
Temporal trends in concentrations of DBCP and nitrate in groundwater in the eastern San Joaquin Valley, California, USA

K. R. Burow · N. M. Dubrovsky · J. L. Shelton

Abstract Temporal monitoring of the pesticide 1,2-dibromo-3-chloropropane (DBCP) and nitrate and indicators of mean groundwater age were used to evaluate the transport and fate of agricultural chemicals in groundwater and to predict the long-term effects in the regional aquifer system in the eastern San Joaquin Valley, California. Twenty monitoring wells were installed on a transect along an approximate groundwater flow path. Concentrations of DBCP and nitrate in the wells were compared to concentrations in regional areal monitoring networks. DBCP persists at concentrations above the US Environmental Protection Agency's maximum contaminant level (MCL) at depths of nearly 40 m below the water table, more than 25 years after it was banned. Nitrate concentrations above the MCL reached depths of more than 20 m below the water table. Because of the intensive pumping and irrigation recharge, vertical flow paths are dominant. High concentrations (above MCLs) in the shallow part of the regional aquifer system will likely move deeper in the system, affecting both domestic and public-supply wells. The large fraction of old water (unaffected by agricultural chemicals) in deep monitoring wells suggests that it could take decades for concentrations to reach MCLs in deep, long-screened public-supply wells, however.

Résumé Les suivis en temps du pesticide 1,2-dibromo-3-chloropropane (DBCP), des nitrates et des indicateurs de l'âge moyen des eaux souterraines ont été utilisés dans le but d'estimer le transport et le devenir des produits agrochimiques dans les eaux souterraines, et de prédire leurs effets à long terme dans le système aquifère régional de la San Joaquin Valley orientale, en Californie. Vingt piézomètres ont été implantés en alignement, approximativement selon une ligne de flux souterrain. Les concen-

trations en DBCP et nitrates mesurées dans les piézomètres ont été comparées aux concentrations dans les réseaux de surveillance du secteur. Le DBCP dépasse continuellement la valeur limite fixée par l'US Environmental Protection Agency, à des profondeurs proches de 40 m sous le niveau piézométrique, et plus de 25 ans après son interdiction. Les concentrations en nitrates supérieures aux limites se retrouvent à des profondeurs supérieures à 20 m sous le niveau piézométrique. Les écoulements verticaux sont prépondérants, du fait des pompes intensives et de la réalimentation par irrigation. Les concentrations élevées (supérieures aux limites) présentes dans la tranche la plus superficielle de l'aquifère sont susceptibles de migrer plus en profondeur dans le système, et d'affecter les puits privés et ceux destinés à l'alimentation en eau potable. Cependant, la large proportion d'eau ancienne (non affectée par les produits agrochimiques) dans les piézomètres profonds suggère que les limites de concentration ne seront pas dépassées avant longtemps dans les puits d'alimentation en potable, qui sont profonds et présentent des hauteurs crépinées conséquentes.

Resumen La monitorización temporal del plaguicida 1,2-dibromo-3-cloropropano (DBCP) y de los nitratos así como indicadores de la media de edad del agua subterránea han sido utilizados para evaluar el transporte y el destino de los compuestos químicos en el agua subterránea y para predecir los efectos a largo plazo en el sistema acuífero regional situado al este del Valle de San Joaquín, California. Se instalaron veinte pozos de control en un transecto situado aproximadamente siguiendo la línea de flujo del agua subterránea. Las concentraciones de DBCP y nitratos en los pozos se compararon con las concentraciones en la red de control regional. DBCP persiste con concentraciones por encima de los niveles máximos contaminantes (MCL) de la Agencia de Protección Medioambiental de Estados Unidos a profundidades cercanas a los 40 m por debajo del nivel piezométrico, más de 25 años después de haber sido prohibido. Las concentraciones de nitratos por encima de MCL alcanzaron profundidades de más de 20 m por debajo del nivel piezométrico. Debido al bombeo intensivo y los retornos de riego, las líneas de flujo verticales son dominantes. Las altas concentraciones (por encima de MCLs) situadas en la parte superficial del sistema acuífero regional probablemente se moverán más profundamente en el sistema,

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afectando a los pozos domésticos y a los pozos de abastecimiento. No obstante, la alta proporción de aguas antiguas (no afectadas por compuestos químicos de origen agrícola) en los pozos de control profundos sugiere que pueden pasar décadas para que se alcancen concentraciones que alcancen MCLs en profundidad, en los pozos de abastecimiento totalmente ranurados.

Keywords Agriculture · Contamination · San Joaquin Valley · Groundwater monitoring · Groundwater age

Introduction

Widespread occurrence of 1,2-dibromo-3-chloropropane (DBCP) and nitrate at concentrations of concern affects both rural and public drinking-water supplies in the eastern San Joaquin Valley, California. DBCP, a soil fumigant used to control nematodes, was applied to crops nationwide beginning in the 1950s. In 1977, agricultural use of DBCP was suspended in California in response to concern about the potential hazardous effects of DBCP on human health; however, DBCP persists in groundwater in this region at concentrations above the US Environmental Protection Agency (USEPA) maximum contaminant level (MCL) of 0.2 µg/L, posing a threat to drinking-water supplies more than 25 years after it was banned from use (California State Water Resources Control Board 2002a). Similarly, nitrate occurrence in groundwater is an issue of concern, in part, because nitrate concentrations persist in oxic groundwater and have increased over time in many areas (Nightingale 1970; Schmidt 1972; Madison and Brunett 1985; Lowry 1987; Anton et al. 1988; Almasri and Kaluarachchi 2004). Nitrate has been widely detected in groundwater in the eastern San Joaquin Valley. Nitrate concentrations exceeded the USEPA MCL of 10 mg/L (as nitrogen) in 24% of domestic wells sampled during 1993–1995 (Dubrovsky et al. 1998), and the Central Valley is one of the top three regions in the state in regards to the number of public drinking-water wells exceeding the USEPA MCL for nitrate (California State Water Resources Control Board 2002b). Nitrate concentrations in groundwater in the eastern San Joaquin Valley are expected to persist over the long term, owing to continued anthropogenic nitrogen inputs and generally oxic geochemical conditions.

Many studies have addressed issues of DBCP and nitrate occurrence and sources in the eastern San Joaquin Valley aquifer (Schmidt 1972; Miller and Smith 1976; Nightingale and Bianchi 1974; Schmidt 1986, 1987; Burow et al. 1998a; Harter et al. 1998; Loague et al. 1998a,b; Loague and Abrams 1999) and some studies have analyzed data on temporal trends in concentration (Nightingale 1970; Schmidt 1972; California State University Fresno Foundation 1994; Kloos 1996; Burow et al. 1998b; Burow et al. 1999); however, long-term monitoring data are scarce, and few wells have been sampled over time spans long enough to assess the potential for long-term degradation of the groundwater resource.

Predicting the long-term fate of agricultural chemicals in groundwater in this region is difficult owing to intensive groundwater pumping, mixing sources of recharge water, and complex flow paths through heterogeneous alluvial fan sediments. Coupling chemical concentrations with groundwater age indicators can aid in understanding groundwater-flow systems and identifying trends in groundwater quality (Cook and Böhlke 1999; Lindsey et al. 2003; MacDonald et al. 2003; Broers and van der Grift 2004; Puckett and Hughes 2005). Understanding the behavior of nonpoint source agricultural constituents such as DBCP and nitrate, is fundamental to predicting the long-term effects of anthropogenic practices on the quality of groundwater in the eastern San Joaquin Valley. Analysis of these constituents can assist in characterizing dominant aquifer processes controlling the fate and transport of a wide range of possible chemicals of concern in the subsurface.

To assess temporal trends in groundwater quality in the study area and determine the possible long-term effects of agricultural management practices on groundwater quality in this region, DBCP and nitrate concentrations in groundwater were analyzed in samples collected from monitoring wells in 1994–1995 and in 2003. The monitoring wells were installed at multiple depths along a transect, representing a range of groundwater ages. The groundwater ages, determined from CFC concentrations, were used to estimate the concentration of DBCP and nitrate in recharge through time. Simulated age distributions for each monitoring well, derived from a groundwater flow and transport model developed for the study site (Weissmann et al. 2002b), were evaluated in relation to DBCP concentrations and compared to previous estimates of the in-situ half-life of DBCP in the aquifer (Burow et al. 1999). Spatial and temporal patterns of nitrate concentrations were also evaluated and compared to nitrogen fertilizer applications. Simulated age distributions (Weissmann et al. 2002b) were used to adjust fertilizer application curves to further interpret apparent changes in nitrate concentration over time. Results of the analysis at the study site were compared to data from regional areal well networks to extrapolate the findings to a larger spatial scale.

Study area

Hydrogeology of Fresno study area

The study area is west of the foothills of the Sierra Nevada and east of the San Joaquin Valley trough on the upper part of the Kings River alluvial fan (Fig. 1). The alluvial sediments consist primarily of interlayered lenses of gravel, sand, silt, and clay deposited by the Kings River in aggradation sequences linked to Pleistocene glacial episodes (Burow et al. 1997; Weissmann et al. 2002a). These sediments were derived from source materials in the Sierra Nevada that consist primarily of granitic rocks, with lesser amounts of metasedimentary and metavolcanic rocks (Page and LeBlanc 1969; Cehrs et al. 1980).

