

**INFLUENCE OF REDOX POTENTIAL ON SELENIUM
DISTRIBUTION IN GROUND WATER, MENDOTA,
WESTERN SAN JOAQUIN VALLEY, CALIFORNIA**

By Neil M. Dubrovsky, John M. Neil, Roger Fujii, Ronald S. Oremland,
and J.T. Hollibaugh

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This report was prepared by the U.S. Geological Survey as part of the Regional Aquifer-System Analysis (RASA) Program. The RASA Program of the U.S. Geological Survey was started in 1978 following a congressional mandate to develop quantitative appraisals of the major ground-water systems of the United States. The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which in aggregate underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system, and accordingly transcend the political subdivisions to which investigations were often arbitrarily limited in the past. The broad objectives for each study are to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to the effective management of the system. The Central Valley RASA study, which focused on the hydrology and geochemistry of ground water in the Central Valley of California, began in 1979. Phase II of the Central Valley RASA began in 1984 and is in progress. The focus during this second phase is on more detailed study of the hydrology and geochemistry of ground water in the San Joaquin Valley, which is the southern half of the Central Valley.

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Conversion Factors

For readers who prefer to use the International System of Units (SI) rather than inch-pound units, the conversion factors for terms used in this report are listed below.

	Multiply	By	To obtain
	foot (ft)	0.3048	meter
	inch (in.)	25.4	millimeter
	mile (mi)	1.6093	kilometer
	pound per square inch (lb/in ²)	6.895	kilopascal

Abbreviations:

g/L	gram per liter
μg/g	microgram per gram
μm	micrometer
μg/L	microgram per liter
μS/cm	microsiemen per centimeter
mg/L	milligram per liter
mL	milliliter
mm/d	millimeter per day
mM	millimole
mV	millivolt
Tu	tritium unit

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$^{\circ}\text{F}=1.8(^{\circ}\text{C})+32$$

Sea Level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929."

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Abstract

The influence of redox potential on selenium transport in shallow ground water was investigated at a site in Mendota, in the western San Joaquin Valley, California. Stratigraphy at the site consists of about 50 feet of complexly interbedded sediments from Sierra Nevada and Coast Range sources, overlying a thick aquifer of Sierra Nevada origin. Under natural conditions, the site was a ground-water discharge area; however, the water table has declined to its present position of 17 to 27 feet below land surface as a result of extensive pumping from the underlying aquifer.

Detailed profiles of ground-water chemistry obtained from wells and from porewater extracted from undisturbed cores show saline water at shallow depths. Specific conductance peaks at greater than 20,000 microsiemens per centimeter at a depth of 36 to 48 feet, and decreases to 3,270 microsiemens per centimeter at a depth of 60 feet. A sharply bounded zone containing water with selenium concentrations greater than 100 micrograms per liter is present at a depth between 18 and 28 feet, with a peak of 1,520 micrograms per liter at a depth of 22.5 feet. Selenium and specific conductance were not correlated in ground water at the site in contrast to the high correlation for ground water from oxidized Coast Range sediments to the west. Redox indicators suggest that the lack of correlation is due to removal of selenium from solution by reduction to a less mobile species. This is inferred by the coincidence of the lower boundary of the high selenium zone with (1) decreasing platinum electrode redox potentials, (2) the disappearance of dissolved oxygen and nitrate, and (3) a rapid increase in iron and manganese concentrations. Laboratory analyses of undisturbed cores indicate that the mechanism of selenium removal is likely microbial reduction to insoluble elemental selenium.

The conceptual model for the site consists of the evolution of saline soil with high selenium concentrations

in a regional ground-water discharge area prior to agricultural development; downward migration of saline, seleniferous ground water due to water-table drawdown; and selenium removal from the downward-migrating ground water by microbially mediated redox reactions.

INTRODUCTION

High concentrations of the trace element selenium in agricultural drain water in the western San Joaquin Valley, California, has been a source of concern since 1983. High selenium concentrations in agricultural drain water entering Kesterson Reservoir apparently were responsible for high mortality rates among waterfowl at the reservoir (Ohlendorf and others, 1986). This finding stimulated research aimed at determining the processes that control the mobility and transport of selenium in ground water in the western San Joaquin Valley. Results of the research show that selenium is correlated with ground-water salinity (Deverel and Fujii, 1988; Deverel and Millard, 1988). Selenium concentrations as high as several thousand micrograms per liter occur in shallow saline ground water that has evolved as a result of leaching of natural soil salts and concentration of dissolved solids by evapotranspiration in areas where the water table is near the land surface (Deverel and Fujii, 1988). Under natural conditions, selenium accumulated in areas with a shallow water table primarily in the ground-water discharge zone near the axis of the valley. Application of large quantities of irrigation water have caused a rapid expansion of areas affected by shallow water tables and salt accumulation problems (Belitz and Heimes, 1990; San Joaquin Valley Drainage Program, 1989).

Research has focused on the Panoche Creek and Cantua Creek alluvial fans in western Fresno County because regional studies showed that these areas have the highest concentrations of selenium in the soil (Tidball and others, 1986) and shallow ground water (Deverel and others, 1984). Cross sections of ground-water chemistry in wells installed in the Panoche Creek alluvial fan show that ground water derived from recent irrigation recharge, identifiable by its tritium concentration, has infiltrated the aquifers to a depth of 50 to 150 ft below the water table (Dubrovsky and Deverel, 1989). This agricultural recharge contains high concentrations of dissolved solids, selenium, and other trace elements.

Although most irrigation water applied in the western San Joaquin Valley is imported from the Sacramento-San Joaquin Delta by canals, large quantities of ground water are still pumped for various uses. Most of this ground water is withdrawn from Sierra Nevada sediments that underlie flood-basin deposits or alluvial-fan sediments derived from the Coast Range. Permeability generally is higher in the Sierra Nevada sediments than Coast Range sediments (Miller and others, 1971; Bull and Miller, 1975). Most water from the Sierra Nevada sediments is of better quality than water from the Coast Range sediments (Miller and others, 1971, p. 39). Ground water in Sierra Nevada sediments generally is more reducing than ground water in Coast Range sediments (Davis and Poland, 1957; Hotchkiss and Balding, 1971; Lettis, 1982; and Dubrovsky, 1989).

An important concern for water management in this area is the potential contamination of the extensively used aquifer in the Sierra Nevada sediments by overlying high-selenium, shallow ground water in Coast Range sediments. The present-day direction of ground-water flow in the western part of the valley trough, where the potential for such contamination is greatest, is downward and eastward. Moreover, downward and eastward flow could be increased by management strategies that use pumping of deep wells in Sierra Nevada sediments to control the water table. There is a possibility, however, that selenium in shallow ground water that moves across the boundary of the Coast Range and Sierra Nevada sediments may be removed from solution due to the low solubility of selenium in the chemically reducing conditions that prevail in the Sierra Nevada sediments.

This research was conducted as part of the Regional Aquifer-System Analysis Program of the U.S. Geological Survey. The purposes of this study

were to determine the vertical distribution of selenium in ground water across the lithologic interface of Coast Range and Sierra Nevada sediments and to evaluate the influence of ground-water redox potential on selenium concentrations. A site at the eastern edge of the Panoche Creek alluvial fan in Mendota was selected for study because the interface of Coast Range and Sierra Nevada sediments is at a shallow depth, facilitating detailed sampling. The site also was selected because a geochemical control on selenium concentrations was indicated by preliminary data showing that selenium concentrations in ground water decreased from almost 500 $\mu\text{g/L}$ in ground water from Coast Range sediments at a depth of 24 ft to less than 1 $\mu\text{g/L}$ in ground water from Sierra Nevada sand at a depth of 60 ft. The approach was to determine the vertical distribution of selenium and other pertinent constituents in the ground water by sampling observation wells and extracting porewater from undisturbed cores. The selenium concentration of the sediments also was determined, and the potential for selenium reduction by microbial processes was evaluated.

HYDROGEOLOGIC SETTING

The study site was in Mendota, California, about 1 mi southwest of the San Joaquin River near the center of the San Joaquin Valley (fig. 1). The climate of the area is semiarid with a mean annual precipitation of about 12 in. The site has never been farmed and, until recently, was on undeveloped land at the Mendota municipal airfield.

STRATIGRAPHY

The general stratigraphy of the study site consists of about 55 ft of predominantly fine-grained deposits underlain by about 400 ft of medium- to coarse-grained, well-sorted sand. The geologic map of the San Joaquin Valley identifies the surficial sediments as recent flood-basin deposits of the San Joaquin River (California Division of Mines and Geology, 1959). A more recent evaluation concluded that the surficial geology of the site consists of fine-grained Coast Range sediments deposited at the toe of the Panoche Creek alluvial fan (Lettis, 1982). Medium- to coarse-grained sand at greater depths is a mixture of river channel and alluvial-fan sediments derived from the Sierra Nevada and deposited at a time when the axis of the San Joaquin Valley was west of its present position.

