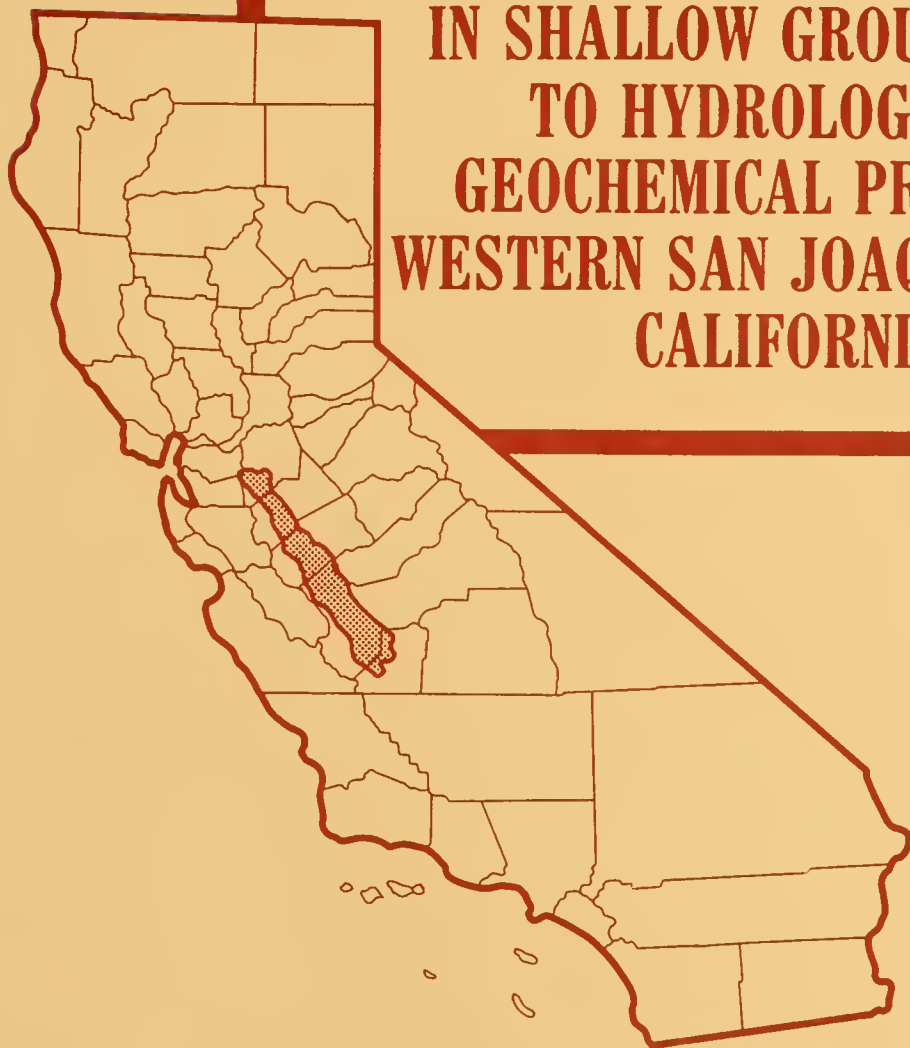


**RELATION OF SALINITY AND SELENIUM
IN SHALLOW GROUND WATER
TO HYDROLOGIC AND
GEOCHEMICAL PROCESSES,
WESTERN SAN JOAQUIN VALLEY,
CALIFORNIA**



**U.S. GEOLOGICAL SURVEY
Open-File Report 88-336
REGIONAL AQUIFER SYSTEM ANALYSIS**

Prepared in cooperation with the SAN JOAQUIN VALLEY DRAINAGE PROGRAM

This report was prepared by the U.S. Geological Survey in cooperation with the San Joaquin Valley Drainage Program and as part of the Regional Aquifer System Analysis Program of the U.S. Geological Survey.

The San Joaquin Valley Drainage Program was established in mid-1984 and is a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the Program are to investigate the problems associated with the drainage of agricultural lands in the San Joaquin Valley and to develop solutions to those problems. Consistent with these purposes, program objectives address the following key areas: (1) Public health, (2) surface- and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

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Sacramento, California 95825-1898

The Regional Aquifer System Analysis (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 have often arbitrarily been limited in the past. The broad objective for each study is 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 an effective management of the system. The Central Valley RASA study, which focused on studying 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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Sacramento, California
1988

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CONVERSION FACTORS

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

<u>Multiply</u> <u>metric unit</u>	<u>By</u>	<u>To obtain</u> <u>inch-pound unit</u>
cm (centimeter)	0.3937	inch
ha (hectare)	2.471	acre
km (kilometer)	0.6214	mile
m (meter)	3.281	foot
m/a (meter per annum)	3.281	foot per year
mL (milliliter)	0.0002642	gallons
mm (millimeter)	0.03937	inch

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

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

Selenium concentrations are given in micrograms per liter (µg/L). One thousand micrograms per liter is equivalent to 1 milligram per liter (mg/L). Micrograms per liter is equivalent of "parts per billion." Isotope composition is expressed in parts per thousand or "per mil."

Abbreviations used:

µS/cm	microsiemens per centimeter at 25 °Celsius
µm	micrometer
TU	Tritium units, tritium atoms on 10 ¹⁸ hydrogen atoms

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--A geodetic datum derived from a 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

Salinity and selenium concentrations in shallow ground water of the western San Joaquin Valley, California, are related to the geomorphology and hydrology of the alluvial fans. The highest salinity and selenium concentrations in shallow ground water occur in alluvium deposited by ephemeral streams and at the margins of the major alluvial fans, where there were naturally saline, fine-grained soils. Low-to-moderate salinity and selenium concentrations in shallow ground water are associated with upper and

middle areas of the major alluvial fans deposited by intermittent streams. Areas with the most naturally saline soils have been irrigated in the last 40 years. These are now the areas of highest salinity and selenium concentrations in the shallow ground water. Present-day (1986) ground-water salinity is significantly correlated with natural soil salinity in these areas. Isotopic data indicate that the highest salinity and selenium concentrations in ground water present at low altitudes resulted from evaporative concentration when the water table was shallow.

INTRODUCTION

Saline soil and ground water have caused water-management problems for agriculture in the western San Joaquin Valley, California, for decades. Recent findings of high-selenium concentrations in agricultural drain water and waterfowl deformities where drain water was discharged (Presser and Barnes, 1985; Deverel et al., 1984, Ohlendorf et al., 1986) have increased environmental concern about agricultural water management in the area. The high-selenium drain water comes from subsurface drainage systems that remove shallow ground water to keep the water table low enough for crop production. Attention is being directed toward management strategies to decrease drain-water flows and selenium concentrations in ground water. Development of effective water-management strategies for the western valley requires an understanding of processes affecting salinity and selenium in shallow ground water.

Previous studies dealt mainly with drained areas where the water table was generally less than 3 m below land surface. Deverel and Millard (1988) and Deverel et al. (1984) evaluated the distribution of and interrelations among chemical constituents in shallow ground water in areas of the western San Joaquin Valley where drainage systems have been installed. The most saline and selenium-enriched ground water occurred in Coast Range alluvial-fan deposits, which includes the Little Panoche Creek, Panoche Creek, Cantua Creek, and Los Gatos Creek alluvial fans, and numerous small fans in between. Selenium and other mobile oxyanions (molybdenum, vanadium, and boron) are correlated with ground-water salinity in Coast Range alluvium (Deverel and Millard, 1988). Selenium concentrations were lower and were not correlated with salinity in ground water underlying the deposits derived mainly from Sierra Nevada rocks.