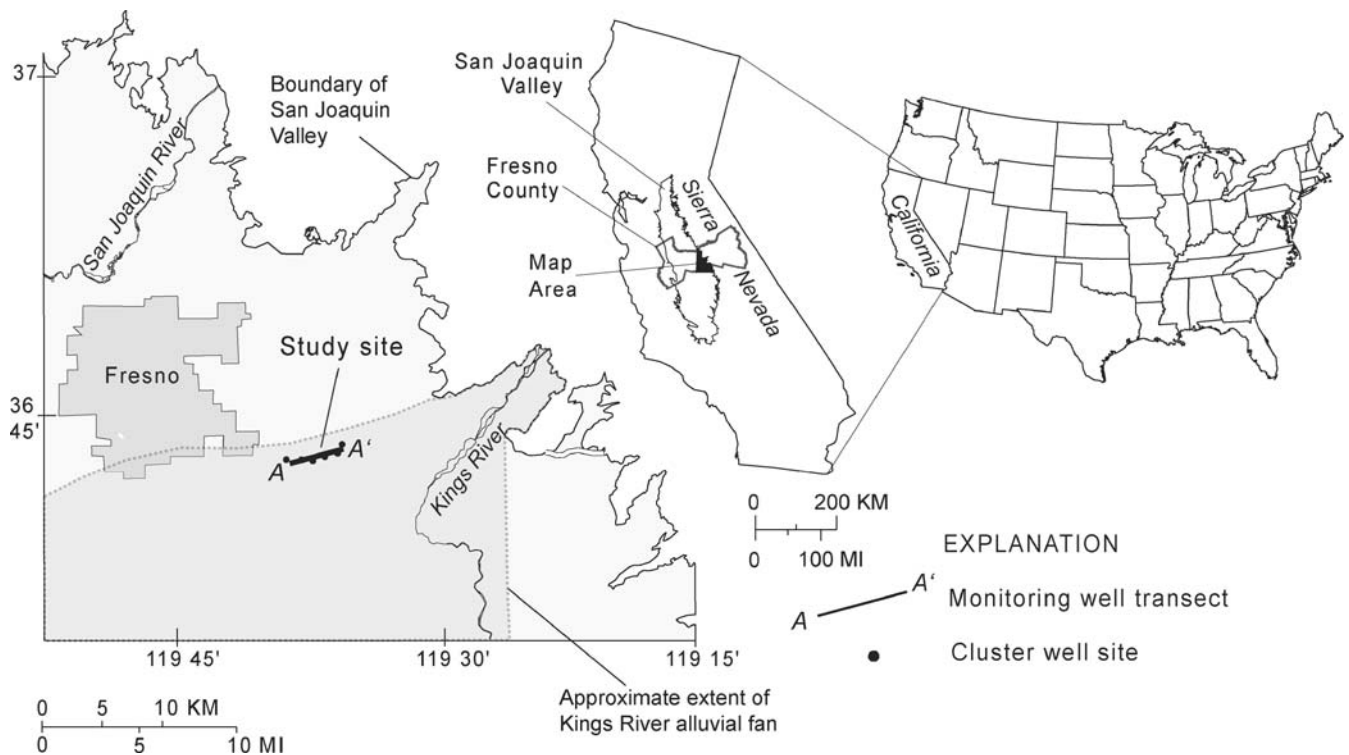


Fig. 1 Study site near Fresno in the eastern San Joaquin Valley, California

The aquifer in the study area is unconfined. Locally, water-bearing layers of sand and gravel are confined by clay layers, but at the regional scale, the sand layers are interconnected (Page and LeBlanc 1969). The transmissivity of the aquifer sediments ranges from about 650 to 2,000 m²/day (Page and LeBlanc 1969); the hydraulic conductivity of the individual hydrogeologic facies units ranges over several orders of magnitude (Burow et al. 1999).

Regional movement of groundwater is southwest, toward the axis of the San Joaquin Valley; however, because of the intensive pumping and irrigation recharge, the dominant flow paths in the aquifer system are vertically downward. The horizontal gradient along the transect is about 0.002, whereas vertical gradients between monitoring wells varied from 0.0003 to 0.1, due to local confining clay layers or pumping of nearby irrigation wells (Burow et al. 1999). Groundwater in the study area is recharged by artificial recharge from canal seepage and infiltration of excess irrigation water; by natural recharge from precipitation, rivers, and streams; and by subsurface inflow from adjacent areas. Pumping is the primary mechanism of groundwater withdrawal in the study area, although some groundwater flows downgradient to adjacent areas or discharges into the San Joaquin and Kings Rivers (Muir 1977).

Groundwater development in the study area began in about 1880. Groundwater withdrawals increased slowly until the 1940s and 1950s when groundwater pumping for irrigation increased sharply (Bertoldi et al. 1991). Beginning in the early 1950s, water from the San Joaquin River, which has low nitrate and DBCP concentrations, was diverted into canals to distribute surface water to farms in

the study area. In 2000, about 14 m³/day of water was used in this region; more than 90% of the water is used for irrigation (Hutson et al. 2004). The relative proportion of surface water and groundwater used for irrigation varies spatially and temporally. Fields adjacent to the irrigation canals likely receive more surface water than fields at greater distances. During wet years, surface-water supplies may be available during the irrigation season, but during dry years, many farmers rely solely on groundwater for irrigation. Although the source of water to specific locations varies from year to year, about 50% of the total urban and agricultural water use is supplied by groundwater (Fred Stumpf, California Department of Water Resources, unpublished data, 1988; Hutson et al. 2004).

Land use and sources of DBCP and nitrate

Agriculture is the predominant land use in the San Joaquin Valley. In the eastern San Joaquin Valley, vineyards occupy about 19% of the more than 1.1 million ha of agricultural land. In eastern Fresno County near the monitoring well transect, grapes have been grown since the late 1800s and the area of harvested grapes has increased steadily from about 570 km² in 1958 to more than 900 km² in the late 1990s (Fresno County Agricultural Commissioner, unpublished data, 2005). The acreage of vineyards near the monitoring well transect has remained relatively constant during the last several decades (Fig. 2); however, some individual fields were converted from vineyards to other crops (primarily orchards) between 1987 and 2000 (California Department of Water Resources 1971, 2001).

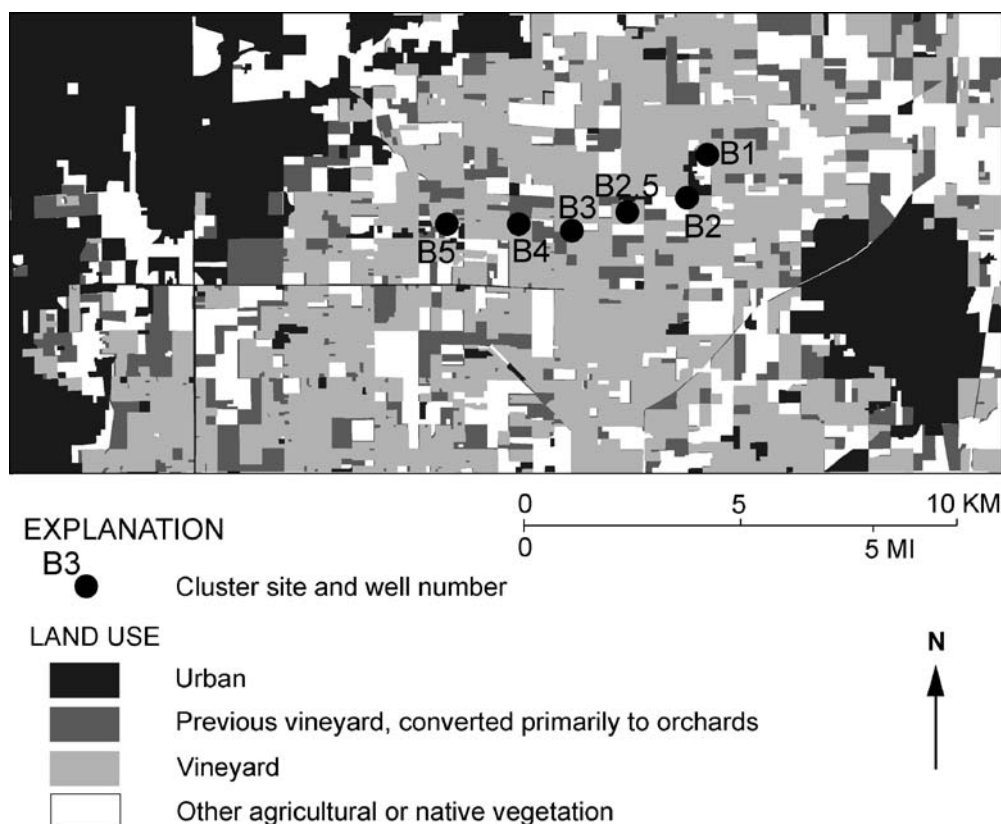


Fig. 2 Land use in the vicinity of the monitoring well transect

Application of DBCP to crops is not well documented, although partial reporting of applications to the California Department of Pesticide Regulation indicates that DBCP was used primarily on vineyards and orchards beginning in the 1950s; the most intensive use was between about 1960 and 1977 (California Department of Food and Agriculture 1973; Domagalski 1997). DBCP was used intermittently to treat nematode problems that occurred especially in older, well-established crops; at many locations it was used only once (California State University Fresno Foundation 1994). In 1977, agricultural use of DBCP was suspended in California in response to concern about the potential hazardous effects of DBCP on human health (California State Water Resources Control Board 2002a).