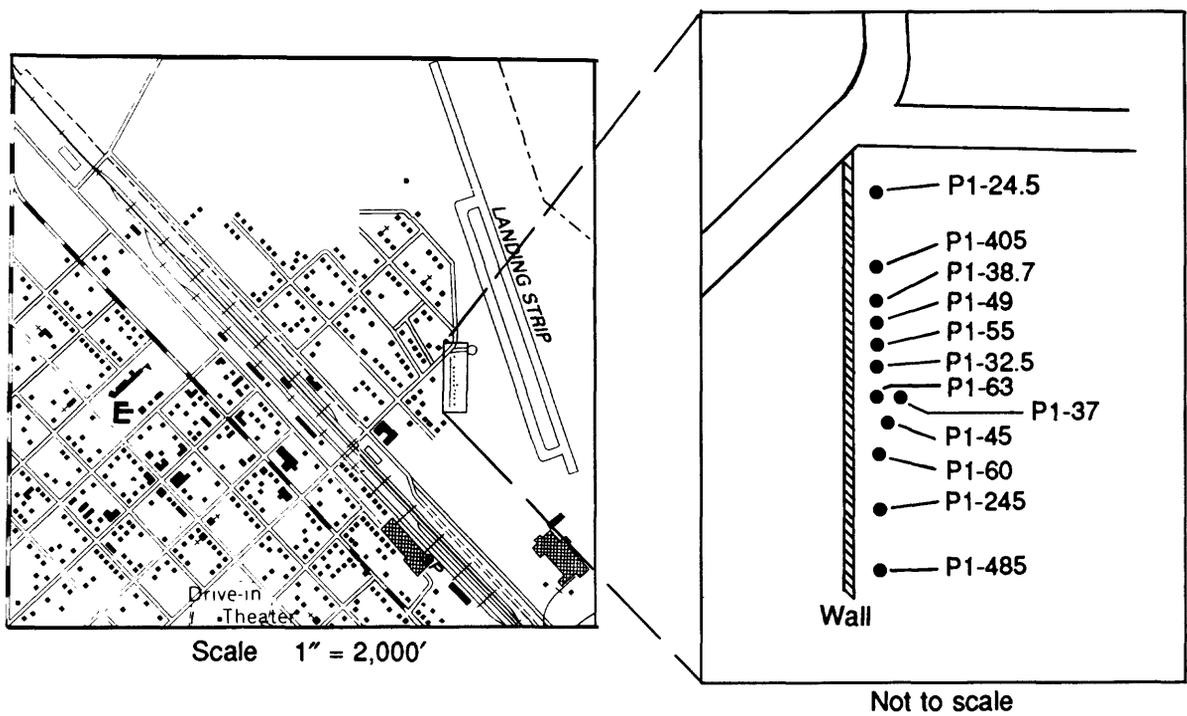
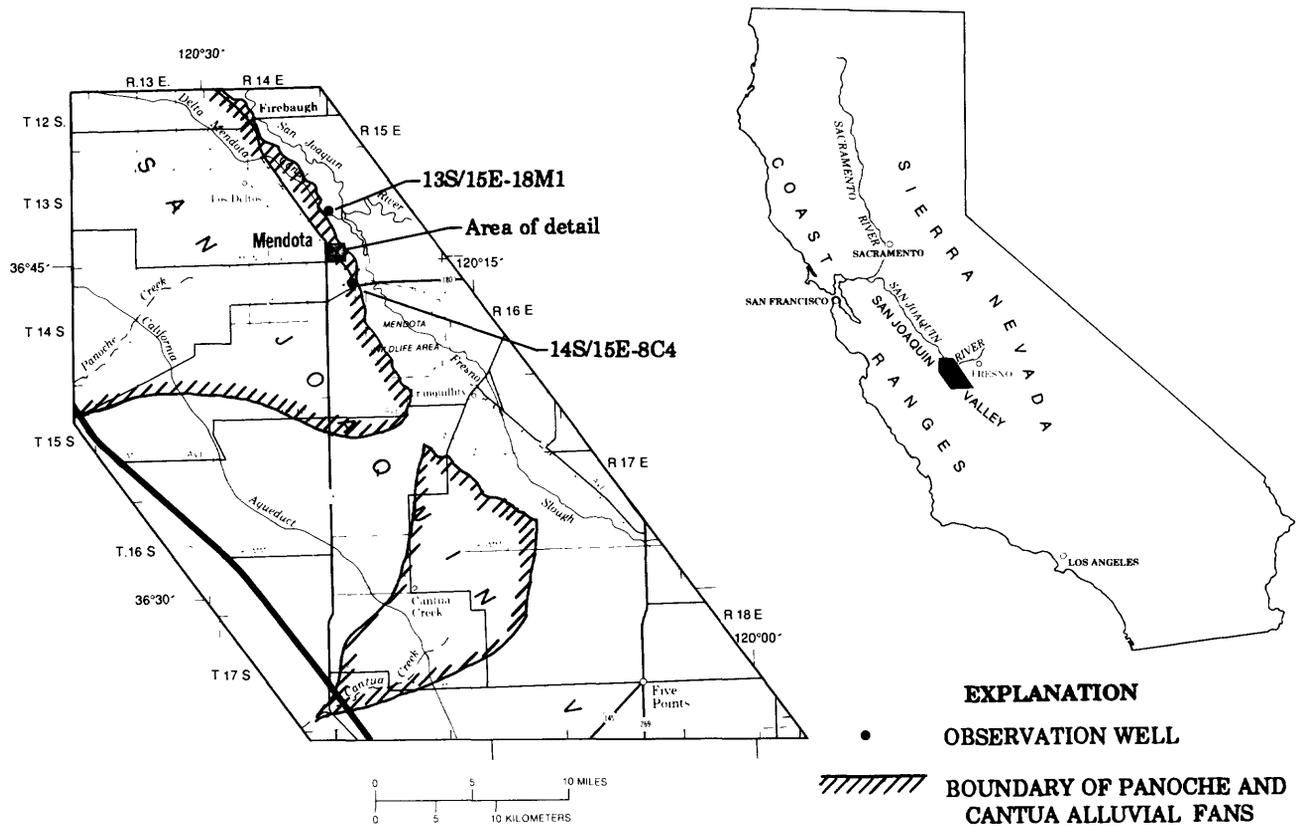


Figure 1. Location of study site.

The upper 60 ft of sediment at the site was continuously cored in the PI- 55 borehole and logged in detail to better define the source area of the sediment and the depositional environment. The lithology in this interval showed a large range in grain size, color, structure, and gypsum content (fig. 2). The upper 11 ft was a buff sandy clay loam with abundant root structure and secondary gypsum and calcite in the upper 7 ft. This was followed by a transition zone where fine-grained layers of clay and silt alternate with thin layers of sand, some of which show strong iron hydroxide staining. Mottling occurred at about 14 ft and intensified over the next 10 ft with reduced gray sediments gradually predominating. From about a depth of 26 to 60 ft, the sediments were blue gray. Medium- to coarse-grained sand predominated from about a depth of 26 to 42 ft, followed by silty sand, and medium- to coarse-grained sand at a depth greater than about 54 ft.

The source of the sediment at the site is important because the concentration of selenium in Coast Range sediments is higher than in Sierra Nevada sediments (Tidball and others, 1986), and reactions between the sediments and ground water may release selenium into solution. The source area usually is determined on the basis of mineralogy and lithic fragments (Meade, 1967, p. 5). On the basis of these criteria, medium- and coarse-grained sand at depths greater than about 26 ft were derived almost exclusively from the Sierra Nevada. Identification on this basis is difficult when the sediment is fine grained. Most of the fine-grained sediment in the upper 26 ft probably is derived from the Coast Range because of its high salinity, geomorphic location, and interbedding with coarser grained Coast Range sediments.

HYDROLOGY

The study site was in the western part of the valley trough where artesian conditions occurred in the semiconfined zone under natural conditions (Mendenhall and others, 1916), and marshland was present prior to development (Hamilton, 1916). Soil at the site was highly saline with greater than 1 percent total soluble solids by weight (Harradine, 1950). The accumulation of soil salts requires a shallow water table, which along with the observations noted above, indicates that the site was an area of ground-water discharge for most of the year. This observation is significant because high selenium concentrations in shallow ground water generally are associated with saline soils in the western San Joaquin Valley (Deverel and Gallanthine, 1989).

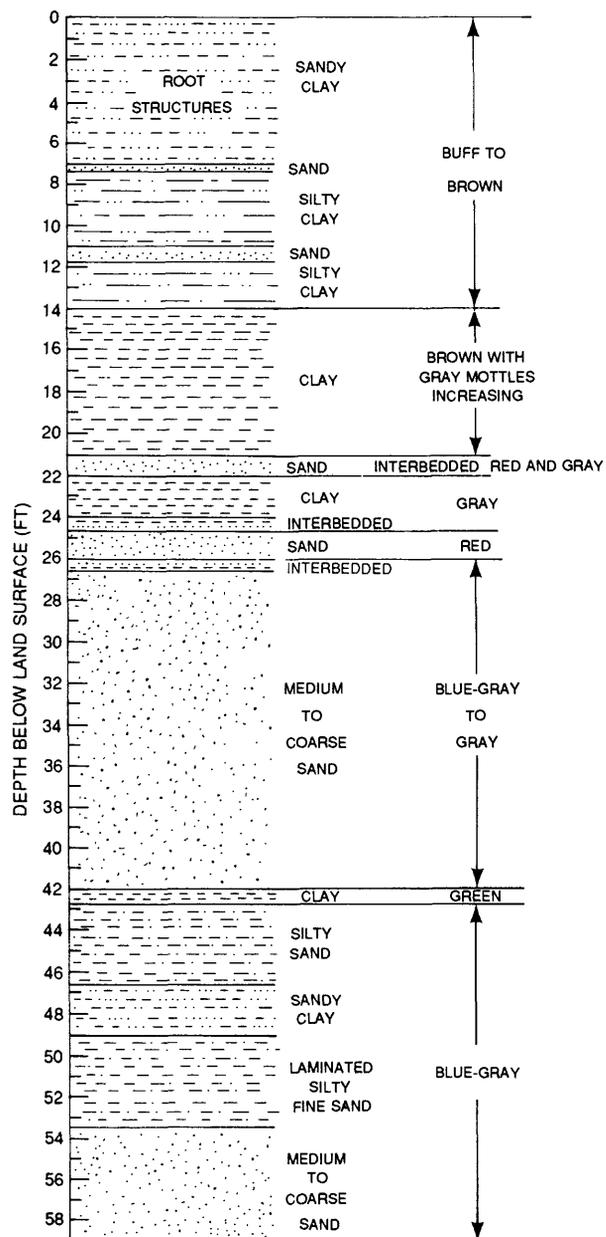


Figure 2. Lithologic log of the upper 60 feet of sediment from continuous core from observation well P1-55.

Prior to construction of reservoirs on the major Sierra Nevada rivers, ground-water recharge to the site was due to seasonal flooding by Sierra Nevada runoff in the San Joaquin River and Fresno Slough. Small amounts of additional recharge may have occurred as a result of sparse annual precipitation and infrequent high flows in Panoche Creek. Maps of the irrigation history of the central western San Joaquin Valley show that by 1955 most of the area

surrounding the site at a distance of 1 mi was irrigated by ground water; however, interviews with local officials indicated that the site has never been irrigated. At present, the town of Mendota and irrigated fields immediately west of the site are the closest source of recharge although the quantity of water that infiltrates from leaking water mains, lawn watering, or other municipal uses is not known.

The rapid development of agriculture, particularly following World War II, required large quantities of irrigation water. Most of this demand was met by ground-water withdrawals, which resulted in regional declines in the water table (Belitz and Heimes, 1990). The large quantities of ground-water withdrawal resulted in a lowering of the water table in distal areas of the alluvial fans. A comparison of water-table maps for the area in 1908 and 1952 shows that the water-table altitude decreased by about 20 ft at the study site (Belitz and Heimes, 1990). Extensive ground-water pumping, and likely additional water-table decline, continued until 1967 after which pumping decreased due to the use of surface water imported by the California Aqueduct (Belitz and Heimes, 1990, fig. 10).

Following the decrease in pumping after 1967, water levels near the site recovered. Data for well 13S/15E-18M1 about 3 mi northwest of the study site indicate a steady decline in water levels from 1959 to 1967 for a total decline of about 25 ft (fig. 3). The water levels were erratic during 1967-75; however, water levels rose about 25 ft during 1978-84 to an altitude equal to or greater than those in 1958. Water

levels for well 14S/15E-8C4 about 2 mi southeast of the study site show no change from 1963 to 1969; however, water-level altitude shows a uniform rate of increase from 1969 through 1984 for a total of about 35 ft of recovery (fig. 3). Although no records are available for the site itself, data for these wells indicate that the water table at the site probably was drawn down 20 to 35 ft or more by ground-water pumping compared to the predevelopment conditions and has recovered since the decrease in ground-water withdrawal in 1967. Recovery may be less than in adjacent areas due to the absence of irrigation recharge at the site, and the present water-table altitude probably is lower than under natural conditions but higher than in the recent past.

Data for the observation wells at the study site showed seasonal fluctuations in the potentiometric heads (fig. 4) from April 1987 through July 1988. In April 1987, the water level in the 24.5-foot well was 18.2 ft below the land surface of 152 ft, and there was a steep downward gradient between the 38.7- and 55-foot wells. From April to August, the water levels declined in all wells almost uniformly, with a slight increase in the downward gradient near the bottom of the section. In September, the water table reached a maximum depth of 26.0 ft below land surface, and there was a reversal in the gradient as the water levels in wells at 55 and 49 ft increased by about 1 ft. The water levels rose in all wells through the autumn and winter, and upward gradients persisted throughout the profile until March. From February to March, water levels in the lower two wells declined by about 2 ft, and downward gradients were again established.