The objective of this study was to identify the geochemical, hydrologic, and geomorphic processes that affect the regional distribution of salinity and selenium in shallow ground water of the central part of the western valley. In this report, regional distributions of various constituents in ground water are evaluated in relation to the geomorphology and hydrology of the alluvial fans. This evaluation serves to identify the processes that affect the distribution of salinity and selenium. Data presented by Deverel et al. (1984) and additional data collected primarily upslope of areas that now have drainage problems were combined and analyzed. The location of the study area and areal distribution of wells sampled for chemical analyses are shown in figure 1. Additional data collected from 28 wells installed in a drained agricultural field (site M2, shown in fig. 1) also were analyzed.

This study is part of a comprehensive investigation of the hydrology and geochemistry of the western San Joaquin Valley by the U.S. Geological Survey. The studies are being done in cooperation with the San Joaquin Valley Drainage Program and as part of the Regional Aquifer System Analysis Program of the U.S. Geological Survey.

GEOHYDROLOGIC SETTING

California's San Joaquin Valley is a trough between the Sierra Nevada on the east and the folded and faulted Coast Ranges on the west. The Sierra Nevada, a fault block that dips southwestward, is composed of igneous and metamorphic rock, mostly of pre-Tertiary age. The Diablo Range of the California Coast Range, which borders the study area to the west, consists of an exposed Cretaceous and Upper Jurassic core assemblage of marine origin overlain and juxtaposed with Cretaceous marine and Tertiary marine and

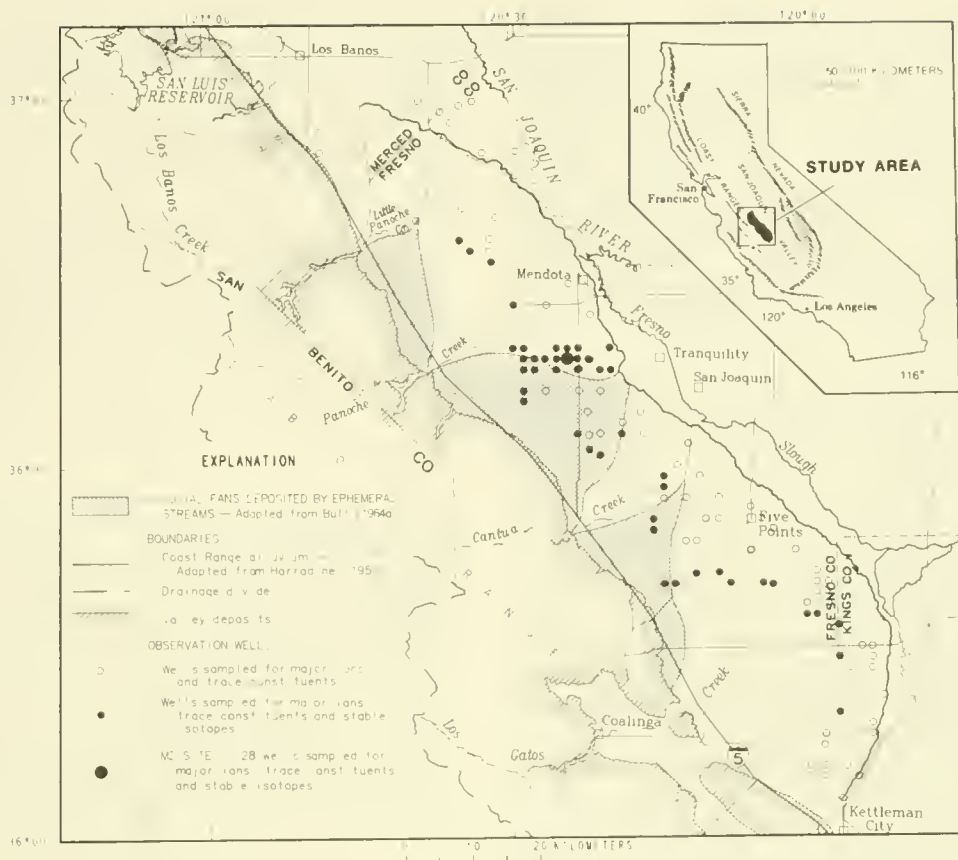


FIGURE 1. Location of study area and areal distribution of wells sampled for chemical analyses.

continental deposits. The alluvial-fan deposits of the western valley are derived exclusively from Diablo Range rocks (Miller et al., 1971). The basin deposits are derived from the Sierra Nevada and the Diablo Range, but are dominated by Sierra Nevada deposits.

The alluvial fans on the westernmost edge of the valley were deposited by intermittent and ephemeral streams (Bull, 1964a, b). Intermittent streams originate in the mountains of the Diablo Range and flow for several months each year. Ephemeral streams originate in the foothills of the Diablo Range and flow only during storms. The fans deposited by

ephemeral streams are smaller than and encircled by the four major alluvial fans deposited by intermittent streams--Little Panoche, Panoche, Cantua, and Los Gatos Creeks (fig. 1). Shallow deposits of the major alluvial fans are typically coarse grained in the upper- and middle-fan areas and fine grained in the lower-fan areas, including the margins of the fans (Harradine, 1950). The fine-grained soils at the margins of the fans generally are poorly drained and often saline.

Under natural conditions, ground-water recharge was primarily from infiltration of water from intermittent streams in the

upper parts of the alluvial fans (Belitz, 1988). Ground water flowed from southwest to northeast, reflecting the general topographic trend of the area. Discharge from the system was by evapotranspiration and streamflow along the valley trough (Mendenhall et al., 1916, Davis and Poland, 1957). Flowing wells mapped by Mendenhall et al. (1916) indicate that artesian conditions prevailed along a broad stretch of the valley trough.

The predevelopment ground-water-flow system was characterized by horizontal flow from the recharge area to the valley trough. Pumpage of ground water for irrigation, which began in the late 1800's and reached a maximum in the 1950's, substantially altered the ground-water-flow system. Percolation of irrigation water past crop roots throughout the western valley became the primary mechanism for ground-water recharge. Evapotranspiration by crops and discharge from wells became the primary discharge mechanisms. The combination of ground-water withdrawals and increased recharge resulted in vertical gradients in the regional ground-water system, causing a substantial component of downward flow.

Ground-water withdrawals until 1952 in the area north of Mendota and until 1967 in the area south of Mendota caused the water table to decline along the fan margins and in the valley trough. When surface water imported from northern California replaced ground water for irrigation, the water table rose throughout the area. The percentage of the area characterized by a water table within 6 m of land surface has increased substantially since 1952 (Belitz, 1988).

METHODS

Differences in chemical compositions of ground water were evaluated using Piper diagrams (Hem, 1985) and the chemical equilibrium model WATEQF (Plummer et al., 1976). Mineral phases affecting the ground-water chemistry were assessed using mineral saturation indices determined by the WATEQF chemical equilibrium

model, where the saturation index is equal to the quotient of the ion-activity product and mineral-solubility constant. Negative saturation index values indicate mineral undersaturation and positive values indicate supersaturation.

The hydrologic history of selected water samples was assessed from the determination of tritium concentrations and deuterium and oxygen-18 enrichment. Tritium concentrations are expressed in tritium units (TU), where 1 TU is equal to one tritium atom in 10^{18} hydrogen atoms.