The persistence of DBCP was documented in laboratory studies, which indicated a half-life ranging from 6.1 years (Deeley et al. 1991) to more than 140 years (Burlinson et al. 1982). The term half-life is a radioactive decay rate that is often used to represent organic chemical transformation. Half-life is used here to represent the time required for the concentration of DBCP to decrease to one-half of the original value, and was determined in laboratory studies by curve-fitting the kinetic data. Several of the chemical and physical properties of DBCP facilitate its transport to groundwater and its continued presence in the aquifer near Fresno. DBCP has a relatively low vapor pressure, 0.8 torr at 21°C, and a moderate water solubility, 700–1,230 mg/L at 20°C (Burlinson et al. 1982; US

Environmental Protection Agency 1985). Using subsurface sediments from the Fresno area, Deeley et al. (1991) determined that DBCP is weakly sorbed (K_D , sorption coefficient, ranged from 0.06 to 0.07 l/kg), owing to the predominantly low organic content of soils in this area. Laboratory experiments by Castro and Belser (1968) indicate that DBCP could undergo biological transformation in soils, but DBCP is resistant to biological transformation in well-oxygenated groundwater (Bloom and Alexander 1990) such as the groundwater in the Fresno area. An apparent half-life for DBCP determined from a contaminant transport modeling study (Burow et al. 1999) is consistent with the 6.1-year half-life determined by Deeley et al. (1991). Results from Burow et al. (1999) indicate that chemical transformation of DBCP to 2-bromoallyl alcohol (BAA) is not a dominant process, however, and the mechanism for decreases in concentrations observed in the Fresno region was not determined. Apparent decreases in DBCP concentrations may be due to unknown transformation processes or the result of physical processes such as hydrodynamic dispersion and pumping and reapplication of irrigation water (Burow et al. 1999).

Nitrate occurs naturally in groundwater; however, in agricultural areas, elevated concentrations of nitrate (above background levels) occur as the result of farming operations where nitrogen fertilizers or manure are applied (Nightingale 1972; Owens et al. 1992), confined animal feeding operations, and rural septic systems. In the study

area, confined animal feeding operations were not present, and background concentrations of nitrate are expected to be less than 3 mg/L (Schmidt 1972). Septic inputs were expected to be small, relative to the contribution from the surrounding crops, although locally they could affect concentrations in water from individual wells. In contrast to DBCP use in the area, nitrogen fertilizer use has generally increased since the 1950s (Alexander and Smith 1990; Battaglin and Goolsby 1994; Ruddy et al. 2006). Nitrogen fertilizers were applied more consistently (spatially and temporally) than DBCP and continued to be applied after DBCP use was banned.

Methods

Twenty monitoring wells were installed in 1994–1995 at depths ranging from 21.3 to 81.7 m below land surface at six cluster sites along a 5.9-km transect southeast of Fresno (Figs. 2 and 3). The length of the screened interval of each well is about 1.5 m (Burow et al. 1997, 1999). The monitoring well transect generally was aligned in the direction of regional groundwater flow in the study area.

Groundwater samples were collected during 1994–1995 and 2003 and analyzed for DBCP and nitrate concentrations. Groundwater samples were also collected

and analyzed for CFCs and SF₆ concentrations to estimate mean groundwater ages along the transect. Concentrations of nitrate plus nitrite are hereafter referred to as nitrate because nitrite was only detected in three samples and accounted for less than 3% of the total nitrate plus nitrite in those samples.

Groundwater samples were collected using protocols developed by the USGS National Water-Quality Assessment (NAWQA) program (Koterba et al. 1995) and are further described in Burow et al. (1999). Analyses of DBCP and nitrate were completed at the USGS National Water-Quality Laboratory (NWQL) in Arvada, Colorado. DBCP samples were collected by filling 40-ml vials with unfiltered water and analyzed by liquid/liquid extraction followed by gas chromatography/electron-capture detection (GC/ECD; Fishman 1993). The detection limit for DBCP using this method was 0.03 µg/L. Nitrate samples were filtered using a 0.45-µm pleated capsule filter and analyzed using standard methods of analysis (Fishman and Friedman 1985). Following collection of the samples described above, a submersible, positive-displacement piston pump with 0.6-cm diameter aluminum tubing was used to collect samples for analysis of CFC concentrations using methods described by Busenberg and Plummer (1992). The samples were analyzed for dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11), and trichlorotrifluoromethane (CFC-113) by the USGS labo-

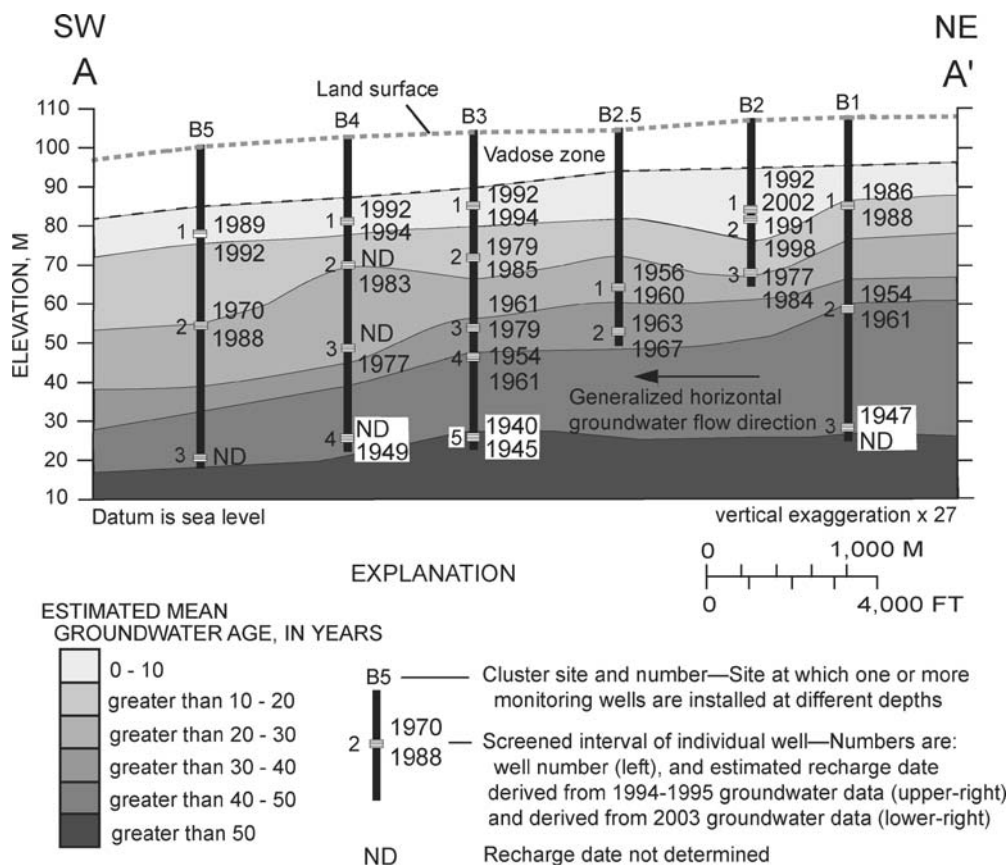


Fig. 3 Monitoring well transect showing estimated groundwater recharge dates determined from chlorofluorocarbon (CFC) concentrations in groundwater samples collected from wells during 1994–1995 and 2003 (refer to Fig. 1 for transect location)

ratory in Reston, Virginia, using a purge-and-trap GC/ECD procedure (Busenberg and Plummer 1992). Samples were collected for dissolved gases (N_2 , Ar, CO_2 , CH_4 , and O_2) and sulfur hexafluoride (SF_6) also. The dissolved gas samples were analyzed by gas chromatography after extraction in headspaces of glass samplers (Busenberg et al. 1998), and SF_6 was determined by methods described in Busenberg and Plummer (2000).

Results and analysis

Groundwater age

Mean groundwater ages (the mean age of groundwater reaching the wells) were estimated along the monitoring well transect using CFC concentrations in samples collected in 1994–1995 (Burow et al. 1999) and in 2003 (Table 1). CFC concentrations were the primary age tracers used in this analysis; SF_6 concentrations were used primarily to corroborate the CFC-determined ages.