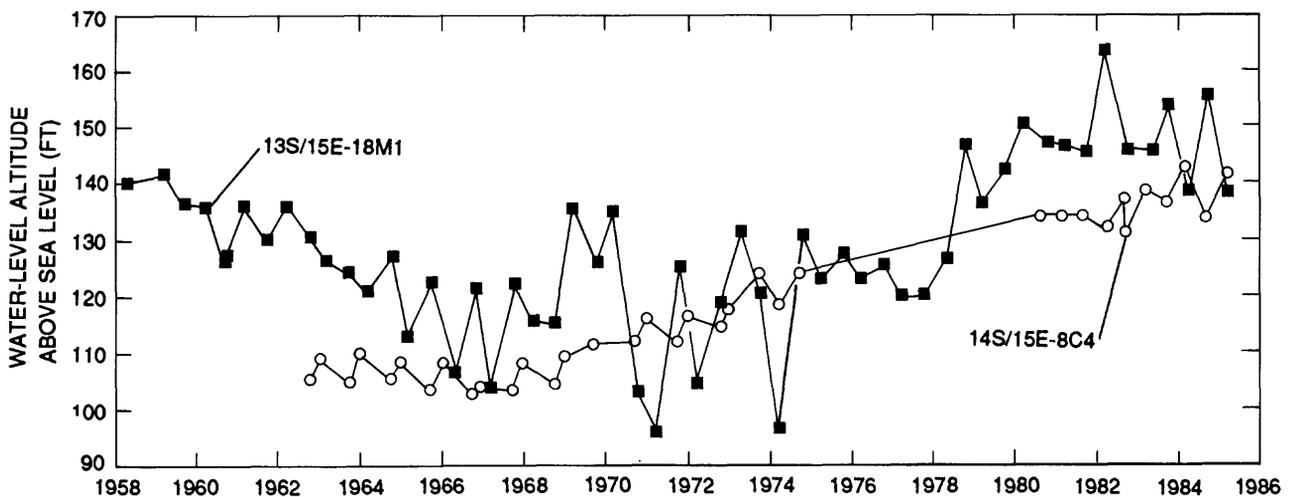


Figure 3. Water-level changes from 1957 to 1985 for two production wells near the study site.

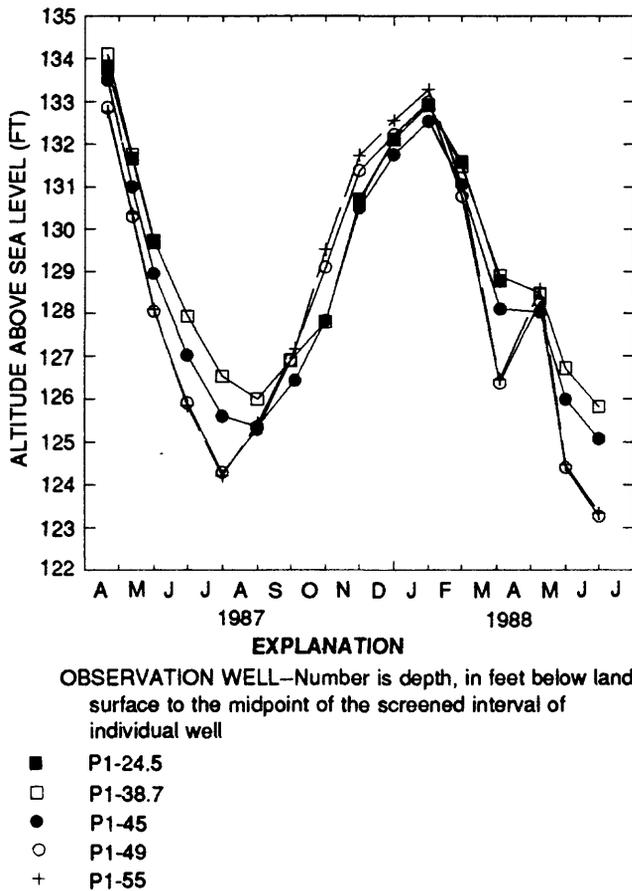


Figure 4. Seasonal fluctuations in potentiometric heads in observation wells, April 1987 through July 1988.

The declining water levels in the spring and summer correspond to a period when the Sierra Nevada sediments are extensively pumped for irrigation and agricultural processing water. The quantity of pumping is greatly decreased in the early autumn, resulting in water-level recovery. This seasonal water use results in maximum fluctuations of more than 7.5 ft in the overlying Coast Range sediment. This is larger than the 1- to 5-foot seasonal fluctuation measured for wells higher up on the Coast Range alluvial fans in irrigated areas that are not drained (Belitz and Heimes, 1990) and probably is larger than the seasonal fluctuation in the predevelopment flow system.

METHODS

FIELD

Data on the hydrology and chemistry of the site were collected by two methods: installation of observation wells and recovery of porewater and sediment samples from undisturbed core. Initially, three wells were drilled and completed at depths of 24 to 245 ft. Subsequently, five additional wells were drilled and completed at depths between 25 and 60 ft in order to obtain more detail on the vertical distribution of ground-water chemistry. All wells at depths less than 60 ft were completed using a hollow stem auger and 2-inch PVC pipe with screen lengths of 2 to 10 ft. The screened interval of these wells was sandpacked and isolated using a bentonite grout. In the deeper wells, 6-inch PVC casings were installed with 10-foot screens using mud rotary drilling, sandpacked, and then grouted to land surface. Wells were monitored for water levels, and water-quality samples were collected.

WELL SAMPLING

Prior to sample collection, wells were purged of three casing volumes of water or until the specific conductance stabilized to within 10 percent in consecutive casing volumes. During this period, a flow-through cell was used to monitor temperature, pH, dissolved-oxygen concentrations, and platinum electrode redox potential (in mV) of the ground water without exposing it to the atmosphere. The pH meters and electrodes used were calibrated using pH 7 and 10 buffers before each measurement. The platinum electrode was checked against ZoBell's solution (Nordstrom, 1977).

CORE SAMPLING

Detailed information on the vertical variation in ground water and sediment chemistry was collected by extracting porewater from continuous, undisturbed cores. Two-foot core intervals were collected by inserting a core barrel lined with two 1-foot long

sections of 2-inch diameter clear plastic tubing down the annulus of a hollow stem auger. Porewater was hydraulically extracted in the field using a procedure similar to the ones described by Siever (1962) and Manheim (1966). Each 1-foot section was subsampled for porewater as soon as each core was recovered. Two sets of cores, P1-55 and P1-63, were processed at the site immediately after collection, and the P1-49 core was returned to the laboratory for porewater extraction. Samples from core P1-37 were sealed and stored on ice immediately upon collection for subsequent analysis of selenate reduction by microbial activity.

Specific conductance was measured on all porewater samples as soon as they were extracted. In addition, samples were collected for the analysis of total selenium, selenium species, major elements, and the stable isotopes of oxygen and hydrogen. The samples for selenium speciation analysis were filtered through a 0.45- μm filter and acidified using concentrated hydrochloric acid, then all samples were chilled.

Water samples to be analyzed for major and trace dissolved constituents were filtered immediately upon collection using 0.45- μm membrane filters and stored in polyethylene bottles. All bottles and sampling equipment were rinsed three times with the water to be sampled prior to sample collection. Samples collected for cation analysis were preserved by using nitric acid. Samples for anion analysis and specific conductance were untreated although the sample for nitrogen species was chilled. An unfiltered sample for analysis of total organic carbon was collected in a glass bottle. Unfiltered samples for tritium and the stable isotopes of oxygen and hydrogen also were collected in glass bottles with polyseal tops. Incremental alkalinity titrations were done on unfiltered samples as soon as the sample was collected.

LABORATORY

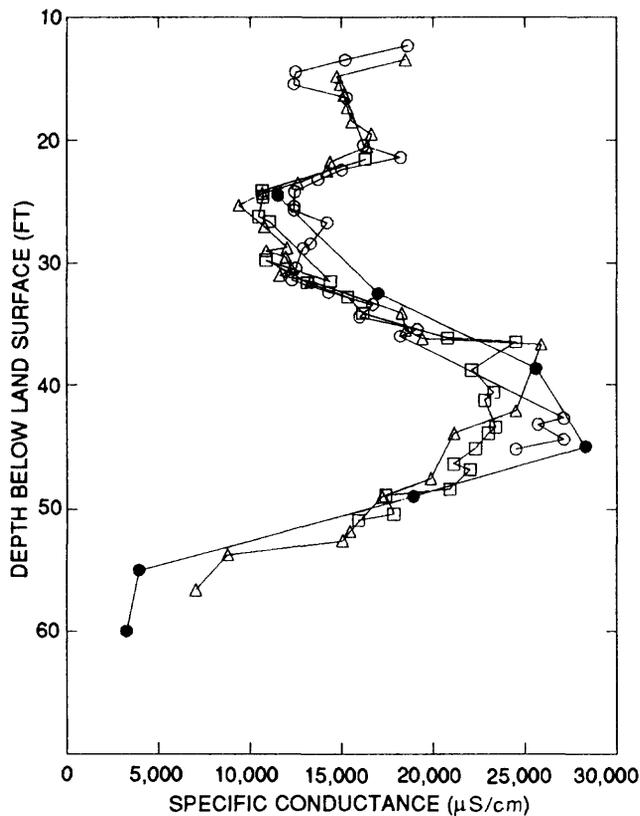
Major and trace elements were analyzed by the U.S. Geological Survey's National Water Quality Laboratory in Arvada, Colorado, by standard methods

described by Skougstad and others (1985). Complete analyses of major constituents were done only on well samples. Arsenic and selenium concentrations were determined by hydride generation and atomic absorption spectrometry.

The porewater samples were analyzed for total selenium and, where a sufficient volume was available, selenium species in the laboratory of the U.S. Geological Survey, Sacramento, California, according to the methods described in Fio and Fujii (1990). Manganese concentrations were analyzed on porewater samples preserved with 0.1 mL nitric acid by standard methods (Skougstad and others, 1985) at the U.S. Bureau of Reclamation Laboratory in Sacramento, California, in 1987 and the U.S. Geological Survey National Water Quality Laboratory in 1988. The stable isotopes of oxygen and hydrogen were analyzed at the Isotope Fractionation Laboratory of the U.S. Geological Survey in Reston, Virginia, according to the methods in Epstein and Mayeda (1953) and Kendall and Coplen (1985), respectively. Stable-isotopes results are reported relative to Vienna Standard Mean Oceanic Water (V-SMOW) in per mil notation (‰). Tritium analysis was done by electrolytic enrichment followed by scintillation counting (International Atomic Energy Agency, 1976) by the Environmental Isotope Laboratory at the University of Waterloo, Ontario, Canada.

GENERAL WATER CHEMISTRY

Both porewater and ground-water samples show a zone of high but variable salinity at depths between 12 and 55 ft. The specific conductance of porewater from three cores collected during more than 1 year, ranged from 7,040 $\mu\text{S}/\text{cm}$ at 56.1 ft below land surface to 27,100 $\mu\text{S}/\text{cm}$ at 43.0 and 44.8 ft below land surface (fig. 5). Ground-water samples show the same profile and indicate that, in addition, specific conductance ranged from 3,000 to 4,000 $\mu\text{S}/\text{cm}$ at depths equal to or greater than 60 ft. Specific conductance at depths less than 60 ft is more than two orders of magnitude greater than specific conductance of surface water draining the Sierra Nevada.



EXPLANATION

- POREWATER SAMPLE EXTRACTED FROM CORES—Core samples were collected during drilling of observation wells
- P1-49
 - △ P1-55
 - P1-63
- GROUND-WATER SAMPLES FROM OBSERVATION WELLS

Figure 5. Specific conductance of porewater samples from three cores and ground-water samples from observation wells.

The major-ion chemistry of ground-water samples is plotted in figure 6 (table 1). In addition to the data for the shallow wells, the analysis of a sample from a well completed at 245 ft, which is typical of deeper ground water at the site, is included for comparison. All ground water sampled was classified as sodium chloride water with sodium always greater than

66 percent of the cation equivalents and chloride always greater than 57 percent of the anion equivalents. Ground water from the wells at depths between 32 and 49 ft have very similar cation ratios. Anion ratios in these samples showed a constant proportion of carbonate plus bicarbonate but an inverse proportionality between chloride and sulfate. Saline sodium chloride ground water also was reported by Davis and others (1959, p. 176) near the valley axis.