The distribution of various chemical constituents in the ground water was compared using geostatistical methods. Kriging was used to generate interpolated values of three constituents (ground-water salinity, soil salinity, and selenium in ground water) based on the spatial variance structure and the measured values. The estimated variance structure is defined by the semivariogram (Journel and Huijbregts, 1978):

$$\gamma(h) = \frac{1}{2}E[(z(x_i) - z(x_j))^2], \quad (1)$$

where

$h = x_i - x_j$ is the distance (lag) between pairs of data,

z is the \log_{10} value of the constituent at site x_i or x_j , and

E designates the expected value of the terms inside the brackets.

The frequency distributions of the constituents evaluated (ground-water salinity, expressed as dissolved solids; soil salinity; and selenium in ground water) were log normal. This was determined by comparing the log normal scores to the logarithms (base 10) of the values of the constituents. The log normal scores were significantly correlated with the logarithms of the values. The correlation coefficients, r , for dissolved solids in ground water, soil salinity, and selenium in ground water are 0.97,

0.98, and 0.98, respectively. All r values are significant at $\alpha=0.01$. The logarithms of the data are used in the geostatistical analysis (Delhomme, 1978; Neuman, 1982). The semivariogram was verified by sequentially estimating each measured value with the remaining data. Kriging of historical soil salinity in the western valley was done with 573 point estimates of subsurface soil salinity from Harradine (1950).

Field

Samples of shallow ground water were collected at 118 observation wells distributed throughout the study area (fig. 1). Seventy-two of the wells were sampled during an 18-day period in spring 1984. Forty-six wells were sampled in the spring of 1986. Samples collected at these 46 wells were analyzed for deuterium and oxygen-18 (fig. 1). The wells are 6 to 10 m deep and constructed of polyvinyl chloride pipe perforated over the entire depth of the well.

An additional 28 wells with 30-cm screens at 3, 6, 10, and 12 m below land surface were installed at the M2 site (fig. 1). The wells were installed along a 300-m transect in January 1986 and were sampled in spring 1986.

Most of the observation wells were sampled using tubing and positive-displacement bladder pumps constructed of Teflon¹. The submersible, 2-cm diameter bladder pump operates by allowing water to enter through a one-way valve in the bottom of the pump. Pressurized nitrogen gas is cycled in and out of a Teflon bladder inside the pump casing, displacing the water up the tubing. Some of the observation wells were sampled using a peristaltic pump to remove water from the well through Teflon tubing into sample containers.

Prior to sampling, each well was pumped until the specific conductance of the water did not vary by more than 10 percent for three consecutive well-casing volumes of water. Electrical conductivity meters were standardized using potassium chloride standards within 2,000 $\mu\text{S}/\text{cm}$ of the well water. Specific conductance and pH were measured several times at each well prior to collection of samples. Before each sample was taken, another well-casing volume was pumped with the bladder pump only.

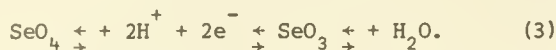
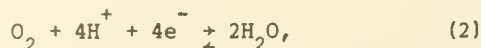
Prior to sampling at each site, all sampling apparatus and containers were rinsed three times with the water to be sampled. Well water was used to rinse filters, filter holders, and sample containers. Prior to collection of samples for laboratory analysis of the inorganic constituents, unfiltered 50-mL samples were titrated incrementally with dilute sulfuric acid for bicarbonate and carbonate concentrations. The pH was measured with portable meters that were calibrated at each site with standardized solutions. Portable pH meters and electrodes were calibrated at each well and for each bicarbonate titration. The calibrations were done using pH buffers maintained at the temperature of the sample water within ± 2 °C. Temperature was measured with mercury thermometers that were checked against a standardized laboratory thermometer.

Samples for analysis of dissolved constituents were pressure filtered through 0.45- μm membrane filters. Samples for determination of major ions and all trace elements were collected and stored in polyethylene bottles with Teflon-lined caps. All samples were acidified with nitric acid to a pH of less than 2 except those collected for determination of chloride, sulfate, bicarbonate, carbonate, pH, and specific conductance, which

¹The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

were untreated. Samples collected for the determination of selenate and selenite were acidified to a pH less than 1 using concentrated hydrochloric acid.

Determination of the oxidation-reduction status of the ground-water samples was done by determining the dissolved-oxygen concentration, the platinum electrode redox potential, and the ratio of selenite to selenate activities. The oxidation-reduction potential was calculated using the Nernst equation and E_0 values (Bard et al., 1985) for the reactions



The platinum electrode redox potential and dissolved oxygen were determined by placing the platinum electrodes in a flow through chamber as described by Wood (1981). Samples for analysis of oxygen- and hydrogen-stable isotopes and tritium were unfiltered and collected in glass bottles with polyethylene lids so that there was no air space.

Laboratory

Calcium, magnesium, sodium, potassium, sulfate, chloride, aluminum, iron, and silica were determined by atomic-absorption spectrometric methods described in Skougstad et al. (1979). Chloride was determined by the ferric thiocyanate colorimetric method. Sulfate was determined by the turbidimetric procedure.

Selenium was determined by hydride generation and atomic absorption spectrometry (Fishman and Bradford, 1982). The method used for selenium in this study is designed to determine the total concentration of all forms of selenium present in the water sample. A sample is first subjected to an oxidative digestion to release any selenium from the organic fraction. The selenium released by this

digestion, together with the inorganic selenium originally present, is then reduced to the selenite form using a stannous chloride and potassium iodide mixture. The selenium hydride is generated by reducing the selenite form using sodium borohydride. The hydride gas is stripped from the solution by a stream of nitrogen gas and its concentration is determined by atomic-absorption spectrometry.

To determine the concentrations of selenate and selenite, three separate analyses were done on each sample. First, the total concentration of the dissolved forms was determined by the above method. Second, the sample was analyzed without performing the oxidative digestion. Third, the sample was analyzed without performing the stannous chloride reduction. The second analysis determines the concentration of the inorganic selenium and the third analysis determines the concentration of the selenate species. The selenite concentration was calculated from the difference between the results of the second and third steps.

The oxygen-isotopic compositions of the water samples were determined using the carbon dioxide equilibration method (Epstein and Mayeda, 1953). Analysis was done with a 60° sector, 150-mm radius double-collecting isotope ratio mass spectrometer. The results are reported relative to Vienna Standard Mean Ocean Water (V-SMOW):

$$\delta^{18}O = \frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{V-SMOW}}}{(^{18}O/^{16}O)_{\text{V-SMOW}}} \times 1,000. \quad (4)$$

The hydrogen-isotopic compositions were determined by analyzing hydrogen quantitatively extracted from water (Kendall and Coplen, 1985). Hydrogen results are reported relative to V-SMOW in the per mil notation. The standard deviation of the laboratory measurements of oxygen- and hydrogen-isotopic compositions are

0.10 and 1 per mil, respectively. The hydrogen- and oxygen-isotopic compositions were determined in the Isotope Fractionation Project Laboratory of the U.S. Geological Survey, Reston, Virginia.

Tritium was determined by scintillation counting after electrolytic enrichment (International Atomic Energy Agency, 1976). All tritium analyses were done by the Environmental Isotope Laboratory at the University of Waterloo, Ontario, Canada.