In the study area, CFC-based mean groundwater age increased with depth (Fig. 3). Groundwater in the shallow aquifer depth zone, less than or equal to 10 m below the water table, was generally less than 15 years old, whereas groundwater in the deep aquifer depth zone, more than 60 m below the water table, was generally more than 45 years old (Table 1). In most samples, concentrations of two or more tracers were evaluated and compared to simple analytical models of groundwater age (e.g., Cook and Böhlke 1999) using the TRACERMODEL software (Böhlke 2005). The groundwater age interpreted from concentrations of the various tracers were generally concordant, indicating a lack of significant mixing between young (1940s or younger) and old, pre-tracer-aged groundwater. The mean groundwater ages determined from CFC concentrations were based primarily on a piston-flow model (Plummer and Busenberg 2004), where the ages of groundwater samples from different depths are nearly uniform. Some samples indicated local contamination problems and other samples had concentrations consistent with the early (1940s) or late (after 1990s) part of the input curve, which resulted in a greater uncertainty in interpreted mean ages. Additional factors considered in the interpretation of mean age included comparison to concentrations of other solutes, knowledge of specific site history, and fitting of a conceptual model for position of the well in the flow system.

Mean groundwater ages determined from groundwater flow and transport simulations (Weissmann et al. 2002b) were older than the CFC-based mean ages—about 25 years in the shallow aquifer depth zone and more than 100 years in the intermediate (10–60 m below the water table) and the deep depth zones. Simulated CFC concentrations were similar to observed concentrations, however (Weissmann et al. 2002b). The mean ages determined from the simulations were older than CFC-based mean ages because the simulated mean ages account for the full distribution of ages of water reaching the well screens, including water that is older than the introduction of the

age-dating tracers into the environment. As noted by Kazemi et al. (2006), it is difficult to accurately represent complex groundwater-flow systems with simple analytical models; however, the simulated age distributions resembled a piston-flow type curve in the shallow part of the system, and resembled an exponential-piston-flow- or dispersion-type curve with depth as the proportion of old, pre-tracer-aged groundwater increased. Conceptually, the piston-flow part of the age distribution curves likely represents the young fraction of water traveling through preferential flow paths, whereas the exponential part of the age distribution curves represent older water traveling along slower flow paths or diffusing from fine-grained sediments. Because the CFC concentrations indicated a lack of significant mixing, the CFC-based mean ages reflect the mean age of the young, piston-flow fraction of water reaching the wells.

Change in DBCP concentrations

DBCP concentrations in 2003 persisted at concentrations above the USEPA MCL at 7 of the 20 wells along the monitoring well transect (Table 1), at depths of nearly 40 m below the water table. DBCP concentrations increased in 6 of the 20 wells between 1994–1995 and 2003 but decreased in 8 other wells. DBCP was not detected in either 1994–1995 or 2003 in the remaining six wells, likely reflecting variability in application patterns and the effects of heterogeneity on transport in the subsurface. The largest changes in concentration were decreases in the high concentrations at site B2 (Table 1) in the shallow and intermediate depths of the aquifer, suggesting that high-DBCP water was replaced by recharge with low-DBCP water at this site (Fig. 4). DBCP concentrations varied greatly near the water table. DBCP was not detected in either 1994–1995 or 2003 at shallow aquifer depths at sites B3 and B4. DBCP was also not detected in the deepest wells at sites B3, B4, and B5 (Fig. 4). DBCP concentrations increased at intermediate aquifer depths at sites B2.5, B3, and B4, and although the concentrations were low, the largest percentage change in concentrations between 1994–1995 and 2003 was at wells with increases in low concentrations (Table 1). The largest percentage change in concentration occurred at B1-3, the deepest well along the transect where DBCP was detected. DBCP concentrations also increased in the intermediate and shallow depth wells at site B1, indicating that high concentrations of DBCP have moved laterally and downward within the aquifer adjacent to site B1.

Persistence of DBCP and initial concentrations

Using the change in concentration of DBCP and estimated groundwater recharge dates derived from CFC concentrations in groundwater samples collected in 1994–1995 and 2003, an in-situ half-life estimate for DBCP in groundwater was calculated. The DBCP half-life was calculated using a first-order decay equation (Domenico and Schwartz 1998),

Table 1 Mean groundwater age determined from chlorofluorocarbon (CFC) concentrations, and 1,2-dibromo-3-chloropropane (DBCP) and nitrate concentrations in groundwater samples in 1994–1995 and 2003 in the eastern San Joaquin Valley, California

Well (Figs. 2 and 3)	Depth below land surface to midpoint of screened interval (m)	Depth below water table (m)	Depth zone ^a	Mean age for 1994–95 samples (years)	Mean age for 2003 samples (years)	DBCP in 1994–1995 (µg/L) ^b	DBCP in 2003 (µg/L) ^b	Difference in DBCP concentration (percent)	Nitrate in 1994–1995 (mg/L) ^c	Nitrate in 2003 (mg/L) ^c	Difference in nitrate concentration (%)
B1-1	22.4	7.2	Shallow	8	16	2.6	3.1	19	8.6	11	28
B1-2	48.9	33.7	Intermediate	41	43	0.29	0.49	69	2.3	2.4	4
B1-3	79.4	64.2	Deep	48	ND	<0.03	0.18	500	1.4	2.1	50
B2-1	22.4	7.2	Shallow	2	2	2.8	0.17	-94	12	20	67
B2-2	25.2	10.0	Shallow	4	6	3.0	0.44	-85	14	18	29
B2-3	38.9	23.7	Intermediate	18	19	6.4	3.6	-44	11	13	18
B2.5-1	40.4	25.2	Intermediate	39	43	<0.03	0.08	170	1.9	2.2	16
B2.5-2	51.7	36.5	Intermediate	32	37	0.86	0.47	-45	3.3	3.9	18
B3-1	19.0	3.8	Shallow	3	9	<0.03	<0.03	0	6.3	30	380
B3-2	32.2	17.0	Intermediate	16	19	0.3	0.08	-73	11	17	55
B3-3	50.1	34.9	Intermediate	33	24	0.04	0.12	200	5.1	8.6	69
B3-4	57.8	42.6	Intermediate	41	43	0.46	0.17	-63	2.9	3	3
B3-5	78.5	63.3	Deep	55	58	<0.03	<0.03	0	2.3	2	-13
B4-1	21.5	6.3	Shallow	2	9	<0.03	<0.03	0	6	14	130
B4-2	32.8	17.6	Intermediate	ND	20	<0.03	<0.03	0	6.1	8.7	43
B4-3	53.8	38.6	Intermediate	ND	26	0.86	1.1	31	4.1	5.1	24
B4-4	77.3	62.1	Deep	ND	55	<0.03	<0.03	0	2.6	2.6	0
B5-1	22.1	6.9	Shallow	6	12	1.3	0.06	-95	31	40	29
B5-2	45.9	30.7	Intermediate	25	16	2.0	1.7	-12	8.1	10	23
B5-3	79.4	64.2	Deep	ND	ND	<0.03	<0.03	0	5	7.9	58

^a *Shallow* includes depths of less than or equal to 10 m below the water table, *intermediate* includes depths of more than 10 m to 60 m below the water table, and *deep* includes depths of more than 60 m below the water table

^b Micrograms per liter

^c Milligrams per liter

ND no data

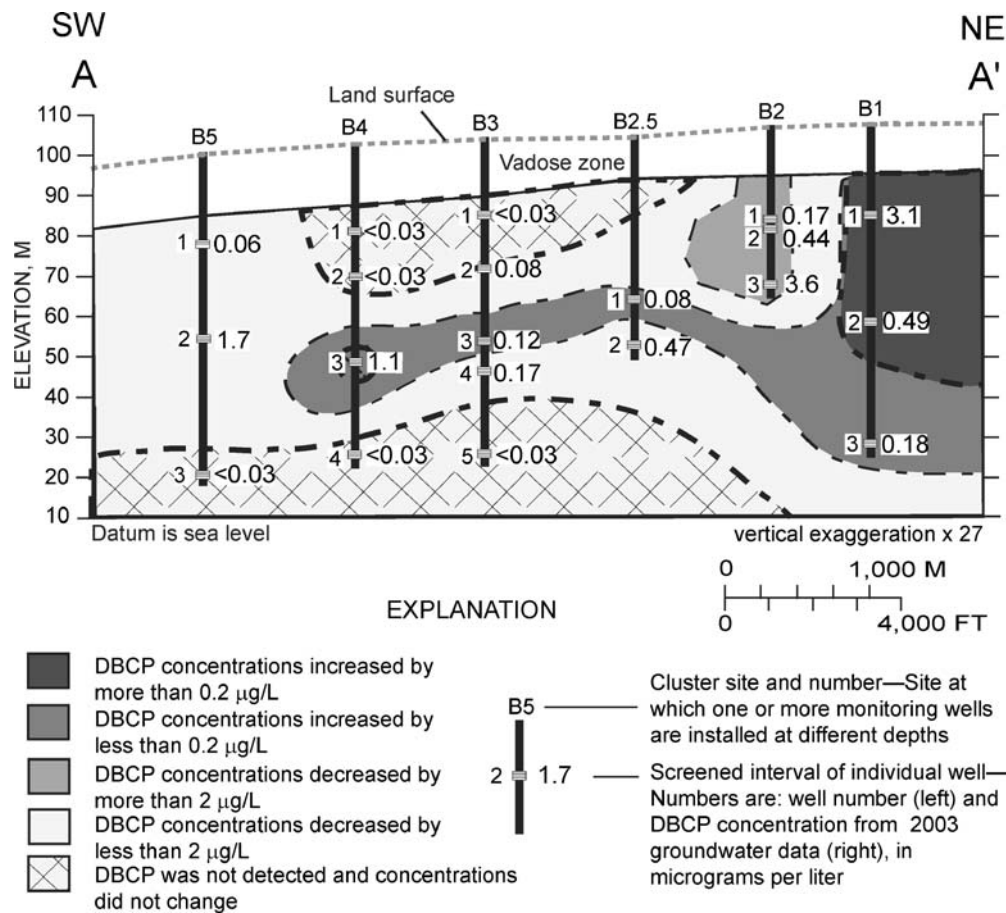


Fig. 4 DBCP concentrations in groundwater samples collected from wells in 2003 and change in DBCP concentrations between 1994–1995 and 2003