The chemical similarity of water from depths of 32.5 to 49 ft indicates a common origin and history attributed to a combination of the concentration of dissolved solids by evapotranspiration and the redissolution of soil salts produced by earlier cycles of desiccation. The decrease in dissolved-solids concentrations from a depth of 45 to 60 ft is the result of mixing shallow, saline ground water with deep ground water with lower dissolved-solids concentrations.

AGE AND ORIGIN OF GROUND WATER

The stable-isotope composition of ground water along with tritium dating were used to help evaluate the age and origin of ground water. The profile of the delta oxygen-18 ($\delta^{18}\text{O}$) in ground-water samples show similar values ranging from -9.00 to -9.95 ‰ at depths of 24.5 to 49 ft (fig. 7, table 2). Delta oxygen-18 was -10.85 ‰ for ground water in wells at depths of 55 and 60 ft. The values for the deeper wells are similar to the value of -11.10 ‰ in the 245-foot well, as well as the $\delta^{18}\text{O}$ of about -11 ‰ for imported canal water (Deverel and Gallanthine, 1989) used for irrigation in the western San Joaquin Valley. The similarity of the irrigation water and the deep ground water precludes identification of the source of the shallow water solely on the basis of oxygen isotopes. Porewater samples from 25.3 to 50.4 ft had $\delta^{18}\text{O}$ values similar to ground water from wells at similar depths (fig. 7, table 3). Porewater data shows a significant enrichment in $\delta^{18}\text{O}$ from -9.90 ‰ at a depth of 25.3 ft to a maximum of -5.70 ‰ at a depth of 13.5 ft, slightly above the water table (fig. 7). Enrichment in $\delta^{18}\text{O}$ indicates that the shallower porewater has undergone evaporation.

EXPLANATION

OBSERVATION WELL--Number is depth, in feet below land surface to the midpoint of the screened interval of individual well

- P1-24.5
- P1-32.5
- ⊕ P1-38.7
- × P1-45
- ◇ P1-49
- ▽ P1-55
- ⊠ P1-60
- ⊡ P1-245

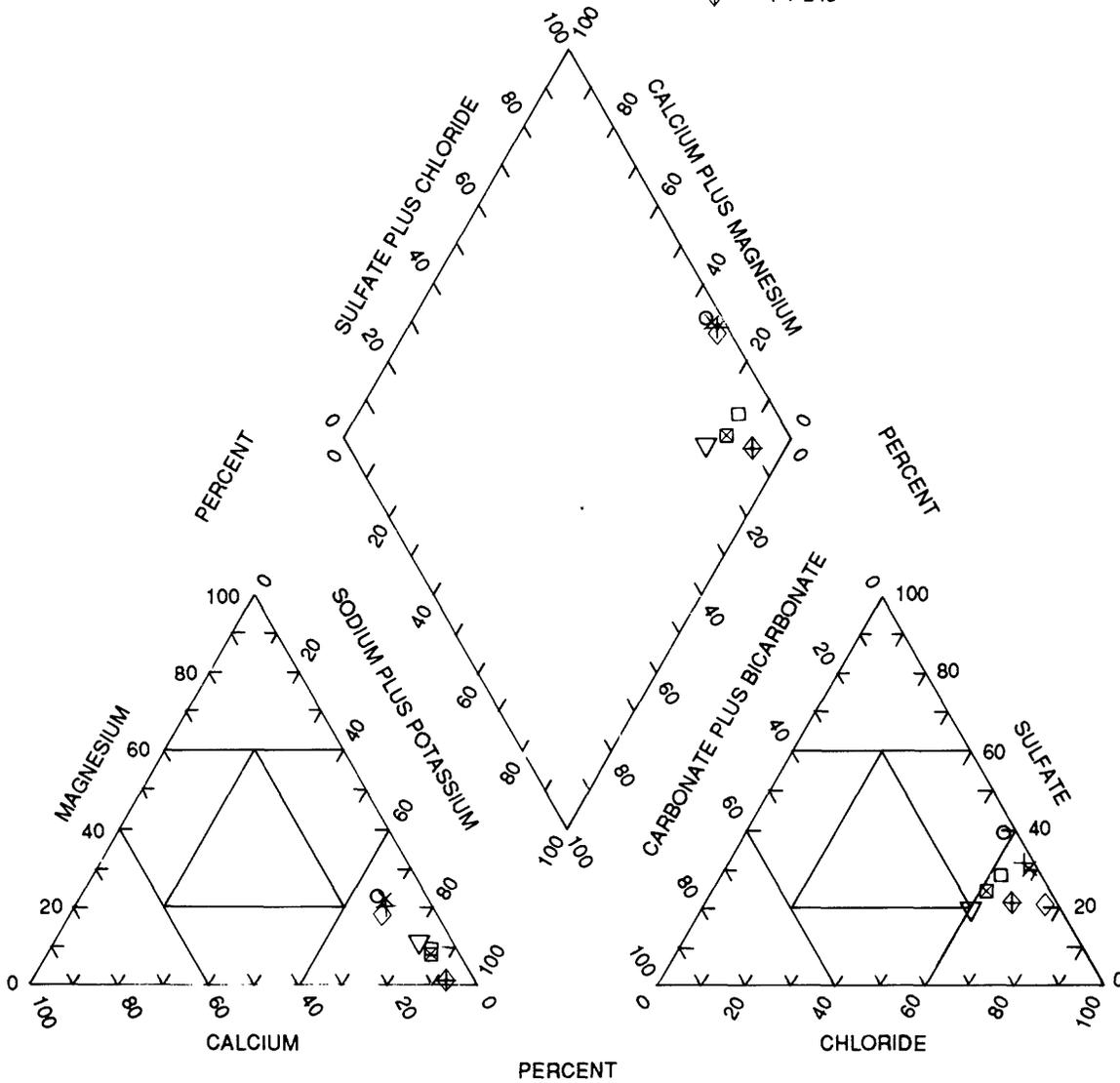


Figure 6. Major-ion chemistry of ground-water samples from observation wells.

Table 1. Analyses of ground-water samples from observation wells for major constituents and selenium

[Observation well: Number is depth, in feet below land surface to the midpoint of the screened interval of individual well. $\mu\text{S/cm}$, microsiemen per centimeter. $^{\circ}\text{C}$, degree Celsius; mg/L , milligram per liter; $\mu\text{g/L}$, microgram per liter. <, actual value is less than value shown]

Observation well	Date	Specific conductance ($\mu\text{S/cm}$)	pH (standard units)	Temperature, water ($^{\circ}\text{C}$)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)
P1-24.5	4-23-87	11,500	7.85	21.0	130	130	2,200	4.6
P1-32.5	4-22-87	17,000	6.80	21.5	410	520	2,900	14
P1-38.7	4-22-87	25,600	7.12	21.5	560	700	4,400	17
P1-45	4-22-87	28,300	7.23	21.5	580	790	4,700	13
P1-49	4-23-87	18,900	7.29	21.5	440	450	3,100	9.8
P1-55	4-22-87	3,960	8.16	23.0	53	44	660	3.3
P1-60	4-23-87	3,270	8.38	22.0	34	30	560	2.7
P1-245	11-20-85	3,840	7.87	20.5	49	6.0	820	5.4

Observation well	Date	Alkalinity, carbonate (mg/L as CaCO_3)	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Solids, sum of constituents, dissolved (mg/L)	Selenium, dissolved ($\mu\text{g/L}$)
P1-24.5	4-23-87	528	1,600	2,600	24	7,030	480
P1-32.5	4-22-87	303	3,900	4,200	24	12,200	<1
P1-38.7	4-22-87	362	4,600	7,200	21	17,800	<1
P1-45	4-22-87	360	5,100	8,500	29	20,000	<1
P1-49	4-23-87	300	2,100	5,600	25	11,900	<1
P1-55	4-22-87	436	390	910	30	2,360	<1
P1-60	4-23-87	224	360	670	31	2,020	<1
P1-245	11-20-85	203	420	990	33	2,450	<1

The plot of delta deuterium (δD) and $\delta^{18}\text{O}$ for ground water and porewater data show that the well data fall along a best-fit line for ground water in western Fresno County calculated on the basis of more than 300 samples (Davis and Coplen, 1989) (fig. 8). Porewater data from the same depths as the wells are shifted slightly to the right, likely as a result of minimal evaporation during handling of the samples due to their small volume. The enriched samples of porewater from depths equal to or less than 23.5 ft are significantly shifted to the right of the local ground-water line due to evaporation. These samples fall along a straight line that extrapolates back to the position of the deeper ground-water samples, indicating that the shallower evaporative water had an initial isotopic composition similar to that of the deeper water.

Large amounts of evaporation and the accompanying isotopic enrichment usually occur when the

water table is close to the land surface. Experimental laboratory studies of evaporation from bare soil observed a maximum evaporation rate of less than 0.5 mm/d from a clay soil with a water table depth equal to the minimum depth (14.5 ft) observed at the P1 study site (Gardner and Fireman, 1958). As the depth to the water table at the P1 site has been greater than 14.5 ft and surface conditions are optimal for evaporation only a fraction of the year, the potential annual evaporation is estimated to be less than 50 mm. Although this rate of evaporation is small, it would be sufficient to cause isotopic enrichment at the water table given sufficient time and in the absence of recharge. Alternatively, the isotopically enriched water evolved at a time when the water table was shallower or migrated to the site from an adjacent area with a shallow water table.

Tritium concentrations in ground-water samples collected from wells at a depth of 60 ft or less in

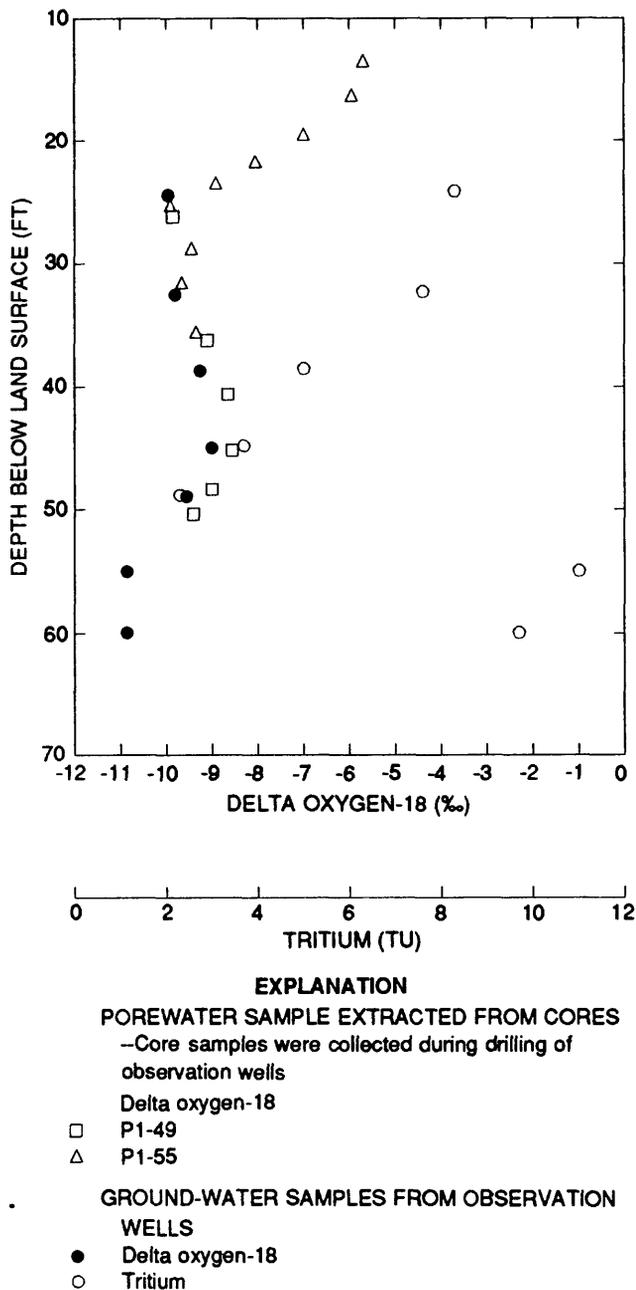


Figure 7. Delta oxygen-18 ratios in ground-water and porewater samples and tritium concentrations in ground-water samples.