RESULTS OF GEOSTATISTICAL ANALYSIS

The kriged values for ground-water salinity, soil salinity, and selenium in ground water were used to evaluate the relation of salinity and selenium in ground water to hydrologic and geochemical processes. The theoretical, isotropic, semivariograms for these three constituents were estimated with spherical models (fig. 2). The values of the variables in the equations describing the variograms are shown in table 1. The spherical equation has the form

$$\gamma(h) = \omega[3/2(h/a) + \frac{1}{2}(h/a)^3] + c, \quad (5)$$

where $\omega + c$, a , and c are the sill, range of influence, and nugget variance, respectively (Journel and Huijbregts, 1978). For all three constituents, the semivariogram was calculated in all directions (isotropic, east-west, north-south, northeast-southeast, and southwest-northeast). No drift was apparent in any direction so the isotropic semivariogram was used to estimate the spherical model to describe the spatial variance structure.

The semivariogram model was verified by estimating the data for each of the three constituents listed above. Each of the

observations was removed sequentially and was kriged using the remaining observations. The semivariogram seems reasonable because the mean estimation error (M_e) for the three constituents was close to zero (table 1) and estimation errors appear normally distributed around zero for the range of estimated values. Also, the standard deviation of the reduced error (σ_{RE}) is close to one (table 1). The original observations estimated by this procedure were significantly correlated ($\alpha=0.01$) with the estimated values for ground-water salinity, soil salinity, and selenium in ground water.

The estimation error (M_e) is defined as

$$M_e = E(\hat{z}_i - z_i), \quad (6)$$

and the standard deviation of the reduced error (σ_{RE}) is defined as

$$\sigma_{RE} = E[(\hat{z}_i - z_i)^2 / s_i^2]^{1/2}, \quad (7)$$

where E denotes the expected value. The symbols \hat{z}_i , z_i , and s_i^2 represent the estimated value of the logarithm of the constituent (ground-water salinity, soil salinity, and selenium in ground water), the actual value of the logarithm of the constituent, and the variance of the estimation at point i , respectively.

The normality of the estimation error for the kriged values was tested by calculating the normal scores and comparing them to the estimation error values. For all three constituents, the r values for the regression of the estimation error values and the normal scores were significant at $\alpha=0.01$. The r values were 0.99 for ground-water salinity, 0.99 for soil salinity, and 0.96 for selenium in ground water. The normalized standard deviation of the kriged estimate (David, 1977) varied normally around zero for the range of the estimated values for all three constituents.

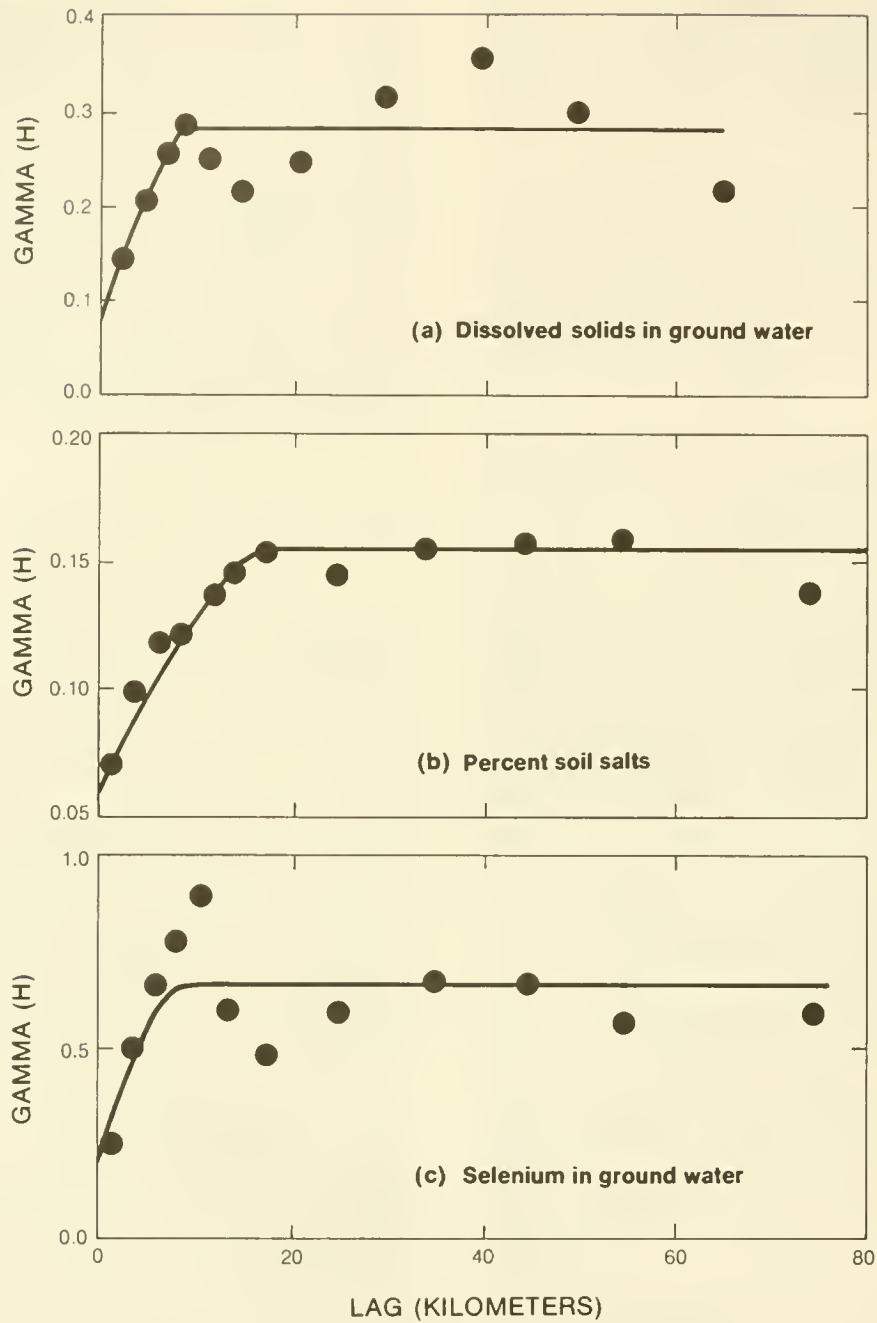


FIGURE 2. Semivariograms for the \log_{10} of (a) dissolved solids in ground water; (b) percent soil salts from Harradine (1950); and (c) selenium in ground water. The solid lines represent the spherical estimates of the semivariograms.

TABLE 1.--Semivariogram model variables, mean estimation error, and standard deviation of the reduced error for \log_{10} of ground-water salinity, soil salinity, and selenium in ground water

[Symbols a, c, and ω are the parameters in the equation $\gamma(h)=\omega[3/2(h/a)+\frac{1}{2}(h/a)^3]+c$]

Constituent	Number of data points	Standard deviation of the reduced error (σ_{RE})	Mean estimation error (M_e)	a	c	ω
Dissolved solids in ground water (mg/L)	111	1.023	0.0023	15	0.07	0.21
Surface soil salinity (percent)	573	.97	.0026	17.5	.06	.095
Selenium in ground water ($\mu\text{g/L}$)	118	.97	.0045	9	.2	.46

RELATION OF SALINITY AND SELENIUM TO HYDROLOGIC AND GEOCHEMICAL PROCESSES

Alluvial-Fan Geomorphology and Hydrology

The distribution of salinity (expressed as dissolved solids) in shallow ground water reflects the geomorphology and hydrology of the alluvial fans, which were deposited by streams originating in the Coast Range and foothills. Dissolved-solids concentrations generally are similar for the three largest alluvial fans associated with intermittent streams. In ground water in the Panoche Creek alluvial fan, dissolved solids generally are less than 3,000 mg/L in the middle-fan areas (fig. 3). In the lower-fan area, dissolved solids are commonly greater than 5,000 mg/L, with some areas at the

fan margins that have dissolved-solids concentrations greater than 10,000 mg/L. Dissolved solids also generally are less than 5,000 mg/L in the middle-fan areas of the Cantua and Los Gatos Creek alluvial fans and generally are greater than 5,000 mg/L, and are as much as to 10,000 mg/L at the margins of the fans. Sparse data prevent evaluation of similar patterns for Little Panoche Creek fan.