$$C_o = C(t)e^{kt}, \quad (1)$$

and

$$k = \frac{0.693}{t_{1/2}}, \quad (2)$$

where C_o is the initial DBCP concentration, $C(t)$ is the DBCP concentration at time t , t is the time since beginning of the reaction, k is the rate constant for a first-order reaction, and $t_{1/2}$ is the half-life for the reaction. The difference in concentrations of DBCP between 1994–1995 and 2003 for wells with similar recharge dates in 1994–1995 and 2003 were used in the half-life calculations (Table 2). Samples were paired if the estimated recharge dates were within 1 year. In most cases, there was only one sample from 1994–1995 and one sample from 2003 for each recharge date. Although the first-order reaction rate may not adequately reflect DBCP reaction rates in the aquifer, limited data were available to characterize the decay function, and previous work was limited to the use of a first-order reaction rate (Burow et al. 1999).

Resulting DBCP half-life estimates ranged from 2 to 6 years, with a median of 4 years. An estimated half-life of in this range is consistent with results of earlier work, in which contaminant transport model results suggested that the effective in-situ half-life of DBCP was about 6 years (Burow et al. 1999). Although the results indicated by this analysis compare generally well with previous estimates

Table 2 Calculated 1,2-dibromo-3-chloropropane (DBCP) half-life from changes in DBCP concentration and groundwater age dates for groundwater samples with common recharge dates in the eastern San Joaquin Valley California

Recharge date	DBCP in 1994–1995 (µg/L) ^a	DBCP in 2003 (µg/L) ^a	Calculated DBCP half-life (years)
1960	0.04	0.17	^b
1977	6.4	1.1	3
1979	0.3	0.12	6
1986	2.6	0.89	5
1989	1.3	3.1	^b
1992	2.8	0.06	2
Mean	2.2	0.91	4
Median	2.0	0.53	4

^a Micrograms per liter

^b Half-life could not be calculated because concentrations increased
Elapsed time between sample dates was 8.5 years

of the in-situ half-life of DBCP determined through contaminant transport modeling, this approach assumes that DBCP is generally well-distributed throughout the profile and that the mixing of older water does not affect the calculations. A mass-balance approach would likely provide a better estimate of in-situ DBCP half-life; however, the data and analysis requirements to attempt a mass balance in this system were prohibitive.

Estimated initial concentrations of DBCP in recharge through time were calculated, again using the first-order decay Eqs. 1 and 2 and the CFC-based and simulated mean groundwater age estimates. Initial concentrations of DBCP calculated using groundwater recharge dates estimated from CFC concentrations and a half-life of 6 years ranged from less than 1 to 70 $\mu\text{g/L}$ (Table 3). Maximum measured concentrations in production wells sampled during the early 1980s were about 50 $\mu\text{g/L}$ (California Department of Pesticide Regulation 1992, 1993, 1994). For comparison, initial concentrations of DBCP were calculated using the simulated mean groundwater age (Weissmann et al. 2002b). Initial concentrations resulting from the simulated mean age were from 2 to 5 orders of magnitude higher than the estimates from the CFC mean age (Table 3). The initial concentration estimates from the simulation-based mean age were extremely high because the simulated age distributions include water that is older than the introduction of DBCP into the environment, and, thus, the simulated mean age does not represent the mean age of the fraction of water containing DBCP. In 6 of 14 wells where DBCP was detected in 2003 (B2-3, B2.5-1, B2.5-2, B3-3, B3-4, and B4-3), estimated groundwater recharge dates from the simulated mean groundwater ages were before 1950, probably before DBCP was used (California State University Fresno Foundation 1994).

The analysis described above indicates that the mean age determined by CFC concentrations better reflects the age of the water containing DBCP than the simulated mean age because the CFC-based mean ages correspond more closely with the timing of the input of DBCP. Additionally, the uncertainty in the simulated mean ages determined in the transport simulations ranged from 10 to 30 years (Weissmann et al. 2002b), suggesting that the simulated mean ages may be a coarse evaluation of age for interpreting changes in chemical concentrations of less than a few decades. To accurately represent the true mean age and predict long-term concentrations in the aquifer, however, a complete distribution of age is needed that includes the age distributions of both the young and old fractions of water.

Change in nitrate concentrations and relation to nitrogen fertilizer use

Nitrate was detected in samples from all wells along the monitoring well transect. Concentrations in 2003 ranged from about 2 mg/L (as nitrogen) in the deepest monitoring wells to 30 to 40 mg/L in the shallow wells (Table 1). Concentrations above the USEPA MCL reached depths of

more than 20 m below the water table. As noted in Burow et al. (1999), and corroborated with dissolved gas data collected in 2003, groundwater along the transect is oxic. Nitrate is expected to be persistent in the aquifer and assumed to be transported conservatively through the system.

Nitrate concentrations increased by more than 1 mg/L between 1994–1995 and 2003 in 12 of 20 wells along the monitoring well transect (Table 1). Increases in nitrate concentrations were the greatest in the shallow part of the aquifer (Fig. 5). Nitrate concentrations in shallow wells at sites B2, B3, B4, and B5 increased by 8–23 mg/L. A plum orchard was in production immediately upgradient from site B3 during the 1990s, and other citrus and nectarine orchards were planted upgradient from site B4 by 2000. Nitrogen fertilizer application rates are typically much higher for orchard crops (158 kg/ha/year) than for grapes (60 kg/ha/year; Rauschkolb and Mikkelsen 1978), although it is not known whether the high nitrate concentrations are due to the differences in crops or whether other sources of nitrate or management practices may have affected concentrations at these sites. Nitrate concentrations increased at a slower rate in wells screened in the intermediate part of the aquifer. Nitrate concentrations generally increased less than 1 mg/L in the deepest wells and remained at concentrations of less than 3.0 mg/L in the intermediate and deep wells at sites B1, B3, and B4.

Nitrate concentrations were compared to nitrogen fertilizer applications to evaluate whether the observed changes in nitrate concentration in recharge through time could be explained by fertilizer use. Using a method outlined by (Böhlke 2002), nitrate concentration in recharge water from nitrogen fertilizer applications were estimated using groundwater recharge dates and data for county-level fertilizer applications. Based on the mean groundwater age from CFC concentrations, a linear groundwater age gradient was characterized, indicating a constant vertical water velocity with depth (Cook and Böhlke 1999). Although the aquifer in the study area is a heterogeneous mixture of alluvial fan sediments, the aquifer receives distributed recharge and lacks extensive confining clays, which is consistent with a generally linear or logarithmic age gradient with depth. The estimated recharge rate, r , was calculated using the equation,

$$r = nZ/\tau, \quad (3)$$

where n is the effective porosity, Z is the saturated thickness of the aquifer, and τ is the mean age of groundwater in the aquifer (Cook and Böhlke 1999; Böhlke 2002). An effective porosity of 0.3 was calculated, assuming an effective porosity ranging from 0.2 to 0.35 and using the proportion of each of the four hydrogeologic facies identified in the study area (Weissmann and Fogg 1999). A saturated thickness of about 50 m was assumed. A mean age of groundwater of 24 years was calculated by averaging the apparent CFC-based mean ages from 1994–1995 and 2003 concentrations (Table 1). The resulting

Table 3 Initial 1,2-dibromo-3-chloropropane (DBCP) concentrations in recharge determined from chlorofluorocarbon (CFC) age dates and simulated age distributions in the eastern San Joaquin Valley, California