1985 and 1987 range from 2.3 to 11 tritium units (Tu) (fig. 7, table 2). Tritium concentrations decrease from a depth of 24.5 to 49 ft below land surface, but are high (9.7 to 11 Tu) in ground water at 55 to 60 ft. These values indicate that all of these water samples contain some component of water that originated as precipitation after the increase in the tritium concentration of precipitation due to atmospheric testing of

Table 2. Analyses of ground-water samples from observation wells for tritium, delta deuterium, and delta oxygen-18

[Observation well: Number is depth, in feet below land surface to the midpoint of the screened interval of individual well. Tu, tritium units; ‰, per mil. <, actual value is less than value shown]

Observation well	Date	Tritium, total (Tu)	Delta deuterium (‰)	Delta oxygen-18 (‰)
P1-24.5	4-23-87	8.3	-76.0	-9.95
P1-32.5	4-22-87	7.6	-76.0	-9.80
P1-38.7	4-22-87	5.0	-71.5	-9.25
P1-45	4-22-87	3.7	-72.0	-9.00
P1-49	4-23-87	2.3	-72.5	-9.55
P1-55	4-22-87	11	-81.0	-10.85
P1-60	4-23-87	9.7	-81.5	-10.85
P1-245	11-20-85	<.8	-84.5	-11.10

nuclear weapons which began in 1952. The sudden increase in tritium from a depth of 49 to 55 ft indicates that water at depths greater than 49 ft is part of a different local flow system with more rapid recharge. This is supported by the rapid change in the dissolved-solids concentration over this depth interval.

The decrease in tritium concentration with depth suggests increasing age, but absolute ages cannot be calculated due to the lack of data on the initial tritium concentrations in precipitation and in the various water used for irrigation in the area. The decrease in tritium concentration with depth may be due to the shift in the primary source of irrigation water from local ground water low in tritium prior to 1967 to canal water high in tritium after 1967. Another possibility is that the decrease in tritium concentration from a depth of about 24 to 49 ft could reflect the decrease in the concentration of tritium present in precipitation from 1963 to 1952. Alternately, young water that has moved downward through the more permeable zones of the profile may have lost tritium due to diffusion into clay lenses containing older water. This also would result in a gradual decrease in the tritium concentration with increasing depth. This phenomena has been observed in other geologic settings where interbedding with large permeability contrasts occur and in dual-porosity systems (Grisak and Pickens, 1980; Desaulniers and others, 1981; Sudicky and Frind, 1981). Regardless of the uncertainty as to the exact mechanism responsible for the tritium concentration profile, all of the proposed processes invoke increasing age from a depth of 24 to 60 ft.

Table 3. Geochemical data for porewater samples from cores P1-55 and P1-49, April 1987; and P1-63, August 9-10, 1988

[ft, feet; $\mu\text{S}/\text{cm}$, microsiemen per centimeter; $\mu\text{g}/\text{L}$, microgram per liter; ‰, per mil; --, no data. <, actual value is less than value shown]

Interval sampled (ft)			Specific conductance ($\mu\text{S}/\text{cm}$)	Manganese ($\mu\text{g}/\text{L}$)	Selenium ($\mu\text{g}/\text{L}$)	Delta deuterium (‰)	Delta oxygen-18 (‰)
Midpoint	Top	Bottom					
Core P1-55, April 1987							
13.5	13.0	14.0	18,500	--	10	-54.7	-5.70
14.8	14.0	15.7	14,700	--	13	--	--
15.5	15.0	16.0	14,900	60	21	--	--
16.4	16.0	16.8	15,200	--	31	-56.0	-5.95
17.4	16.8	18.0	15,300	66	73	--	--
18.5	18.0	19.0	15,600	--	174	--	--
19.5	19.0	20.0	16,200	--	487	-61.0	-7.00
20.5	20.0	21.0	16,400	60	918	--	--
21.8	21.5	22.0	14,400	--	1,240	-67.5	-8.05
22.5	22.0	23.0	14,200	24	1,520	--	--
23.5	23.0	24.0	12,600	--	967	-72.5	-8.90
24.3	24.0	24.6	10,700	--	358	--	--
25.3	24.6	25.9	9,400	154	33	-77.0	-9.90
26.2	25.9	26.5	--	--	--	--	--
26.3	26.0	26.5	--	--	196	--	--
27	--	--	10,800	--	--	--	--
28.0	27.5	28.5	--	--	107	--	--
28.8	28.5	29.0	12,000	--	26	-75.5	-9.45
29	--	--	10,900	--	--	--	--
29.5	29.0	30.0	11,900	1,460	93	--	--
30.5	30.0	31.0	12,300	--	79	--	--
31	--	--	11,600	--	--	--	--
31.5	31.0	32.0	13,400	2,200	4.0	-76.0	-9.65
34.1	--	--	18,300	--	--	--	--
35.5	35.0	36.0	18,500	--	13	-73.5	-9.35
36.2	--	--	19,400	--	--	--	--
36.7	36.6	36.8	25,900	--	--	--	--
42.1	42.0	42.2	24,500	--	--	--	--
43.9	43.8	44.0	21,200	--	--	--	--
47.6	47.4	47.7	19,800	--	--	--	--
48.5	48.0	49.0	17,200	--	--	--	--
52.1	51.8	52.4	15,400	--	--	--	--
52.6	52.4	52.7	15,000	--	--	--	--
53.6	53.4	53.7	8,780	--	--	--	--
56.1	55.4	56.8	7,040	--	--	--	--
Core P1-49, April 1987							
21.6	21.4	21.7	16,300	--	1,410	--	--
24.1	24.0	24.2	10,600	--	412	--	--
24.6	24.2	25.0	10,700	146	190	--	--
26.2	25.9	26.5	10,400	220	181	-77.5	-9.85
26.6	26.5	26.7	11,000	--	104	--	--
29.8	28.0	31.5	10,900	--	29	--	--
31.5	--	--	14,400	--	73	--	--
31.6	31.5	31.7	13,200	--	9	--	--
32.8	31.7	34.0	15,400	--	23	--	--
34.1	34.0	34.2	16,200	--	20	--	--
36.2	35.9	36.4	20,800	8,000	13	-72.0	-9.10

Table 3. Geochemical data for porewater samples from cores P1-55 and P1-49, April 1987; and P1-63, August 9-10, 1988--Continued

Interval sampled (ft)			Specific conductance (µS/cm)	Manganese (µg/L)	Selenium (µg/L)	Delta deuterium (‰)	Delta oxygen-18 (‰)
Midpoint	Top	Bottom					
Core P1-49, April 1987--Continued							
36.5	36.4	36.6	24,500	--	12	--	--
38.8	38.4	39.2	22,100	3,700	8.9	--	--
40.6	40.2	41.0	23,300	--	2.0	-70.0	-8.65
41.2	41.0	41.5	22,800	--	2.0	--	--
43.4	43.0	43.8	23,400	--	12	--	--
43.9	43.8	44.0	23,000	--	5.0	--	--
45.2	44.8	45.5	22,300	--	2.4	-70.5	-8.55
46.4	46.3	46.5	21,100	--	5.0	--	--
46.8	46.5	47.2	22,000	--	6.1	--	--
48.4	48.0	48.8	20,900	1,104	1.9	-72.5	-9.00
48.9	48.8	49.0	17,400	--	3.0	--	--
50.4	50.0	50.8	17,800	--	<.1	-75.0	-9.40
50.9	50.8	51.0	15,900	--	2.0	--	--
Core P1-63, August 9-10, 1988							
Interval sampled (ft)			Specific conductance (µS/cm)	Manganese (µg/L)	Selenium (µg/L)		
Midpoint	Top	Bottom					
12.8	12.4	13.4	18,600	--	--		
14.0	13.5	14.5	15,200	35	14.0		
15.0	14.5	15.5	12,500	--	--		
16.0	15.5	16.5	12,400	--	--		
16.9	16.6	17.2	15,300	59	116.0		
17.8	17.2	18.2	15,600	120	207.0		
18.8	18.2	19.2	15,300	66	682.0		
19.9	19.4	20.4	16,400	79	962.0		
20.9	20.4	21.4	16,200	51	1,440.0		
21.9	21.4	22.4	18,200	44	1,200.0		
22.9	22.4	23.4	15,000	41	1,510.0		
23.7	23.2	24.2	13,700	53	1,030.0		
24.7	24.2	25.2	12,400	--	1,100.0		
25.6	25.4	25.7	12,400	520	488.0		
26.2	25.7	26.7	12,400	--	370.0		
27.2	26.7	27.7	14,200	190	121.0		
28.6	28.4	28.8	13,300	3,300	9.0		
29.3	28.8	29.8	12,900	--	5.0		
30.9	30.4	31.4	12,500	3,800	20.0		
31.9	31.4	32.4	12,300	--	2.0		
32.9	32.4	33.4	14,300	9,600	1.7		
33.9	33.4	34.4	16,700	10,000	.2		
34.9	34.4	35.4	16,000	14,000	1.0		
35.9	35.4	36.4	19,100	13,000	1.5		
36.2	36.0	36.4	18,200	12,000	1.8		
43.0	42.7	43.2	27,100	--	.1		
43.7	43.2	44.2	25,700	2,700	1.8		
44.8	44.4	45.2	27,100	5,500	2.5		
45.7	45.2	46.2	24,500	2,700	<.1		

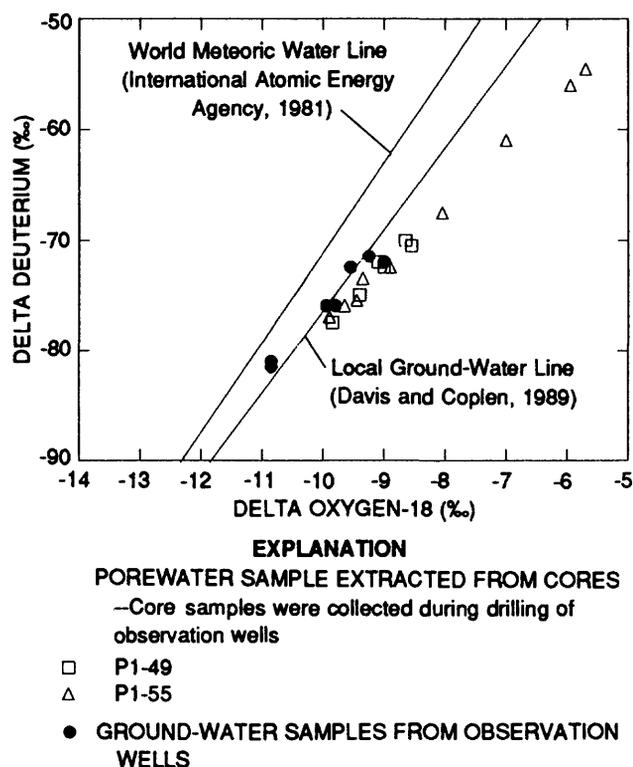


Figure 8. Delta deuterium and delta oxygen-18 for ground-water and porewater samples.

The following model for the origin of the ground water at the study site can be constructed based on the hydrologic, stable-isotope, and tritium data.

1. Under natural conditions prior to irrigation and ground-water development, the site was a discharge area for regional ground-water flow from the Panoche Creek alluvial fan. Saline soil conditions evolved due to evaporative concentration of ground water from a shallow water table.

