest correlation between simazine concentrations and the concentrations of the degradates (DES+DACT, spearman correlation coefficient = 0.46,

**Table 3. The 1994 and 1996 (Sampling 1) analytical data for 30 domestic wells. Reporting limit = 0.05 µg L<sup>-1</sup> all analyses.**

Well	Simazine		DES		DACT		Bromacil		Diuron		Sum triazines, 1996	Residues detected, 1996
	1994	1996	1994	1996	1994	1996	1994	1996	1994	1996		
1	0.06	0.10	<0.05	0.16	N/A	0.14	0.18	0.09	<0.05	0.12	0.40	5
2	0.08	0.11	0.41	0.65	N/A	0.27	0.27	0.28	0.37	0.76	1.0	5
3	0.16	0.14	N/A	0.68	N/A	0.60	1.2	1.20	0.26	0.49	1.4	5
4	0.30	0.26	N/A	1.2	N/A	0.16	<0.05	<0.05	<0.05	<0.05	1.6	3
5	0.09	0.12	N/A	0.41	N/A	0.16	0.75	0.75	0.15	0.15	0.69	5
6	0.06	0.08	N/A	0.07	N/A	<0.05	<0.05	<0.05	0.21	0.07	0.15	3
7	<0.05	0.07	0.25	0.28	N/A	0.20	<0.05	0.14	<0.05	<0.05	0.55	4
8	0.27	0.24	0.15	0.11	N/A	<0.05	<0.05	<0.05	0.09	<0.05	0.35	2
9	0.19	0.15	0.05	0.08	N/A	<0.05	0.28	0.13	0.57	0.35	0.23	4
10	0.13	0.19	0.38	0.65	N/A	0.09	<0.05	<0.05	<0.05	<0.05	0.93	3
11	0.23	0.22	0.82	0.81	N/A	0.85	<0.05	<0.05	<0.05	0.13	1.9	4
12	0.11	0.11	1.2	1.2	N/A	0.34	0.12	0.22	0.22	0.41	1.7	5
13	0.36	0.26	0.79	0.72	N/A	0.06	<0.05	<0.05	0.08	<0.05	1.0	3
14	0.12	0.16	0.30	0.23	N/A	0.18	<0.05	<0.05	<0.05	<0.05	0.57	3
15	<0.05	0.07	0.34	0.34	N/A	0.14	<0.05	<0.05	<0.05	<0.05	0.55	3
16	0.10	0.12	0.06	0.10	N/A	0.08	<0.05	<0.05	<0.05	<0.05	0.30	3
17	0.23	0.41	3.3	3.0	N/A	0.43	<0.05	<0.05	0.44	0.60	3.8	4
18	0.19	<0.05	0.60	0.68	N/A	0.26	<0.05	0.70	<0.05	0.20	0.94	4
19	0.30	0.23	N/A	1.6	N/A	0.43	0.35	0.19	0.62	0.49	2.3	5
20	0.67	0.28	N/A	1.3	N/A	0.51	0.09	0.61	<0.05	<0.05	2.1	4
21	0.09	0.09	0.30	0.28	N/A	0.34	<0.05	<0.05	<0.05	<0.05	0.71	3
22	0.15	0.16	0.28	0.31	N/A	0.25	0.05	<0.05	0.97	0.76	0.72	4
23	0.18	0.17	N/A	0.60	N/A	0.58	2.5	3.2	0.41	0.66	1.4	5
24	0.22	0.23	0.66	0.62	N/A	0.37	<0.05	0.05	0.17	0.13	1.2	5
25	0.21	0.16	N/A	0.43	N/A	0.20	1.2	0.62	1.8	1.4	0.79	5
26	0.17	0.15	N/A	0.60	N/A	0.13	0.9	1.4	0.95	1.5	0.88	5
27	0.21	0.26	0.44	0.62	N/A	0.10	<0.05	<0.05	<0.05	<0.05	0.98	3
28	0.16	0.12	0.08	0.12	N/A	0.10	<0.05	<0.05	0.07	0.06	0.34	4
29	0.18	0.26	1.8	1.5	N/A	0.27	<0.05	<0.05	0.37	0.44	2.0	4
30	0.22	0.22	<0.05	0.07	N/A	<0.05	<0.05	0.05	0.23	0.23	0.29	3

† N/A, not analyzed.