Well (Figs. 2 and 3)	Estimated recharge date from CFC age dates in 1994–1995 (year)	Estimated recharge date from CFC age dates in 2003 (year)	Initial DBCP concentration from CFC age dates in 1994–1995 using a half-life of 6 years ($\mu\text{g/L}$) ^a	Initial DBCP concentration from CFC age dates in 2003 using a half-life of 6 years ($\mu\text{g/L}$) ^a	Simulated mean age ^b (years)	Estimated recharge date from simulated mean age ^b (year)	Simulated fraction of groundwater younger than 50 years ^b (%)	Initial DBCP concentration from simulated mean age using a half-life of 20 years ^b ($\mu\text{g/L}$) ^a
B1-1	1986	1988	6.6	20	22	1981	100	40
B1-2	1954	1961	33	70	ND	ND	ND	ND
B1-3	1947	ND	ND	ND	ND	ND	ND	ND
B2-1	1992	2002	3.5	0.2	32	1971	70	6.8
B2-2	1991	1998	4.8	0.9	33	1970	70	20
B2-3	1977	1984	51	32	57	1946	60	2,600
B2.5-1	1956	1960	ND	11	81	1922	60	920
B2.5-2	1963	1967	35	32	140	1863	40	5.0E+6
B3-1	1992	1994	ND	ND	18	1985	90	ND
B3-2	1979	1985	1.9	0.7	34	1969	70	4.1
B3-3	1961	1979	1.8	1.9	87	1916	60	2,800
B3-4	1954	1961	52	24	97	1906	40	12,000
B3-5	1940	1945	ND	ND	ND	ND	ND	ND
B4-1	1992	1994	ND	ND	19	1984	100	ND
B4-2	ND	1983	ND	ND	44	1959	70	ND
B4-3	ND	1977	ND	22	100	1903	30	110,000
B4-4	ND	1949	ND	ND	120	1883	<1	ND
B5-1	1989	1992	2.6	0.2	24	1979	70	1.0
B5-2	1970	1988	36	10	52	1951	60	690
B5-3	ND	ND	ND	ND	120	1883	0	ND

^a Micrograms per liter^b Simulations from Weissmann et al. 2002b

ND No data

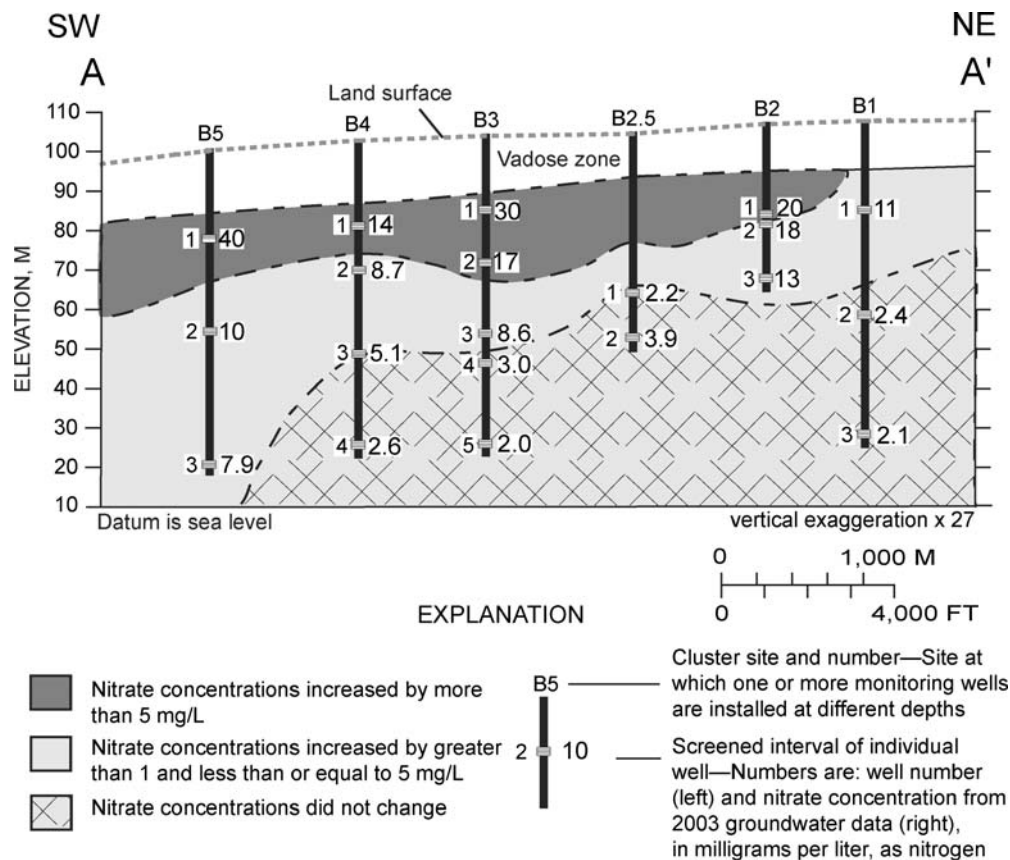


Fig. 5 Nitrate concentrations in groundwater samples collected from wells in 2003 and change in nitrate concentrations between 1994–1995 and 2003

estimated recharge rate was 0.6 m/year. The mean age of groundwater used in the estimate of the recharge rate is based on the CFC mean ages because the elevated nitrate concentrations are likely contained within the piston-flow component of the age distribution, which appears to be adequately represented by the CFC-based ages. The nitrogen application was estimated by dividing the reported application by the area of fertilized land in the county, as determined from annual crop estimates, and assuming that 50% of the nitrogen fertilizer reached the water table.

Estimated initial nitrate concentrations in recharge, represented as observed nitrate concentrations and estimated groundwater recharge dates, generally increased over time (Fig. 6). Estimated nitrogen fertilizer applications also generally increased over time. The axes representing initial nitrate concentration and nitrogen fertilizer application are quantitatively related through the recharge rate such that the application amount on one axis corresponds to the expected concentration in recharge on the other axis (Fig. 6). The estimated nitrogen fertilizer applications were higher than observed nitrate concentrations before about 1980. After this time, the observed nitrate concentrations appear to have increased significantly, whereas the nitrogen fertilizer applications leveled off.

The analysis using nitrogen fertilizer applications may cause the amount of nitrogen expected in the groundwater

samples from annual fertilizer applications to be overestimated because the applications do not account for the wide range of ages represented in each groundwater sample: each fertilizer application amount is associated with only 1 year. Therefore, the nitrogen fertilizer applications were corrected using the distribution of groundwater age from simulations of Weissmann et al. (2002b). The estimated fertilizer application was applied to the fraction of water for each year for each well for which an age distribution was simulated. Before about 1970, the resulting age-corrected nitrogen fertilizer applications correspond more closely to the observed nitrate concentrations than the uncorrected applications, but after 1970, the age-corrected applications appear to be much lower than the observed concentrations (Fig. 6). Local variability in management practices may have contributed to the high observed nitrate concentrations in recent years. The highest observed concentrations are at site B5; concentrations of nitrate were 31 mg/L in 1994–1995 and 40 mg/L in 2003. The history of land use at this site includes vineyards and corn in 1986 and vineyards and orchards in 2000; vineyards comprise about 50% of the area around the well. Consistently high nitrate concentrations relative to those at the other sites along the transect may be due to the presence of orchards and/or corn, which typically receive much more nitrogen fertilizer than vineyards. Concentrations of 30 to 40 mg/L were observed in samples from other wells in the eastern San

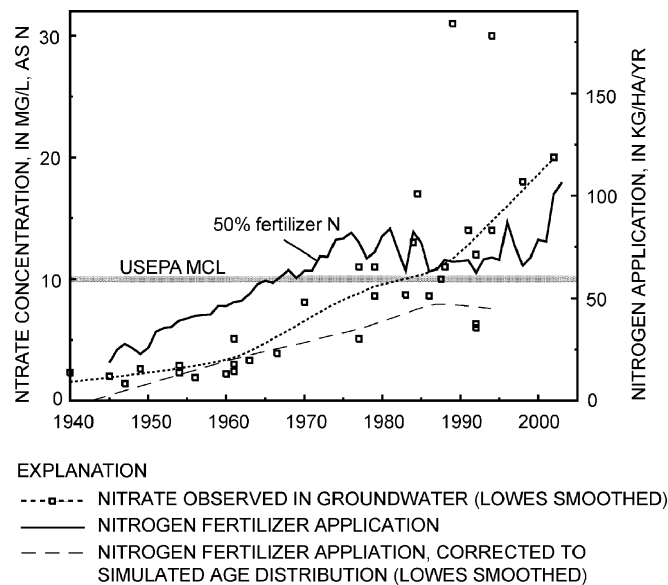


Fig. 6 Estimated initial nitrate concentrations in recharge and nitrogen concentrations estimated from county-level annual nitrogen fertilizer applications. The fertilizer loading curves represent 50% of the nitrogen fertilizer applications divided by the area of fertilized land, dissolved in 0.6 m/year of recharge. Fertilizer loads are also shown corrected for simulated distribution of ages at monitoring wells. USEPA US Environmental Protection Agency; MCL maximum contaminant level

Joaquin Valley representing groundwater beneath almond orchards and corn, alfalfa, and vegetable crops (Burow et al. 1998a).

The discrepancy between observed nitrate concentrations and nitrogen fertilizer applications may also have been caused by evapoconcentration of nitrate as groundwater containing nitrate was pumped and reapplied as irrigation water (Nightingale and Bianchi 1974). Burow et al. (1999) indicated that recycling of groundwater through groundwater pumping and reapplication of irrigation water was likely a dominant process in the study area. This process is likely to result in increasing concentrations of nitrate even without increasing fertilizer applications. Because of the complexity of the groundwater system in this area, however, it is difficult to separate the effect of the recycling of groundwater from other processes such as the mixing of groundwater and surface water used for irrigation and local variability or changes in management practices over the long term. Surface water supplied for irrigation has low nitrate concentrations and using this water would result in lower nitrate concentrations in recharge than groundwater-derived irrigation water.