2. During the period in which the water table was drawn down due to extensive pumpage, the site was not directly irrigated and recharge to the water table was by lateral flow from adjacent irrigated areas and municipal water use.

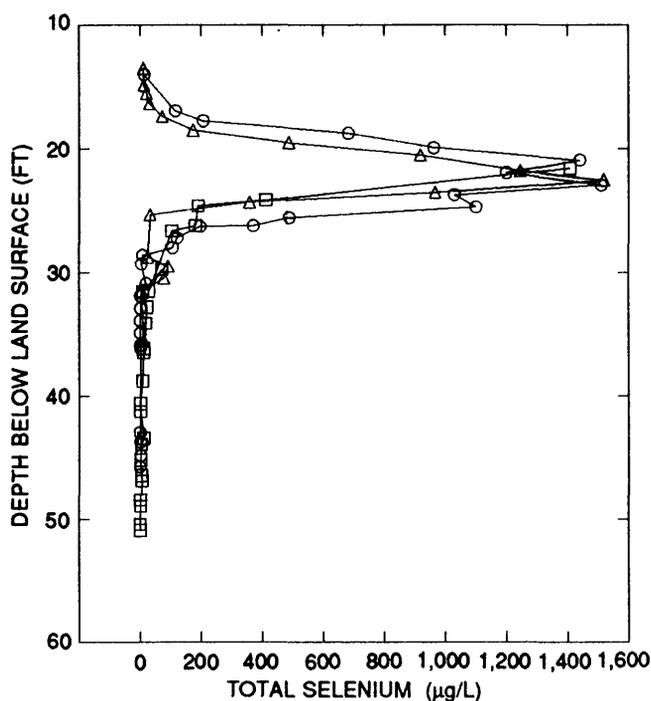
3. At the time during which the ground water presently between about 25 and 50 ft below land surface was recharged, the water table in the contributing areas must have been sufficiently deep to limit evaporation from the water table, as indicated by the lack of isotopic enrichment in water from these depths. The high dissolved-solids concentration in this zone must therefore be due to leaching of preexisting soil salts.

4. Following the introduction of surface water, ground-water pumpage decreased and the water-table altitude in the area contributing recharge to the site increased to within several feet of the surface and was subject to evaporative concentration.

DISTRIBUTION OF SELENIUM

Analyses of ground-water samples from the first wells installed at the site showed a total selenium concentration of 480 $\mu\text{g/L}$ at a depth of 24.5 ft and a selenium concentration of less than 1 $\mu\text{g/L}$ at 60 ft. Data on ground-water chemistry at other locations in the Coast Range alluvial fans of the San Joaquin Valley showed that the logarithms of selenium concentration and specific conductance are highly correlated (Deverel and Fujii, 1988; Deverel and Millard, 1988). Specific conductance was used as a predictor for selenium concentration so that screened intervals of additional wells would provide the best definition of the depth distribution of selenium concentrations in the ground water. Wells at depths of 32.5, 38.7, 45, 49, and 55 ft below land surface were situated to sample ground water representing the entire range of the specific conductance values measured on porewater extracted in the field.

Selenium concentrations in all samples of ground water from wells screened at depths of 32.5 ft or greater were less than the detection limit of 1 $\mu\text{g/L}$ (table 1). Selenium analyses for porewater that was hydraulically extracted from undisturbed cores showed that concentrations of total selenium are extremely high in a narrow, sharply bounded zone with a peak concentration at a depth of 20.9 to 24.7 ft (fig. 9, table 3). Selenium concentration profiles were similar in all three cores taken at the site with maximum concentrations of 1,520 $\mu\text{g/L}$ at 22.5 ft in core P1-55, 1,410 $\mu\text{g/L}$ at 21.56 ft in core P1-49, and 1,510 $\mu\text{g/L}$ at 22.9 ft in core P1-63 (fig. 9). Selenium concentrations decrease rapidly to less than 100 $\mu\text{g/L}$ at depths of greater than about 28 ft and at depths of less than 18 ft. Selenium concentrations in porewater from depths greater than 30 ft below land surface are low, but almost always greater than the detection limit. The presence of detectable selenium in porewater samples extracted from depths at which no selenium was detected in the well samples may be the result of mobilization of adsorbed selenium due to the applied pressure (less than 2,000 lb/in^2) (Manheim, 1966) or the solubilization of small amounts of reduced selenium minerals due to oxidation during sample preparation.



EXPLANATION

POREWATER SAMPLE EXTRACTED FROM CORES
 -Core samples were collected during drilling of
 observation wells

- P1-49
- △ P1-55
- P1-63

Figure 9. Selenium concentrations in porewater samples.

Analysis of selenium species showed that essentially all of the selenium in solution is hexavalent selenate (SeO_4^{2-}). The concentration of tetravalent selenite (SeO_3^{2-}) was less than $1 \mu\text{g/L}$ in all of the ground-water samples from wells except for the sample from 24.5 ft. This sample contained $19 \mu\text{g/L}$ of selenite, which constituted 4 percent of the total selenium present in the sample. The sample from a depth of 27.2 ft in the P1-63 core was the only porewater sample that contained a measurable, though small ($9 \mu\text{g/L}$), amount of selenite.

Along with the specific conductance data, the similarity of the selenium concentration profiles in the three cores indicate that the vertical chemical distribution pattern is consistent in porewaters at sites 10 to 20 ft apart. Furthermore, the water table was at a depth of 27.6 ft, or 10 ft deeper, when the August 1988 cores were taken than when the April 1987 cores were taken. Most of the porewaters with high

selenium concentrations in the 1988 profile are in fact above the water table at the time of sampling, and the similarities between the 1987 and 1988 profiles for specific conductance and selenium concentration indicate little actual movement of water in spite of the large change in hydraulic head. This likely is due to the high field capacity of the fine-grained sediments in the upper part of the stratigraphy. It seems that short-term seasonal fluctuations in water levels do not result in much solute movement.

Fluctuations in the depth to the water table will, however, affect the depth of penetration of atmospheric oxygen and, hence, the depth of oxidizing conditions in the sediments. Evidence of this is the mottling of the sediments described previously from a depth of 14 to 24 ft. The peak selenium concentrations occur in this zone, indicating that changes in redox potential, possibly related to water-table fluctuations, influence the location of high selenium concentrations in ground water.

The most notable feature of the selenium data is that, unlike the ground-water chemistry in other areas on Coast Range alluvial-fan deposits, the concentration of selenium is not correlated with specific conductance or the dominant anions, chloride and sulfate, in ground water. The lack of correlation indicates that processes other than leaching of preexisting soil salts and evaporative concentration are controlling the distribution of selenium in ground water at this site.

The solubilities of selenate minerals generally are high (Elrashadi and others, 1987). The concentration of selenium in oxidizing ground water in the western San Joaquin Valley is not limited by solid phase solubility control by a discrete selenium solid phase. For example, although selenium concentrations of several parts per million occur in sodium and magnesium sulfate evaporite minerals currently precipitating from saline seeps in the Coast Range west of the study area, no selenate minerals were identified in these deposits (Presser and others, 1990). In shallow ground water in the western San Joaquin Valley, selenium concentrations are high where solutes are leached from saline soils, and concentrations increase further in areas where evapotranspiration from a shallow water table causes a general increase in solute concentration.

The solubilities of the reduced forms, elemental selenium (Se^0) and selenide (Se^{2-}), are low (Elrashadi and others, 1987), and the mobility of selenite (SeO_3^{2-}) is severely limited by adsorption (Balistrieri and

Chao, 1987; Neal and others, 1987a, 1987b; Goldberg and Glaubig, 1988). The tendency for selenium to be removed from ground water by reduction of selenate to a less soluble form has been recognized in various geologic settings (Harshman, 1972; Masscheleyn and others, 1989; Oremland and others, 1989; Weres and others, 1989). Most pertinently, work done by researchers from Lawrence Berkeley Laboratory at Kesterson Reservoir has shown that although there was widespread infiltration of agricultural drain water into the aquifer underlying the evaporation pond, selenium only entered the aquifer in zones where the ground water remained oxidizing (White, 1988). These field observations, which have been confirmed by laboratory column experiments (Lawrence Berkeley Laboratory, 1987) and in situ injection tests (Benson and others, 1988; Lawrence Berkeley Laboratory, 1988) indicate that the redox potential of the ground water strongly influences the mobility of selenium in ground water in the western San Joaquin Valley.

INFLUENCE OF REDOX POTENTIAL ON SELENIUM DISTRIBUTION

Ground-water redox potential is difficult to assess quantitatively and apparent redox disequilibrium often occurs in ground water due to (1) chemical and/or biological kinetics, (2) mixed potentials because different redox couples are not at thermodynamic equilibrium, and (3) precipitation or oxidation reactions at the platinum electrode surface (Langmuir, 1971; Whitfield, 1974; Stumm and Morgan, 1981,

p. 490; Bricker, 1982; Thorstenson, 1984). Measured relative abundances of redox-sensitive species, therefore, often do not correspond to speciation predicted from thermodynamic calculations using platinum electrode potentials (Lindberg and Runnells, 1984). Measured speciation of an element, however, is useful for predicting solid phase solubility and sorption behavior. The redox potential of the ground water at the site was assessed on the basis of platinum electrode measurements and the abundance of several dissolved constituents which are sensitive to redox conditions.

The most reliable platinum electrode potential measurements were made by pumping ground-water samples from wells through a flow-through cell that excludes atmospheric contamination. Measurements show a maximum of 391 mV at 24.5 ft and decreasing values with depth to a minimum of 66 mV at 55 ft (table 4, fig. 10). Values measured on pore-waters extracted under a nitrogen atmosphere were consistently higher and likely were affected by contamination with small amounts of atmospheric oxygen during sample handling.

Dissolved oxygen and nitrate in ground water are electron acceptors and hence usually indicative of oxidizing conditions. The dissolved-oxygen concentration of ground water at the site, measured using a flow-through cell, was less than 1 mg/L in all wells except the shallowest well at 24.5 ft (table 4). The dissolved-oxygen concentration in this well ranged from 0.2 to 7.9 mg/L for the five measurements made between April 1986 and February 1988. Measured

Table 4. Indicators of redox potential for ground-water samples from wells

[Observation well: Number is depth, in feet below land surface to the midpoint of the screened interval of individual well. mV, millivolt; mg/L, milligram per liter; µg/L, microgram per liter. <, actual value is less than value shown]

Observation well	Date	Eh (mV)	Dissolved oxygen (mg/L)	Nitrate (mg/L as N)	Iron (µg/L)	Manganese (µg/L)
P1-24.5	4-23-87	391	0.2	1.5	20	450
P1-32.5	4-22-87	203	.3	<.1	11,000	12,000
P1-38.7	4-22-87	170	.2	<.1	10,000	12,000
P1-45	4-22-87	130	.2	<.1	14,000	11,000
P1-49	4-23-87	136	.2	<.1	1,600	4,100
P1-55	4-22-87	66	.2	<.1	100	180
P1-60	4-23-87	97	.2	<.1	250	210