$p = 0.011$ ), indicating that wells with high simazine concentrations also tended to have greater degradate concentrations. However, nearly all of the wells (28 of 30) were selected from a larger population of wells in which simazine had previously been detected. This selection criterion all but eliminated wells that did not contain simazine but may have contained detectable concentrations of degradates. Because of this bias in well selection, the simazine and degradate concentrations may not be representative of the entire population of triazine-positive domestic wells in Fresno and Tulare Counties. Sampling for degradates has been limited, and there potentially may be a large number of wells containing degradates but not the parent simazine. Additional data will be required to further evaluate the apparent correlation between simazine and degradate concentrations.

Herbicide concentrations and frequencies of detection were different between the coarse and hard-pan soil sections. Bromacil detections were more frequent in the hard-pan soil sections than the coarse sections (11 detections in 15 wells and 3 detections in 15 wells, respectively,  $p = 0.003$ , chi-square test). This result is attributable to land-use patterns. Bromacil is registered for use only on citrus; the higher bromacil detection frequencies in the hard-pan sections reflect the predominance of citrus production in the vicinity of the hard-pan section wells.

The median concentrations of both the sum of triazines [DES + DACT + simazine] and diuron were greater in the hard-pan soil sections than the coarse soil sections ( $1.4$  vs.  $0.77 \mu\text{g L}^{-1}$ ,  $p = 0.029$ , and  $0.46$  vs.  $0.14 \mu\text{g L}^{-1}$ ,  $p = 0.037$ , respectively, Wilcoxon rank sum test). The higher triazine and diuron concentrations in the hard-pan soils as compared to coarse soils could result from several factors, including the potentially different mechanisms for transport to groundwater in the hard-pan soil sections vs. coarse soil sections (Troiano et al., 1997, Bartkowiak et al., 1997), the differences in herbicide application timing and frequency, the higher simazine and diuron application rates in citrus than in grapes, and different irrigation practices.

All 30 wells in the first sampling had been sampled for simazine, diuron, and bromacil in summer 1994, but DES was determined in only 21 of these wells. A comparison of 1994 and 1996 concentrations in the wells indicates that concentrations did not change over the 2 yr interval (nondetections assigned a value of 0,  $p = 0.22$ , Wilcoxon signed rank test).

## Sampling 2: Chlorofluorocarbons

The CFC-estimated recharge ages generally increase with depth below the water table (Fig. 4). Data for five monitoring wells and six domestic wells sampled in this study, and 17 monitoring wells previously sampled in 1994 by USGS as part of the NAWQA program (Dubrovsky et al., 1998), are included in Fig. 4. Only six domestic wells are shown because construction records and well screen depths were not available for the remainder of the domestic wells. All of the wells shown in Fig. 4 are located in predominately coarse soils where grapes are grown, and are within 13 miles of each other. The perforated intervals of monitoring wells were 1.5 m in length. In general, the shallowest wells in the area yielded the youngest recharge ages. The perforated intervals for the six domestic wells ranged from 9 to 30 m in length. Although samples from the domestic wells are integrated samples that probably consist of a mixture of waters spanning a range of ages, the results from the domestic wells generally follow the pattern of increasing recharge age with depth observed for the monitoring wells.