Long-term changes in water quality in the regional aquifer

Nitrate concentrations from samples collected from the local network of monitoring wells along the transect were compared to nitrate concentrations in regional areal networks to evaluate whether concentrations observed along the monitoring well transect near Fresno were reflected in regional areal networks in the eastern San Joaquin Valley. Concentrations along the transect were compared to networks of domestic and monitoring wells sampled as part of the NAWQA program (Burow et al.

1998a,b) that represent shallow groundwater conditions throughout the aquifer underlying the eastern San Joaquin Valley, an approximately 16,000 km² area. Concentrations along the transect were also compared to concentrations in nearby public-supply wells sampled for regulatory compliance monitoring (Wright et al. 2004). The public-supply wells are typically deep and have long screened intervals.

Nitrate concentrations from wells in the regional areal networks sampled in 2001–2002 were grouped by well type and well depth below the water table to characterize nitrate concentrations in the different parts of the used resource and to extrapolate concentrations areally to other parts of the regional aquifer. In the regional aquifer, domestic wells are generally screened in the shallow part of the aquifer, whereas public-supply wells tend to be screened in the deeper part of the aquifer. Monitoring wells included in the analysis from the regional areal networks are screened near the water table. Similar to conditions observed along the transect, groundwater in the areal networks is typically oxic (Burow et al. 1998a,b). Nitrate is expected to be persistent in the aquifer and assumed to be transported conservatively through groundwater.

Nitrate concentrations are the highest and most variable in the shallow monitoring wells in the areal networks; variability and concentration decrease with depth (Fig. 7). Highly variable concentrations of nitrate at the water table are expected, even with relatively constant fertilizer applications, because of the heterogeneous distribution of sediments and the high variability of nitrate in the moderately thick vadose zone (Harter et al. 1998). The observed decrease in concentration with depth could be due to dispersion and mixing as nitrate moves farther from the source of nitrate in recharge; however, the decrease in

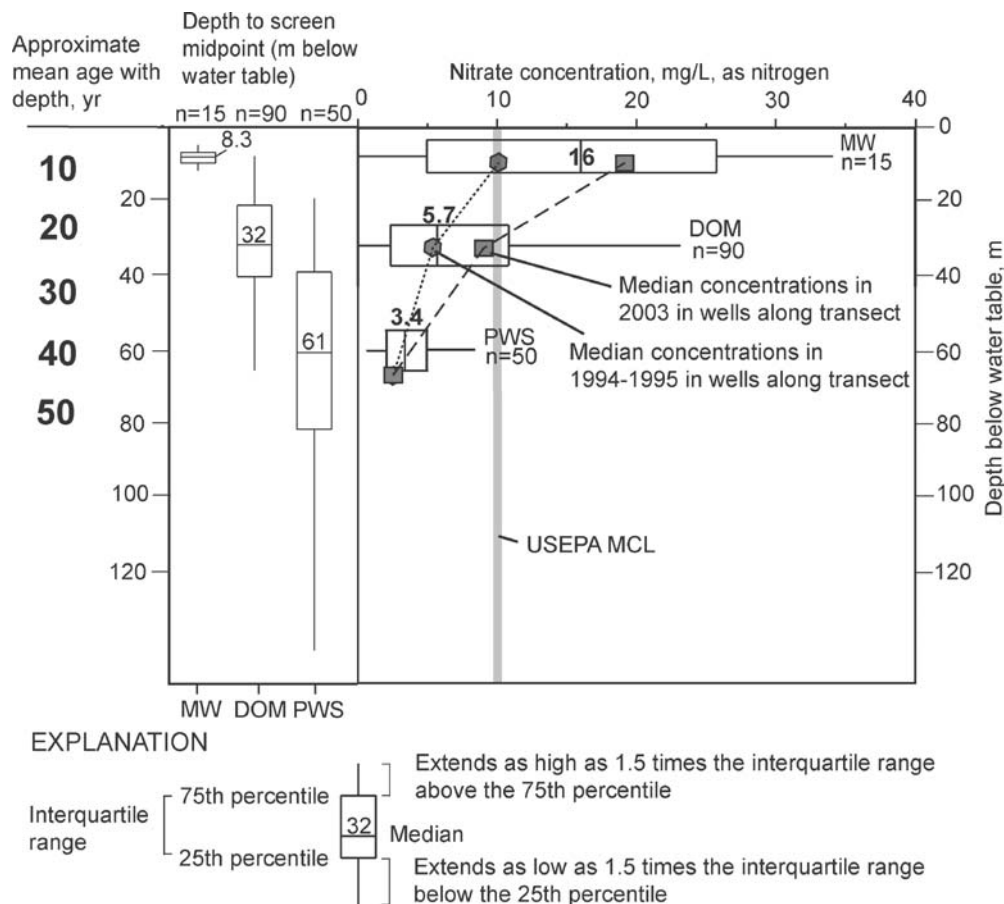


Fig. 7 Relation among nitrate concentration, well type, well screen depth below water table, and groundwater age in the eastern San Joaquin Valley, California. Concentrations in samples from wells along monitoring well transect are grouped by well type. *Boxplots* are concentrations of nitrate sampled in the 2000s from monitoring and domestic well networks (Burow et al. 1998a). Boxplot of concentrations in public-supply wells from Wright et al. (2004). *MW*, monitoring well; *DOM*, domestic well; *PWS*, public-supply well; *n* number of samples; *USEPA*, US Environmental Protection Agency; *MCL*, maximum contaminant level

concentrations with depth is also consistent with an increase in nitrogen fertilizer applications over time (Fig. 6). In the shallow and intermediate depths in the aquifer, concentrations increased between 1994–1995 and 2003 to concentrations similar to those observed at the water table in 1994–1995, indicating that the elevated concentrations at the water table did not attenuate significantly as groundwater moved deeper in the system.

CFC-based mean groundwater age in the monitoring wells along the transect were used to estimate the mean age of groundwater at the depths of the domestic wells; the groundwater in the domestic wells was estimated to be about 20–30 years old. However, mean groundwater age of about 6 years was determined from 18 domestic wells sampled for CFC concentrations in eastern Fresno and Tulare Counties (Spurlock et al. 2000). Despite the apparent differences in groundwater ages, nitrate concentrations observed in the local network of monitoring wells along the transect are within the range of observed concentrations in the areal networks at the same depths. The estimated age of groundwater in domestic wells could be younger than monitoring wells screened at the same depths because of pumping.

Using a similar analysis as described above, CFC-based mean groundwater age at the depths of the public-supply wells are about 30–50 years old. To the extent that the areal networks reflect processes observed in the local network of monitoring wells along the transect and based on chemical data indicating that the aquifer is generally oxic, high nitrate concentrations at the water table in the regional aquifer will likely move deeper in the system without significant attenuation of concentrations over time. However, the proportion of water older than the age-dating tracers increases with depth. The simulated age distributions in the deepest monitoring wells along the transect indicate that groundwater at the depth of the public-supply wells contains from 0 to 40% young water and mean ages are 100 years or more (Weissmann et al. 2002b). Although some young water containing elevated concentrations of nitrate concentrations may reach the deeper wells relatively rapidly along preferential flow paths, the distribution of ages of the old fraction of water reaching the well will control the length of time for concentrations of nitrate to reach levels of concern (MCLs) in the public-supply wells.

Although DBCP was applied less consistently throughout the eastern San Joaquin Valley, causing detection frequencies to vary more, a similar analysis was done using wells from areal networks representing the almond and vineyard land-use settings (Burow et al. 1998a). DBCP was used most commonly on permanent crops such as orchards and vineyards. In contrast to nitrate concentrations, water along the monitoring well transect having the highest median DBCP concentrations of 0.17 $\mu\text{g/L}$ was in the intermediate depth zone, at a depth comparable to that of the areal domestic well networks (Fig. 8). DBCP was detected in 49% of the domestic wells in the areal network; 33% exceeded the USEPA MCL of 0.2 $\mu\text{g/L}$. DBCP was detected in less than 50% of the areal domestic network wells, and, therefore, detection frequencies instead of concentrations were used for comparison to concentrations along the monitoring well transect. The median DBCP concentration in the shallow wells along the monitoring well transect, 0.12 $\mu\text{g/L}$, was lower than the concentration in the intermediate depth zone. Similarly, detection frequencies for the areal networks were lower for the shallow depth wells than the intermediate depth

wells. DBCP was detected in 30% of the areal monitoring well networks at shallow depths; 10% exceeded the USEPA MCL. Because overall detection frequencies and concentrations at the water table appear to be about one-half of those at the depth of the domestic wells, and concentrations of DBCP in the shallow monitoring wells along the transect decreased between 1994–1995 and 2003, DBCP concentrations in domestic wells likely will not increase in the future. DBCP was not detected in public-supply wells in Fresno above the detection limit of 0.5 $\mu\text{g/L}$ (Wright et al. 2004); however, small increases in concentration along the monitoring well transect suggest that DBCP detections and concentrations may increase at the depths of the public-supply wells in the future.