Dissolved-solids concentrations in areas of ephemeral-stream alluvial fans generally are higher than at similar positions in adjacent intermittent-stream alluvial fans. Ground water in the middle-fan areas of the ephemeral-stream deposits north of Cantua Creek has dissolved-solids concentrations that generally are between 3,000 and 5,000 mg/L and are as much as 10,000 mg/L. In the lowest altitudes of these ephemeral-stream deposits, dissolved solids are commonly greater than 10,000 mg/L.

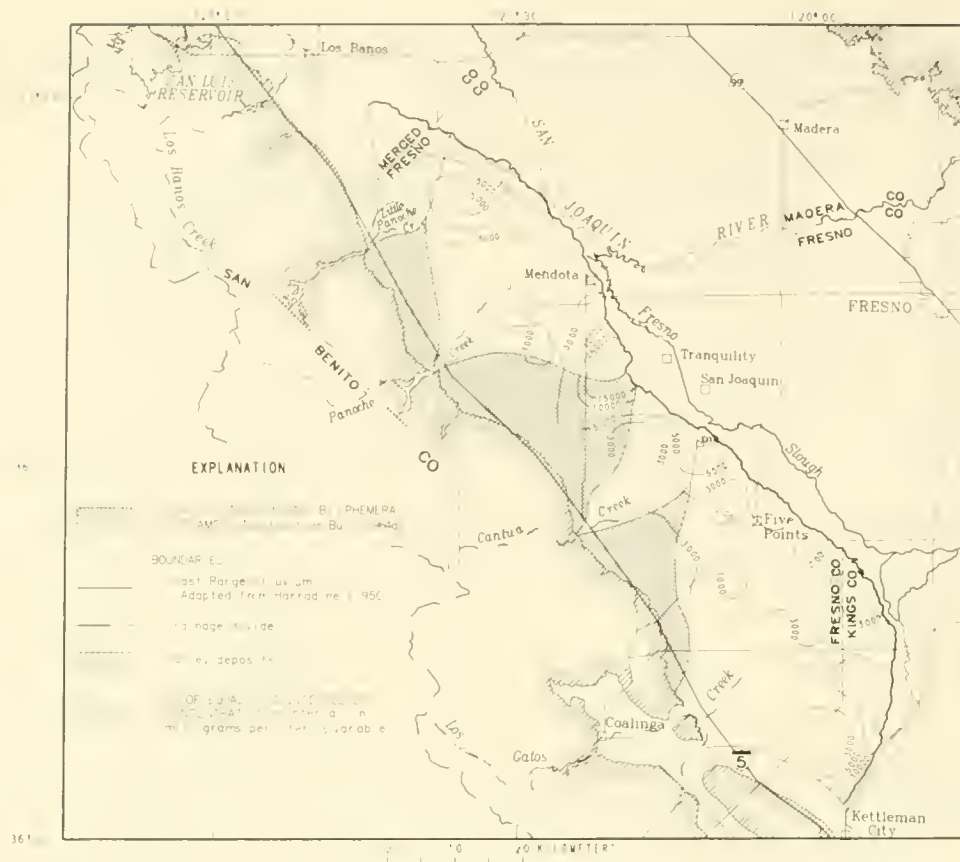


FIGURE 3. Dissolved solids in shallow ground water, 1986.

Over geologic time, smaller quantities of water flowed in the ephemeral streams originating in the foothills than in the larger intermittent streams. The soils of all parts of the alluvial fans associated with these ephemeral streams have been subject to less natural leaching than the soils of the middle and upper parts of the alluvial fans of the intermittent streams. Thus the soils of the ephemeral-stream fans were historically more saline than the middle and upper parts of the intermittent-stream fans. Harradine (1950) estimated percent soil salts in the 1940's at 573 points that are shown in figure 4. Subsurface soil

salinity based on Harradine (1950) and the area of flowing artesian wells defined by Mendenhall et al. (1916) are shown in figure 5. Soils that have 0.5 percent salt or greater are present in the middle-fan areas of the alluvial fans that were deposited by ephemeral streams. Saline soils that have greater than 0.75 percent salt extend into the middle-fan areas in the ephemeral-stream fan deposits to the north of the Cantua Creek alluvial fan. In contrast, soils of the alluvial fans deposited by intermittent streams are less saline in the upper- and middle-fan areas, with soils that have 0.5 percent salt or less.

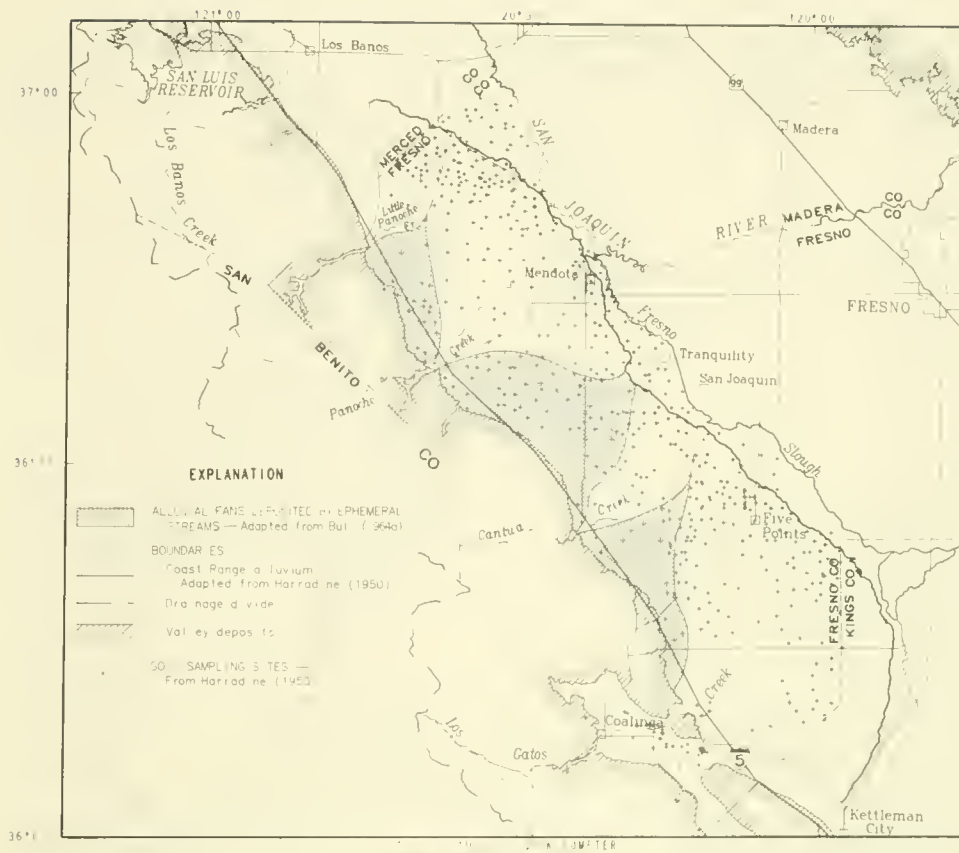


FIGURE 4. Distribution of soil-sampling sites.