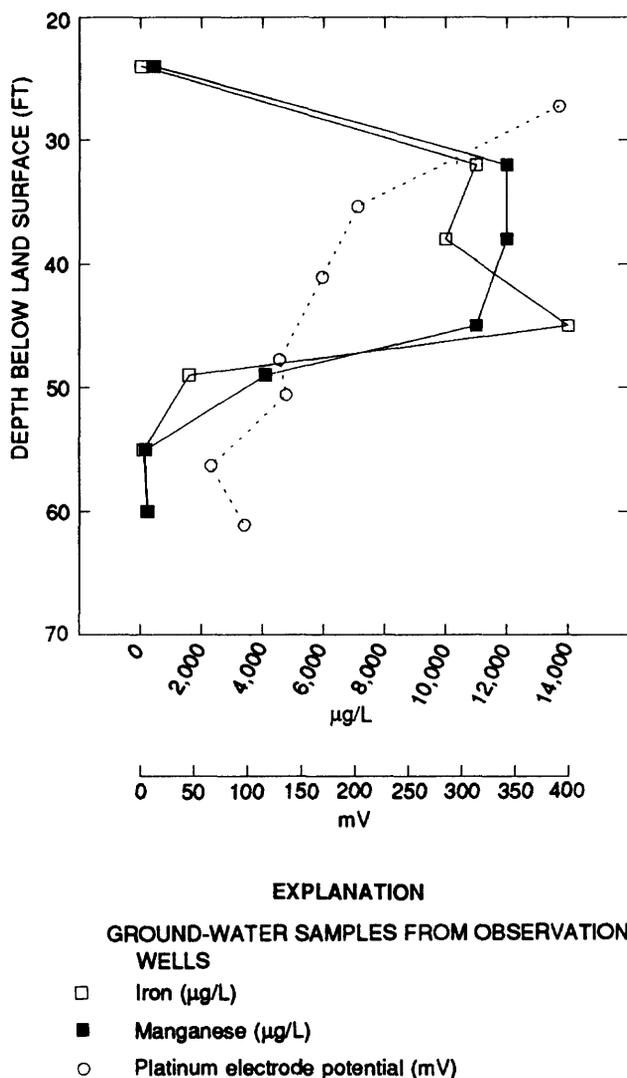


Figure 10. Platinum electrode redox potential and concentrations of iron and manganese in ground-water samples.

values in the deeper wells range from 0.2 to 0.3 mg/L; however, these values are near the detection limit and most of the ground water at the site likely has a dissolved-oxygen concentration of 0.1 mg/L or less. Similarly, nitrate concentrations were less than the detection limit of 0.1 mg/L in all wells except for the shallowest well, which had 1.00 to 1.5 mg/L in the six samples analyzed between 1985 and 1988. Nitrate concentrations for porewater samples taken above the water table in August 1988 (P1-63) show a maximum concentration of 19.5 mg/L at 11.4 ft, 5.98 mg/L at 12.4 ft, and less than 5 mg/L

at 15.5 ft and deeper. The dissolved-oxygen and nitrate data indicate that the ground water is oxidizing above the water table but becomes depleted in these electron-acceptors several ft below the water table.

The concentration of iron and manganese in oxidizing, near-neutral solutions is limited by the low solubilities of the oxyhydroxides of the oxidized species (Fe^{+3} and Mn^{+4}) of these two metals. The more reduced, divalent forms of iron and manganese have relatively high solubilities, and therefore the presence of iron and manganese is a good indicator of a reducing redox potential. The concentrations of iron in ground-water samples show an almost three order of magnitude increase from 20 µg/L at a depth of 24.5 ft to a maximum of 14,000 µg/L at 45 ft (table 4, fig. 10). The vertical distribution of manganese is similar, with a minimum concentration of 450 µg/L at the 24.5-foot depth and a maximum concentration of 12,000 µg/L at the 32.5- and 38.7-foot depth (table 4, fig. 10). The high concentrations of iron and manganese in ground water at depths equal to or greater than 32 ft indicate that the ground water in this interval is moderately reducing. Decreasing concentrations at depths greater than 50 ft are due to mixing with more dilute water (fig. 5). The location of the transition from oxidizing to reducing conditions is defined even more clearly by the profile of manganese concentration in porewater samples (table 3). The porewater data show that manganese concentrations begin to increase at depths greater than 24.6 ft below land surface then rise rapidly at about 30 ft (fig. 11).

In summary, high concentrations of nitrate above the water table indicate that oxidizing conditions dominate in the unsaturated zone. Just below the water table, both nitrate and dissolved oxygen disappear from solution, and the ground water becomes moderately reducing, as indicated by the high concentrations of iron and manganese. This pattern is consistent with the decrease in platinum electrode redox potential with increased depth below the water table. The relation between the concentration of selenium and the redox potential of the ground water can be seen by overlaying the profiles of the selenium and manganese analyses (fig. 11). The data show that the selenium concentration decreases rapidly at the same depth at which manganese concentrations increase, strongly indicating that the decrease in selenium is due to a process that occurs under reducing conditions.

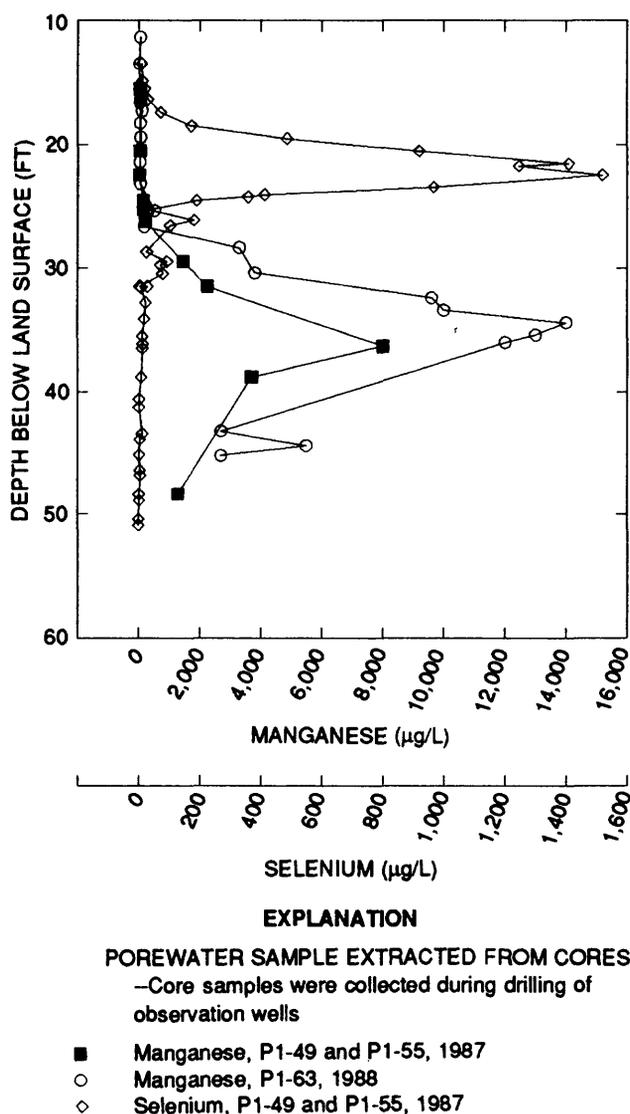


Figure 11. Concentration of manganese in porewater samples from 1987 (P1-55 and P1-49) and 1988 (P1-63). Selenium concentrations in porewater samples from 1987 cores also are shown.

The respiratory reduction of selenate to elemental selenium is a process mediated by anaerobic bacteria (Macy and others, 1989; Oremland and others, 1989). Therefore, the presence of this bacterial activity in selected subsurface sediments from the study site was evaluated. This was achieved by measuring loss of ⁷⁵Se-selenate from solution in samples of slurried core materials. This basic approach was previously used to measure selenate reduction in estuarine sediments (Oremland and others, 1989). Core material (P1-37) was stored at approximately 5 °C for 17 days before processing. Core sections were subsampled

(5-8 samples/section) with 3 cc plastic syringes (hub-end removed), which were sealed with rubber stoppers (size 000). Samples were extruded into serum bottles (25 mL) under a flow of N₂ and mixed with 3 mL of 50 percent ABW solution (salinity = about 10 g/L; pH = 7.3; Oremland and Polcin, 1982). The serum bottles were sealed under N₂ and injected with a deoxygenated stock solution of ⁷⁵Se-selenate (about 8 nano Curies/sample). After about 2 hours to allow for particle settling, the bottles were reopened, subsampled (0.5-1.0 mL), and resealed under N₂. Subsamples were centrifuged and radioactivity was measured in the supernatant solution (Oremland and others, 1989). All samples were incubated statically at 20 °C, and subsampled after 1, 3, and 8 days as indicated above. In addition, selected samples were incubated with 20 mM sodium acetate, a substrate for selenate-reducing bacteria, which increases their activity when added to sediments (Oremland and others, 1989).

Results show that after 3 days of incubation there was no loss of selenate from solution in the core materials from 22.8 to 27.8 ft, and at 30.8 ft (table 5, fig. 12). In contrast, 78 percent of the labeled selenate in solution was lost in the core from 28.8 ft and 20 percent from the core at 29.8 ft. After 8 days, loss of selenate from solution was significant in all nine samples analyzed; however, the samples from 27.8 ft and deeper showed a higher bacterial activity than the shallower samples. In addition, acetate accelerated the selenate loss from the samples at 28.8 and 30.8 ft. These results indicate that all the depths assayed have the bacteria present which will reduce selenate; however, the samples from 27.8 ft and deeper have a microbial population capable of reducing selenate at a significant rate while sediments at shallower depths do not. This depth interval corresponds to the zone at which the porewaters become reducing (fig. 10), which is in agreement with the observation that microbial reduction of selenate is an anaerobic process (Oremland and others, 1989).

Analyses of the selenium solid phase that was precipitated in earlier experiments on selenate reduction showed that the selenate was reduced to either the amorphous red elemental selenium or, less frequently, black crystalline elemental selenium (Oremland and others, 1989). The same researchers also reported that very little of the labeled selenium remained in the sample as selenite because this species is a transient intermediate in the reduction of selenate to elemental selenium.

Table 5. Selenate reduction potential in sediment samples from undisturbed core P1-37 collected August 1988; expressed as percentage of total $^{75}\text{SeO}_4$ removed from solution

[ft, feet; --, no data]

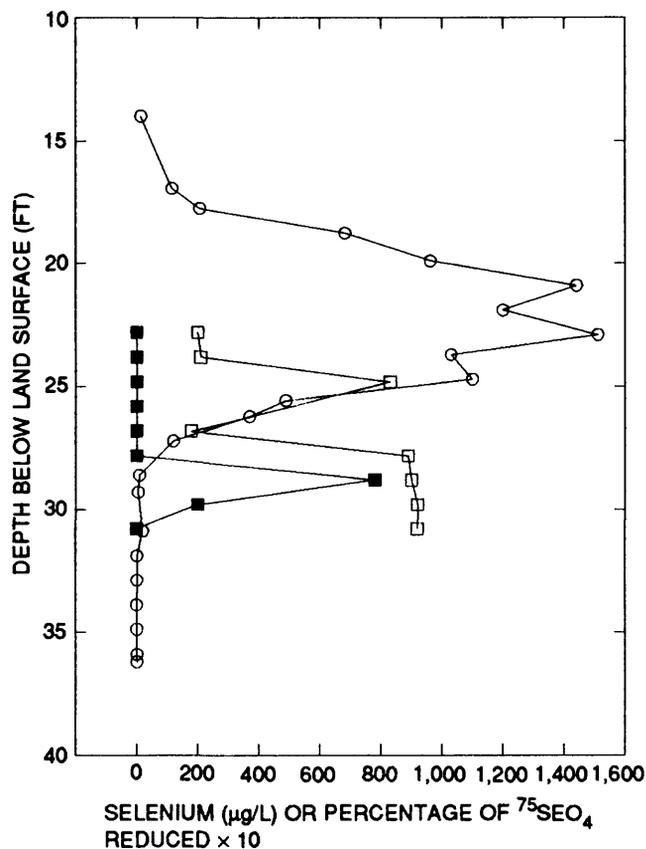
Depth (ft)	Amendment	Selenate reduction: percent of pool reduced in	
		3 days	8 days
22.8	None	0	20
23.8	None	0	21
24.8	None	0	83
25.8	None	0	--
25.8	Acetate	0	12
26.8	None	0	18
27.8	None	0	89
28.8	None	78	90
28.8	Acetate	87	¹ 95
29.8	None	20	92
30.8	None	0	92
30.8	Acetate	92	92

¹About 25 percent of the selenate in this sample was reduced in the first 24 hours.