Because of the dominantly vertical-downward flow paths in the aquifer system and the lack of significant attenuation mechanisms, high concentrations of DBCP and nitrate are expected to move downward over time, which would result in increasing concentrations in the deeper domestic and public-supply wells in the future. The length of time to reach concentrations of concern will depend on the age mixtures in water in the wells. Further

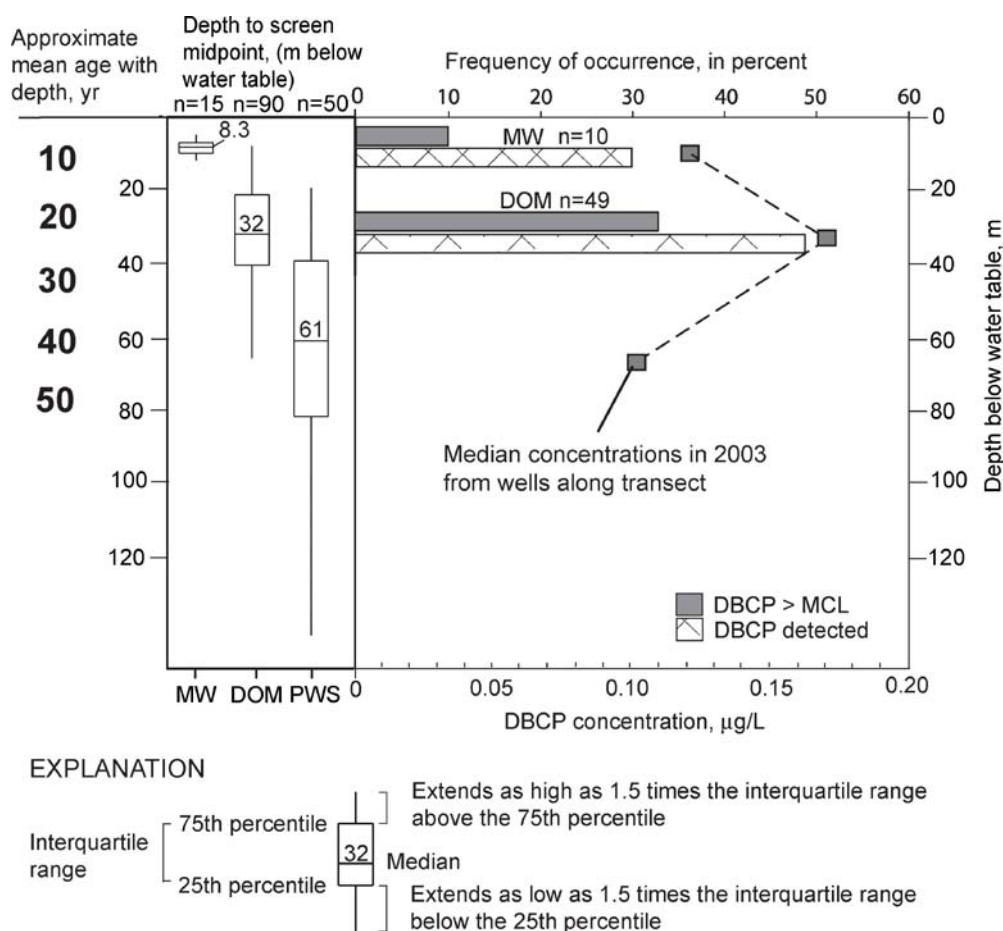


Fig. 8 Relation among DBCP concentration, DBCP detection frequency, well type, well screen depth below water table, and groundwater age in the eastern San Joaquin Valley, California. Concentrations in samples from wells along monitoring well transect are grouped by depth category. Bar charts correspond to frequency of detection of DBCP in wells sampled in the 2000s from monitoring and domestic well networks (Burow et al. 1998a) in the eastern San Joaquin Valley. MW, monitoring well; DOM, domestic well; PWS, public-supply well; n number of samples; > greater than

characterization of ages of the older fraction of water in the regional aquifer is needed to better predict future impacts on the aquifer resource.

Conclusions

Mean groundwater ages determined from CFC concentrations along a monitoring well transect in the eastern San Joaquin Valley, California indicate that groundwater less than about 10 m below the water table is generally less than 15 years old, whereas mean ages of water at depths of more than 60 m below the water table are generally more than 45 years old. DBCP concentrations in groundwater persist at concentrations above the USEPA MCL more than 25 years after its use was banned, although high concentrations of DBCP in the shallow and intermediate depths of the aquifer have been replaced by recharge consisting of water with low DBCP concentrations. DBCP concentrations increased in samples from deep wells along the transect as DBCP moved deeper in the aquifer.

Using the changes in concentration of DBCP and the difference in mean groundwater age between samples collected in 1994–1995 and 2003, an estimated half-life of 2–6 years with a median of 4 years was determined. This half-life is in the range of earlier analysis and contaminant transport modeling results indicating a half-life of about 6 years (Burow et al. 1999). Initial concentrations of DBCP calculated assuming first-order decay and using groundwater recharge dates estimated from CFC concentrations and a half-life of 6 years were consistent with historical data on observed maximum concentrations in the aquifer. Calculations of initial concentrations of DBCP using simulated mean groundwater ages at the study site (Weissmann et al. 2002b) were inconsistent with observed concentrations because the simulated mean age accounts for ages of groundwater that are older than the age-dating tracers. Although the full age distributions are needed to interpret overall travel times in the aquifer and predict future impacts, the mean age of the young fraction of water determined using CFC concentrations better reflects the age of the water containing DBCP than the simulated mean age in this analysis of temporal changes in DBCP concentrations.

Nitrate concentrations ranged from about 2 mg/L in the deepest monitoring wells to 30 to 40 mg/L in the shallow wells, with concentrations above the USEPA MCL reaching depths of more than 20 m below the water table. Nitrate concentrations increased from 8 to 23 mg/L in the shallow part of the aquifer between 1994–1995 and 2003. Estimated initial concentrations of nitrate in recharge indicate an overall increase in nitrate concentrations during the last 50 years, which is generally consistent with increases in nitrogen fertilizer applications. Transport simulation results were used to correct estimates of nitrogen fertilizer loads to account for the full groundwater age distribution reaching the well screens (Weissmann et al. 2002b). Elevated nitrate concentrations resulting from pumping groundwater with high nitrate concentra-

tions and reapplying it as irrigation water may explain elevated concentrations in later years.

DBCP and nitrate concentrations along the monitoring well transect were compared to concentrations in areal monitoring networks. Overall, concentrations along the monitoring well transect were similar to concentrations in the areal networks, suggesting that the dominant processes affecting nitrate concentrations may be similar at both local and regional scales. Nitrate concentrations were the highest and most variable in the shallow monitoring wells in the regional areal monitoring networks; the variability in nitrate concentrations and median values decreased with depth. Because of intensive pumping and irrigation recharge, the dominant groundwater flow paths in the aquifer system are vertically downward. High concentrations in the shallow part of the aquifer could be expected to move downward over time, which would result in increasing concentrations in the deeper domestic and public-supply wells in the future as water with high nitrate concentrations moves deeper in the groundwater system. Therefore, to the extent that the areal networks reflect processes observed in the monitoring wells along the transect and based on chemical data supporting that the regional aquifer is generally oxic, it is likely that high nitrate concentrations at the water table in the regional aquifer will move deeper in the system without significant attenuation of concentrations over time, affecting both domestic and public-supply wells in the regional aquifer. In contrast to nitrate concentrations, the highest DBCP concentrations were in intermediate depths in the aquifer. DBCP concentrations in shallow and intermediate depths in the regional aquifer represented by domestic wells will likely not increase in the future; however, increasing detection of low concentrations of DBCP may occur in public-supply wells open to the deepest parts of the aquifer as DBCP moves deeper in the system.

The analysis of spatial and temporal data on agricultural constituents such as DBCP and nitrate and indicators of mean groundwater age, are a useful approach to understanding the movement and fate of agricultural chemicals in the aquifer and in predicting future impacts on the resource. The data indicate that anthropogenically impacted water containing DBCP and nitrate has reached the deepest wells along the transect, at depths that corresponding to the depths of typical public-supply wells open to the regional aquifer. Mean ages determined from CFC concentrations correlate with the age of the anthropogenically impacted water; however, the CFC-based ages did not characterize the distribution of pre-tracer-aged groundwater. The simulated groundwater age distributions in the monitoring wells (Weissmann et al. 2002b) indicate that these wells contain a large fraction of old water, resulting in mean ages of 100 years or more. Assuming that DBCP and nitrate will continue to move deeper in the system, the length of time for concentrations of DBCP and nitrate to reach levels of concern in the public-supply wells in the regional aquifer will depend on the distribution of ages in water from those wells. Further characterization of the distribution of ages in the regional aquifer is

needed to better predict future impacts of anthropogenic chemicals on the regional aquifer.

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