Low-lying areas of high salinity and selenium were natural ground-water-discharge areas (Mendenhall et al., 1916; Davis and Poland, 1957). Figure 5 shows the area of flowing artesian wells described by Mendenhall et al. (1916) in relation to soil salinity mapped by Harradine (1950). The proximity and overlap of areas of highest soil salinity and flowing artesian wells indicates that the probable reason for naturally saline soils was evaporative ground-water discharge at the margins of the alluvial fans.

Salinity of ground water and soils also reflects irrigation patterns since the

early 1900's. Figure 6 shows the areas that were irrigated with ground water as of 1940 (Bull and Miller, 1975). At the time of Harradine's sampling in the 1940's, the areas of highest salinity were at the southern and northern margins of the Panoche Creek fan, and at the margins of the Cantua Creek and Los Gatos Creek fans (fig. 5). These saline areas, which include the middle-fan areas of the ephemeral-stream fans, probably were avoided for irrigated agriculture until after 1940 because of the high soil salinity. Unirrigated areas at higher altitudes probably were not irrigated because of greater depths to ground water.

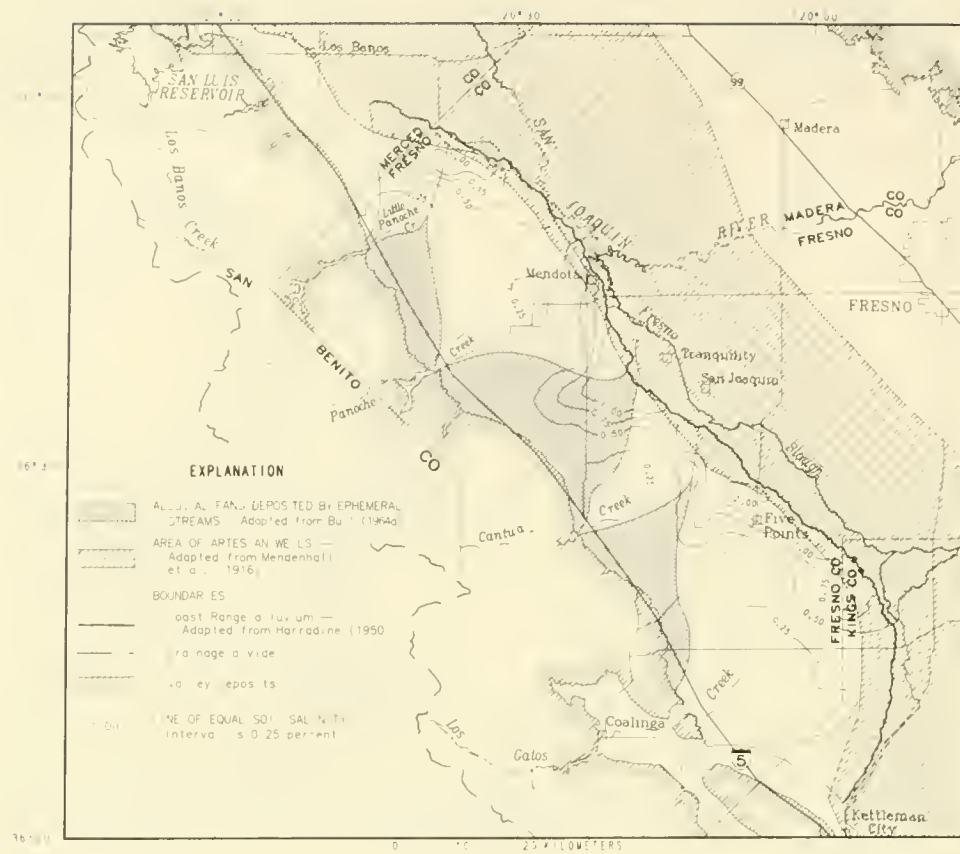


FIGURE 5. Subsurface soil salinity, 1950.

In the area irrigated after 1940, the present-day ground-water salinity is partly the result of leaching of soluble soil salts by irrigation. Figure 7 shows the comparison of 989 kriged values for \log_{10} of ground-water salinity and soil salinity. Ground-water and soil salinity are significantly correlated ($r=0.5$, $\alpha=0.01$).

The texture of the alluvial deposits also affects the relation of ground-water salinity to soil salinity in this area. About 50 estimated points denoted in figure 7 are in a single area south of the Cantua Creek alluvial fan, where coarse-textured deposits predominate below 3 m (Julie Laudon, U.S. Geological Survey, written commun., 1988). By

removing these points, which generally represent low ground-water salinity values and high soil salinity values, the resulting correlation coefficient, r , is 0.66. The coarser texture of the deposits of this area relative to the other deposits in the area irrigated after 1940 probably resulted in more rapid leaching of soluble salts by irrigation water that percolated through the root zone. Present-day ground-water salinity is uncorrelated with soil salinity as reported by Harradine (1950) ($r=0.19$) in the area irrigated before 1940. The Wilcoxon rank sum test (Hollander and Wolfe, 1973) indicated that soil salinity was significantly ($\alpha=0.01$) greater in the area irrigated after 1940.

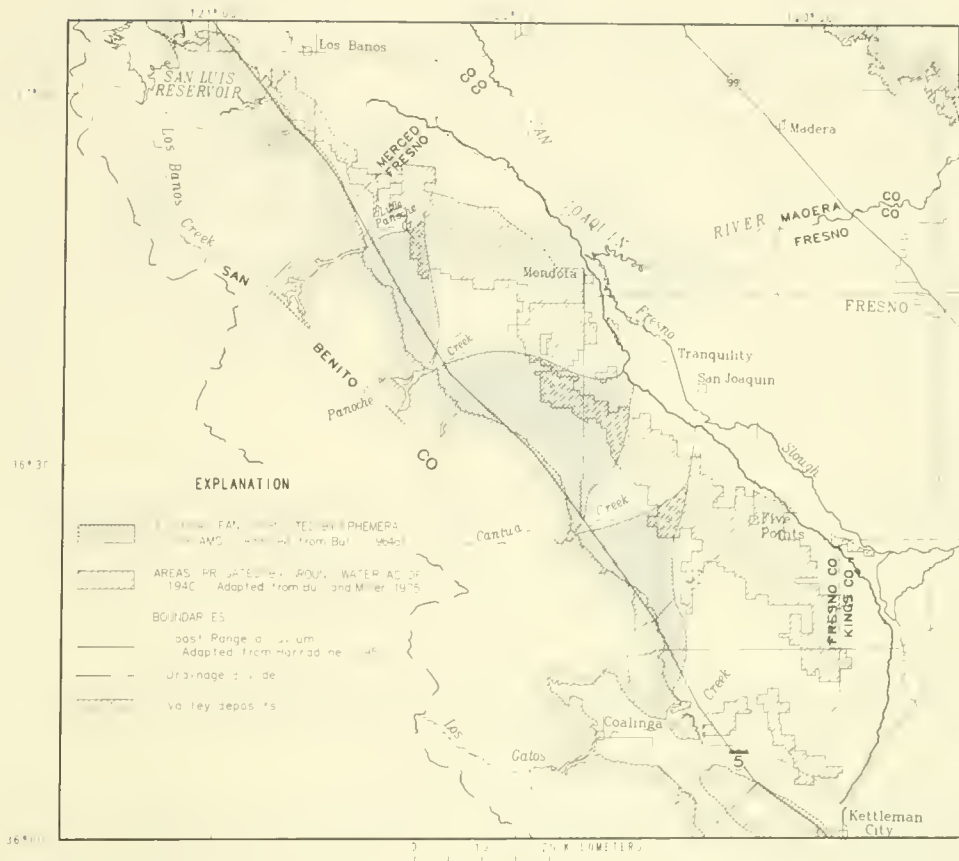


FIGURE 6. Areas irrigated as of 1940.