The observation that the selenate is removed from solution requires that selenium accumulate in the solid phase. Quantitative recovery of elemental selenium in the solid phase was demonstrated with estuarine sediments (Oremland and others, 1989). In addition, this activity was detected in agricultural waste-pond sediments (Oremland and others, 1990) as well as in a broad survey of sediment types ranging from freshwater to hypersaline (Steinberg and Oremland, 1990). Loss of selenium by degassing of methylated selenides (Frankenburger and others, 1986, 1987) is unlikely to be important below the water table at the site due to the low redox potential and competing anaerobic demethylation reactions (Oremland and Zehr, 1986). Several sediment samples were analyzed in order to determine if there is a zone of higher selenium concentration in the sediments below the peak selenium concentration in the ground water.

Figure 13 shows the range in selenium concentration in two sets of data on San Joaquin Valley soils: data on the selenium concentration in 297 soil samples (0- to 12-inch depth) collected valleywide, and 721 soil samples (66- to 72-inch depth) from the Panoche and Cantua alluvial fans (Tidball and others, 1986). A map of the total selenium concentration of soils in the San Joaquin Valley shows that soil

developed from Sierra Nevada sediments almost always contained less than $0.13 \mu\text{g/g}$ selenium (Tidball and others, 1986), while 90 percent of the soil in the Panoche-Cantua alluvial fans contain greater than $0.32 \mu\text{g/g}$ selenium (fig. 13). These data suggest that if Sierra Nevada sediments at the site contain selenium concentrations greater than $0.13 \mu\text{g/g}$, then these concentrations may be due to addition of selenium to the sediments by reductive removal from infiltrating ground water.



EXPLANATION

POREWATER SAMPLE EXTRACTED FROM CORES
 - Core samples were collected during drilling of observation wells

○ Selenium concentration, P1-63, August 1988

PERCENTAGE OF TOTAL $^{75}\text{SeO}_4$ LOST FROM SOLUTION BY REDUCTION, P1-37 CORE

■ Percentage reduced by 3 days

□ Percentage reduced by 8 days

Figure 12. Selenium concentrations in porewater samples from the P1-63 core and results of assays of potential selenate reduction for sediments from the P1-37 core, expressed as percentage of total $^{75}\text{SeO}_4$ lost from solution. (See table 5.)

SAN JOAQUIN VALLEY

PANOCHÉ AND CANTUA
ALLUVIAL FANS

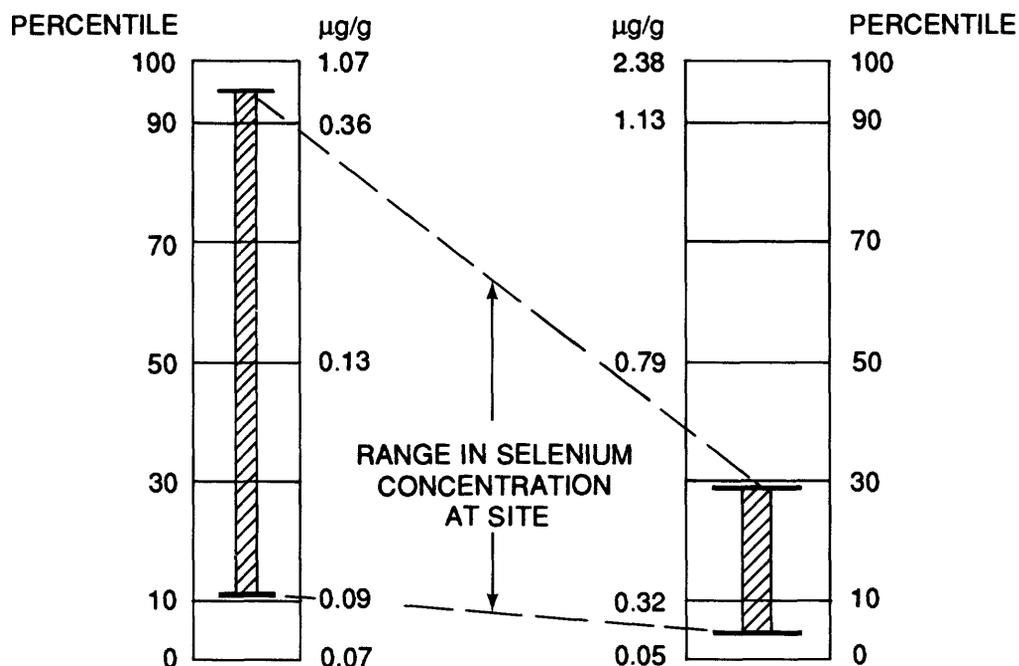


Figure 13. Selenium concentrations in two sets of soil samples in the San Joaquin Valley: 297 soil samples from 0 to 12 inches collected valleywide (left) and 721 soil samples from 66 to 72 inches from the Panoche and Cantua alluvial fans (modified from Gilliom, 1989).

Total selenium concentrations in the sediments ranged from the detection limit of 0.1 µg/g to a maximum of 0.6 µg/g at the same depth as the peak selenium concentration in solution (table 6, fig. 14). Given that the precision of the analysis is ± 0.1 µg/g, for sediments at depths greater than 25 ft, only the samples from 26.6 and 43.9 ft have a selenium concentration greater than expected for Sierra Nevada sediments. There is, therefore, no evidence of a zone of accumulation of solid-phase selenium due to removal from the saline ground water at greater depths. A zone of selenium accumulation would be difficult to identify if either the zone was very narrow, and therefore easily missed, or if the selenium was dispersed in a broad zone in the sediments. A more detailed investigation of the vertical variation of major and trace element concentrations in sediments from the site is in progress.

Table 6. Selenium concentrations in sediment samples from cores P1-55 (1) and P1-49 (2), April 1987

[ft, feet; µg/g, microgram per gram; µg/L, microgram per liter]

Depth (ft)	Core	Selenium, total in solid (µg/g)	Selenium in porewater (µg/L)
21.6	2	0.4	1,410
22.5	1	.6	1,520
24.1	2	.4	412
25.3	1	.2	33
26.6	2	.3	104
29.5	1	.1	93
31.6	2	.2	9
36.5	2	.1	13
43.9	2	.4	5
50.9	2	.2	2

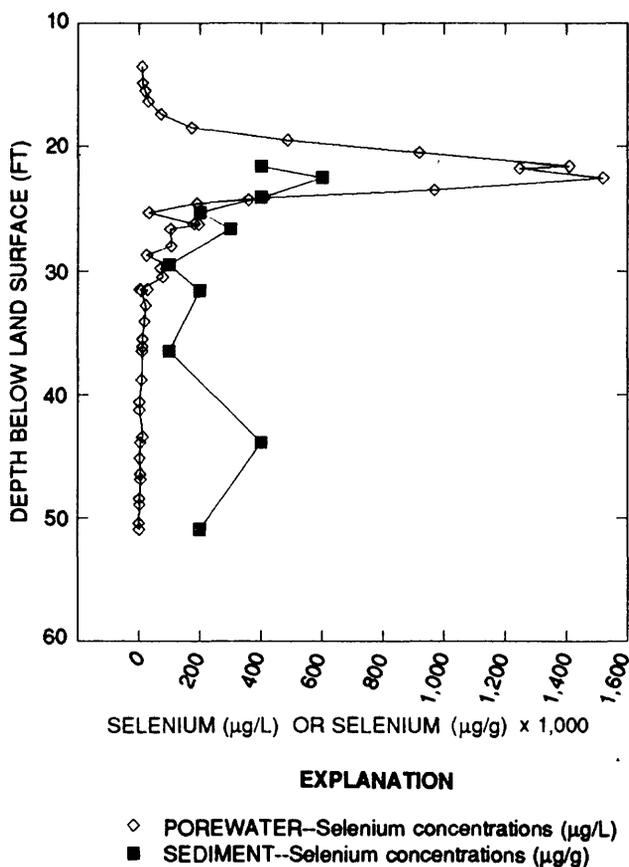


Figure 14. Selenium concentrations of porewater and sediment samples extracted from cores during drilling of observation wells P1-49 and P1-55.

SUMMARY AND CONCLUSIONS

The influence of redox conditions on selenium transport in shallow ground water was investigated at a site in Mendota, in western San Joaquin Valley, California, where about 50 ft of complexly interbedded sediments from Sierra Nevada and Coast Range sources overlie a thick aquifer of Sierra Nevada origin. The medium- and coarse-grained sand at depths greater than 26 ft below land surface is derived primarily from the Sierra Nevada; however, the fine-grained sediments that dominate the shallower stratigraphy are derived primarily from the Coast Range. Under natural conditions, the site was a

discharge area; however, heavy pumping from the underlying aquifer has lowered the water table. Fluctuations in the water-table altitude were caused by deep pumping, and the depth of the water table ranged from 17.6 ft in February 1987 to a maximum of 27.6 ft in August 1988.

Detailed profiles of ground-water geochemistry obtained from wells and porewater extracted from undisturbed cores show saline water at shallow depths. Specific conductance peaks at greater than 20,000 µS/cm at a depth of 36 to 48 ft, and decreases to 3,270 µS/cm at a depth of 60 ft. All shallow ground water at the site was a sodium chloride type with similar ratios of major cations and anions. Stable-isotope data showed that most of the well water and porewater was similar to local deep ground water and imported irrigation water; however, ground water from 23.5 ft and shallower had been subject to evaporative concentration. Tritium data indicated all of the shallow ground water recharged after 1952, and the age of the ground water decreased with decreasing depth from 60 ft to the water table.

The selenium analyses of ground water samples from observation wells showed a concentration of 480 µg/L at 24.5 ft and concentrations of less than 1 µg/L at all wells 32.5 ft and deeper. Analyses of selenium concentrations in porewater samples from undisturbed cores showed a sharply bounded zone with most selenium concentrations greater than 100 µg/L between 18 and 28 ft, and a peak of 1,520 µg/L at 22.5 ft. Essentially, all of the selenium occurs as selenate, and the maximum concentration of selenite was 19 µg/L (4 percent of the total concentration). Selenium and specific conductance were not correlated in ground water at the site, in contrast to the high correlation observed for ground water from oxidized Coast Range sediments to the west.

Redox potential of ground water greatly affects the distribution of selenium in San Joaquin Valley ground water due to the low mobility of the reduced selenium species. Redox potential of ground water at the site was evaluated on the basis of platinum electrode potential and the abundance of redox-sensitive dissolved constituents. These redox indicators suggest that the lack of correlation of selenium and salinity is due to removal of selenium from solution by reduction to a less soluble species. This is inferred by the

coincidence of the lower boundary of the high selenium zone with (1) decreasing platinum electrode redox potentials, (2) the disappearance of dissolved oxygen and nitrate, and (3) a rapid increase in iron and manganese concentrations.

Laboratory analyses of undisturbed cores indicate that the potential for microbial selenate reduction is significant at depths greater than 27 ft below land surface. These results, along with results of other researchers working in similar geochemical systems, indicate that the mechanism of selenium removal likely is microbial reduction to insoluble elemental selenium. Analysis of sediment samples showed no zone of accumulation of selenium as would be expected if high concentrations of selenium had been transferred from the solution to the solid phase; however, such a zone would have gone undetected if it were a narrow zone that was missed or a broad zone resulting in little increase above background.

The conceptual model for the site consists of the evolution of saline soil with high selenium concentrations in a regional ground-water discharge area prior to agricultural development; downward migration of saline, seleniferous ground water due to water-table drawdown; and selenium removal from the downward-migrating ground water by microbially mediated redox reactions.

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