The principal sources of groundwater recharge are rainfall and irrigation to meet crop ET. The average annual grape ET in the southern San Joaquin Valley is 0.7 m (Univ. of California, 1984, Dep. of Water Resources, 1993). Maximum obtainable irrigation efficiencies (crop ET requirement/applied water) are about 60 to 90% depending on irrigation method (Solomon, 1988). In practice, typical California irrigation efficiencies are probably around 65% (Snyder et al., 1986; Hanson, 1994). Approximately 70% of the annual 0.3 m rainfall occurs during the months of December through March when ET is minimal. These data yield an order of magnitude estimate of net annual recharge from irrigation and rainfall in grape-growing areas of 0.5 m. The monitoring well data in Fig. 4 show a vertical gradient in recharge age of approximately  $1 \text{ yr m}^{-1}$ . Assuming an aquifer porosity in the range of 0.3 to 0.4, this gradient corresponds to an average recharge of about 0.3 to 0.4  $\text{m yr}^{-1}$ . While this CFC-based average recharge is a gross estimate, it is consistent in light of the estimated annual groundwater recharge of 0.5 m previously mentioned, the estimate of annual groundwater pumpage in the area of about 0.3 to 1.0  $\text{m yr}^{-1}$  (Williamson et al., 1989), and the relatively constant springtime depth to groundwater in the area during the last 30 yr (U.S. Bureau Reclamation, 1990).

**Table 4. Summary of analytical results for ground water samples collected during first sampling of Wells 1 to 30 (July 1996).**

Variable	Triazines				Diuron	Bromacil
	Simazine	DES†	DACT†	Sum		
% Wells with a detection	97	100	87	100	63	47
Median conc. ( $\mu\text{g L}^{-1}$ )‡	0.16	0.60	0.19	0.91	0.13	—§
Mean conc.‡	0.17	0.65	0.24	1.1	0.30	0.32
SD	0.08	0.62	0.20	0.79	0.40	0.66
Maximum conc.	0.41	3.0	0.85	3.8	1.5	3.2
Minimum conc.	<0.05	0.07	<0.05	0.15	<0.05	<0.05

† DES = deethylsimazine, DACT = diaminochlorotriazine.

‡ Median and mean concentrations calculated assuming nondetections ( $<0.05$ ) = 0.

§ More than 50% of bromacil analyses were  $<0.05$ .

Of the 23 domestic wells sampled for CFCs, samples from five wells were not dated because their calculated vadose atmosphere concentrations for at least two of the three CFCs exceeded the respective maximum historical North American continental atmospheric concentrations by more than 10%. Limited observations of local atmospheric excesses in rural areas up to about 10% have been reported (Oster et al., 1996), while annual excesses ranging from 6 to 13% have been reported near the New York City metropolitan area (Ho et al., 1998). Thus, it appears that local atmospheric CFC excesses of the magnitude required to explain the elevated levels observed here are unlikely, indicating that individual wells may have been contaminated by an individual local point sources. Sewage has, in some cases, been observed to contain high levels of CFCs (Busenberg and Plummer, 1992), so sewage contamination is one potential source of high CFC concentrations. As noted in other studies, CFC-113 was particularly problematic; concentrations in 13 of 29 wells yielded anomalously high calculated CFC-113 mixing ratios.

In general, the three CFCs are discrete compounds with separate uses and sources. Therefore, the decision rule to date those wells with at least two viable ages was used because it is unlikely that two or three CFCs in any particular sample would simultaneously be present due to contamination at relative levels that would also yield similar recharge ages, and in multiple wells with a frequency sufficient to strongly bias the estimate of median recharge ages. The within-well SD of recharge ages ranges from 0 to 6.6 yr, with a mean of 3.8 yr. Thus, the viable ages within wells are consistent. This result, along with the previously discussed order-of-magnitude regional recharge estimate obtained from the recharge age gradient below the water table (Fig. 4) indicates that, in aggregate, the CFC data yield a reasonable estimate of approximate median recharge age in the study area.