Saline soils are shown in an area irrigated by surface water prior to 1940 at the northern margin of the Panoche Creek fan, where ground-water salinity is now low. Because this area has been irrigated with surface water since the early 1900's, an irrigation-induced rise in the water table probably led to saline conditions in the unsaturated zone because of evapotranspiration. The soils of this area were mapped as nonsaline in 1915 (Nelson et al., 1919). Installation of drainage systems in this area since 1950 has allowed displacement of saline ground water and leaching of soil salts. This is probably the reason that the present-day ground-water salinity of the area is low.

The relative distribution of selenium in ground water is similar to the salinity distribution (fig. 8), and selenium in ground water and salinity are significantly correlated (Deverel and Millard, 1988). Selenium concentrations generally are less than 20 $\mu\text{g/L}$ in ground water in the middle-fan areas of the alluvial fans deposited by intermittent streams. In the lower-fan areas, principally at the northern and southern margins of the Panoche Creek fan, concentrations are as much as several hundred micrograms per liter. Selenium concentrations in ground water in the middle-fan areas of alluvial fans deposited by ephemeral streams range from 50 to 500 $\mu\text{g/L}$. High selenium in ground water generally corresponds to the

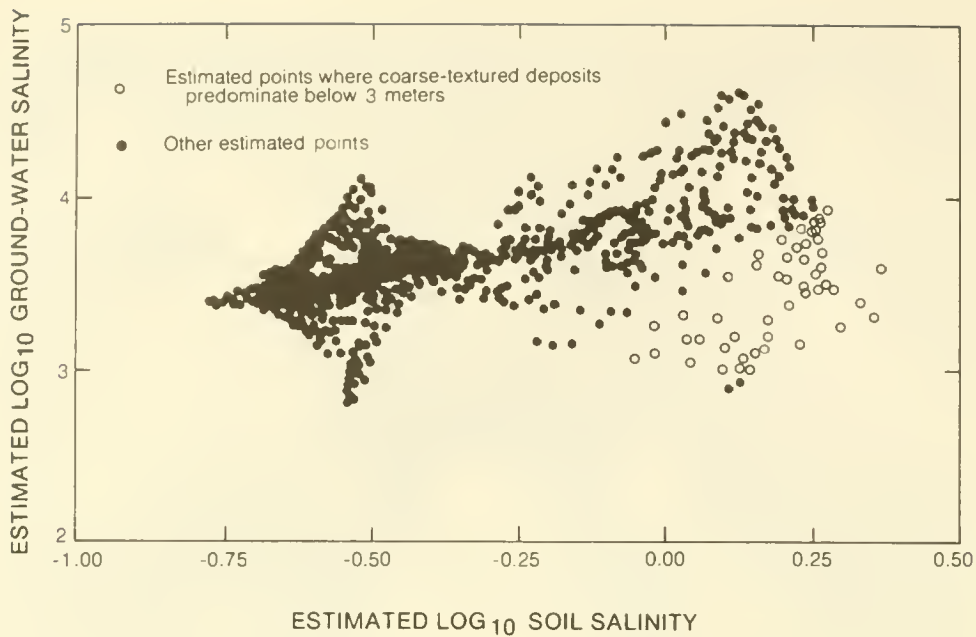


FIGURE 7. Comparison of estimated \log_{10} of ground-water salinity and soil salinity for the area irrigated after 1940.

saline soil areas. Therefore, leaching of salts from saline soils, particularly in areas that were irrigated after 1940, probably contributed substantial amounts of selenium to the shallow ground water.

Tidball et al. (1986) assessed the distribution of selenium in soil in the western San Joaquin Valley. The highest selenium concentrations (99th percentile) were in the upper-fan areas of the ephemeral-stream fans between the Cantua Creek and Panoche Creek alluvial fans. These are areas that have been irrigated only since the 1960's and were subjected to little natural leaching. High soil selenium concentrations (95-99th percentile) also were along the margin of the Panoche Creek fan and at the base of the ephemeral-stream deposits south of the Panoche Creek alluvial fan. These high soil concentrations are mostly the result of evapotranspiration from a shallow water table.

Studies by Amundson et al. (1986) and Fujii et al. (1988) provide information about the nature and fate of the total soil selenium. Amundson et al. (1986) examined changes in potassium phosphate (K_2HPO_4) extractable selenium in soils on the Panoche Creek alluvial fan from 1946 and 1985. Soil samples collected from the same locations in 1946 and 1985 showed substantial decreases in K_2HPO_4 extractable selenium. Soils irrigated after 1940 were higher in K_2HPO_4 extractable selenium in 1946 than the soil irrigated before 1940. All 1985 K_2HPO_4 extractable selenium values were about 10 percent of the 1946 value. Fujii et al. (1988) also found that selenium in irrigated soils is presently in a form resistant to leaching. They showed that only a small part of the total selenium in soils sampled in 1985 in fields irrigated for more than 30 years is in water soluble or extractable forms. The most mobile forms of selenium apparently have been mostly removed from the soils in the study area by irrigation.

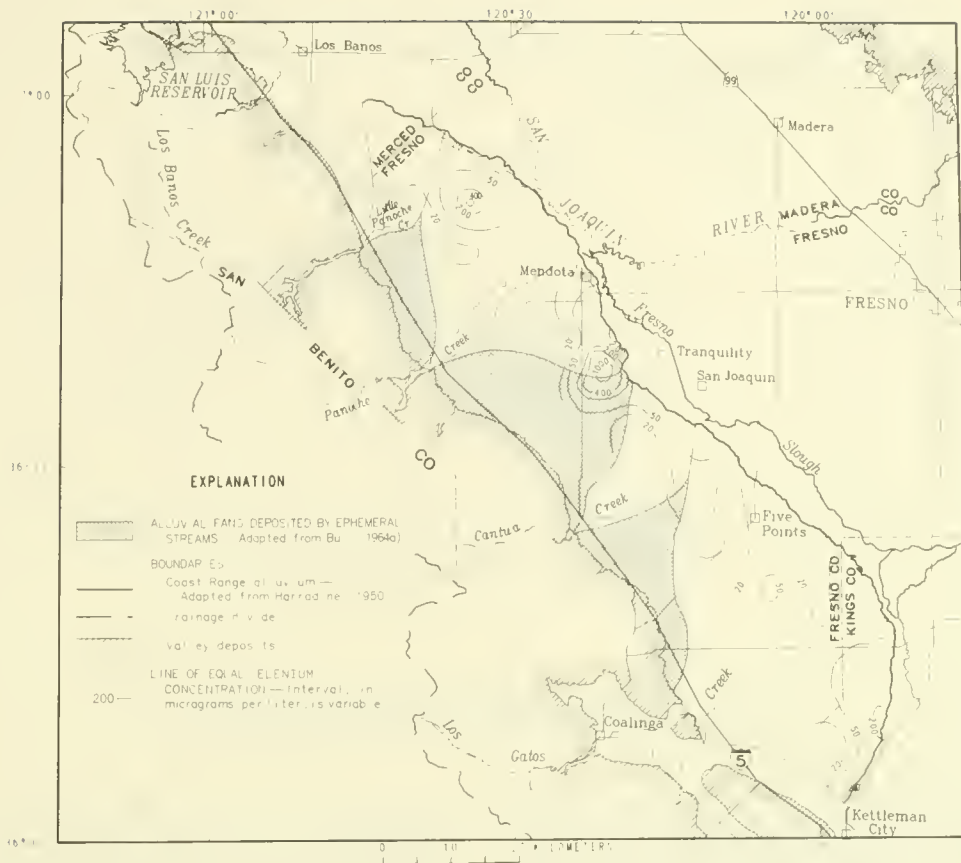


FIGURE 8. Selenium concentrations in ground water, 1986.