The estimated recharge ages of the 18 domestic wells ranged from 1 to 31 yr, with a median age of 6 yr

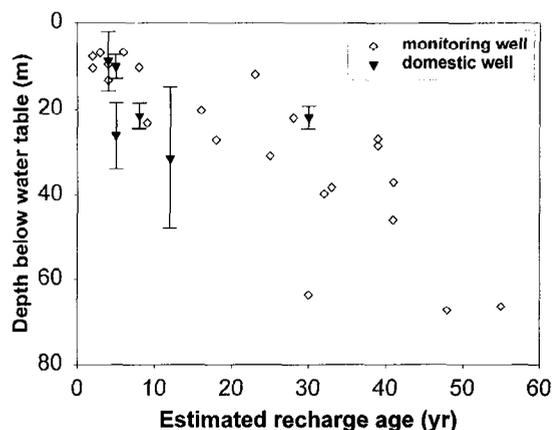


Fig. 4. CFC-estimated recharge age vs. depth below the water table for five monitoring wells and six domestic wells sampled in this study, and 17 monitoring wells sampled in 1994 as part of the USGS NAWQA study (Leahy et al., 1990). Domestic well error bars show span of perforated interval; perforated intervals for monitoring wells are approximately equal to the size of the data symbols.

(Fig. 5). The estimated time between application of the herbicides and their detection in groundwater is equal to the recharge age plus the travel time from the ground surface to the water table. An estimated annual vertical solute transport velocity of approximately  $5 \text{ m yr}^{-1}$  was thus obtained using the LEACHM model, corresponding to an estimate of vadose-zone travel time of 1 to 3 yr. This travel time estimate is probably greater than the actual mean travel time because the herbicide front is modeled as a uniform plane moving downward through the soil. In reality, preferential flow typically leads to more rapid downward movement than predicted by one-dimensional leaching models, especially in coarse soils (Rice et al., 1991). Thus, CFC age-dating combined with the modeling indicates that the detections in the 18 domestic wells are associated with herbicide applications ranging from 2 to 33 yr ago, with more than half of the detections associated with applications in the last 7 to 9 yr.

## CONCLUSIONS

In the Fresno and Tulare County wells that were sampled in this study, simazine constituted only a fraction of the total triazines present, about 10 to 20%. While no samples in this study contained *total* triazine concentrations (simazine + DES + DACT) that exceeded the simazine MCL of  $4 \mu\text{g L}^{-1}$ , samples from several wells approached this level. The maximum total triazine concentration measured in this study was  $3.8 \mu\text{g L}^{-1}$ , or 95% of the simazine MCL. The prevalence of triazine degradates observed in this and other studies indicate that drinking water standards based on total triazines may be most appropriate, particularly if the triazine species display a common mode of toxicological action. More than two-thirds of the wells also had detectable concentrations of diuron and/or bromacil, whereas one-third had detectable concentrations of all five residues: bromacil, diuron, simazine, DES, and DACT (reporting limit of  $0.05 \mu\text{g L}^{-1}$ ).

There was no detectable change in herbicide concentrations in the 30 domestic wells between 1994 and 1996.

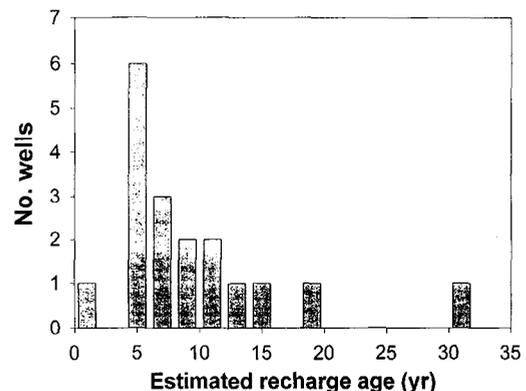


Fig. 5. Histogram of CFC-estimated recharge ages for 18 domestic wells. Five additional domestic wells had CFC concentrations too high to be explained by atmospheric equilibration and may have been contaminated. The median estimated effective recharge age (travel time from water table to well screen depth) for the 18 wells shown is 6 yr.

Estimated times between herbicide application and subsequent detection in well water ranged from 2 to 33 yr, with more than half of the detections associated with applications made within the last 7 to 9 yr. The aggregate data indicate that many of the widespread preemergent herbicide detections are associated with relatively recent agricultural management practices. The data further indicate that any changes in groundwater quality arising from widespread modifications of herbicide use or changes in other agricultural management practices will probably not be discernible for at least a decade.

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