Evaporative Concentration

Although the leaching of natural soil salts by irrigation water was probably the primary process that initially formed saline shallow ground water, subsequent evaporative concentration caused further increases in salt and selenium concentrations. Figure 9 shows the isotopic composition for 46 selected samples collected throughout the study area (fig. 1). Samples collected at the lowest altitudes (50 to 58 m above sea level) are mostly enriched in the heavy isotopes and follow an evaporative trend line. Deverel and Fujii (1988) reported that ground-water isotopic data collected in drained agricultural fields fit a similar evaporative trend line. At higher

altitudes, where selenium concentrations generally are low (fig. 8), the ground water is more depleted and has been subject to little or no evaporation.

Most of the shallow ground-water samples collected at the higher altitudes (71 to 100 m above sea level) represent a local meteoric water line (Davis and Coplen, 1988). The isotopic composition of ground water collected from deep parts of the regional unconfined aquifer (at 100 to 200 m below land surface) in areas where the most isotopically enriched shallow ground-water samples were collected, is similar to the approximate intercept of the evaporative trend line with the apparent local meteoric water line (fig. 9). This ground water was applied as irrigation water throughout

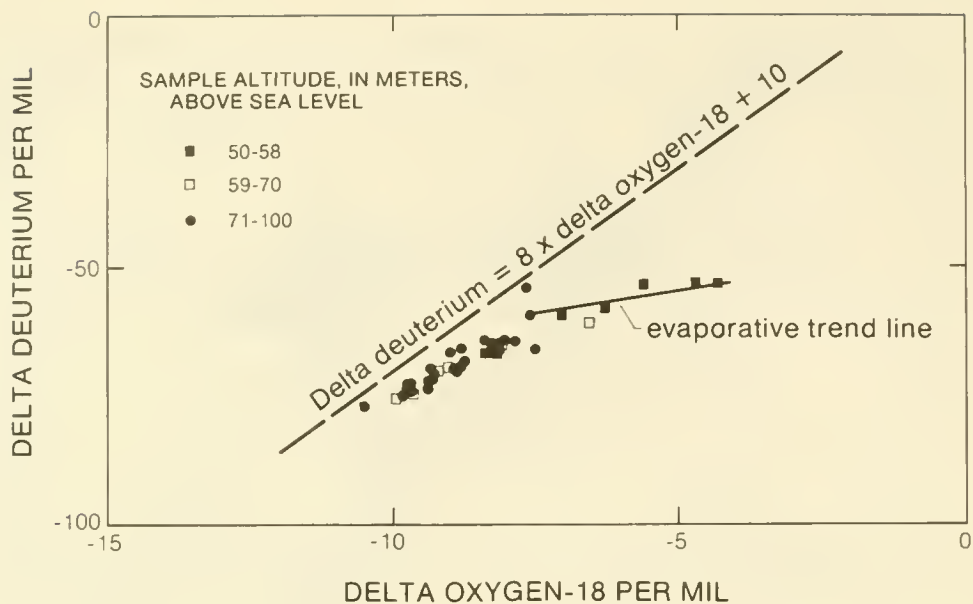


FIGURE 9. Comparison of delta deuterium and delta oxygen-18 for samples collected from various altitudes.

the study area prior to 1970 when the water table was too deep for evaporative concentration to occur. The saline shallow water collected at the lower altitudes seems to be regional ground water that was applied as irrigation water and then evaporated where the water table was shallow.

The two samples collected at low altitudes had tritium concentrations of 1.4 and 1.7 TU and isotopic compositions of $\delta D = -52.5$ and $\delta^{18}O = -4.30$ and $\delta D = -53.0$, $\delta^{18}O = -5.60$ per mil, respectively. The low tritium values in these two samples indicate that this partially evaporated water is composed primarily of water that infiltrated prior to the introduction of atmospheric tritium. In this area, where there is probably little ground-water recharge from rainfall, we assume that most of the tritium in the ground water was introduced since about 1970, when water from the Federal Central Valley Project was first introduced. The tritium values in 13 samples from higher

altitudes ranged from 7.5 to 31.5 TU (median, 15.25 TU), indicating that the ground water infiltrated at land surface since about 1970. Irrigation water collected from the Federal Central Valley Project in spring 1986 had 13 TU.

The most probable explanation for the lower tritium values at the lower altitudes is the greater depth below the water table at which the samples were collected. All wells sampled are perforated over their entire length such that wells at the lower altitudes penetrate farther into the saturated zone. Wells sampled at the lower altitudes probably intercept older evaporated water. Wells at the higher altitudes intercept only the top 1 to 3 m of the ground water.

Clusters of wells that were installed at the M2 site (fig. 10) at various depths and screened over small intervals (0.3 m) provide additional information about the processes of leaching and evaporation. Figure 10 shows a comparison

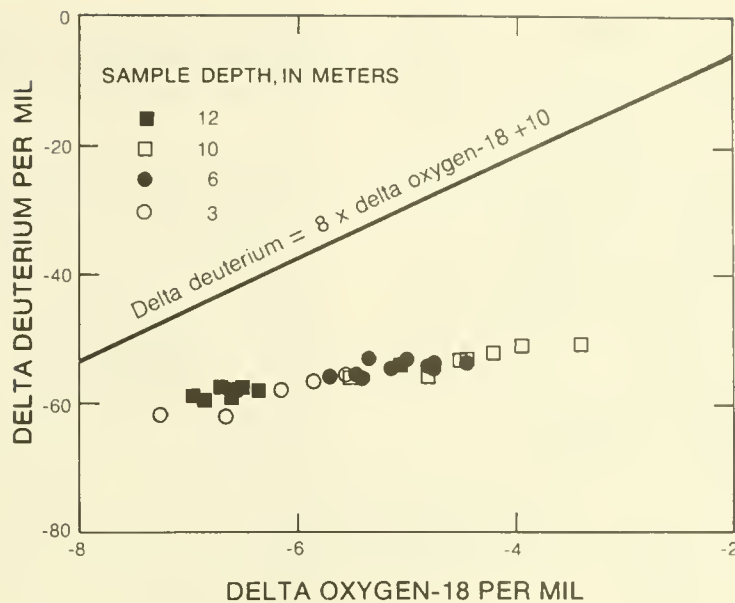


FIGURE 10. Comparison of delta deuterium and delta oxygen-18 for samples collected at various depths at the M2 site.

of δD and $\delta^{18}O$ for samples collected from wells along a 300-m transect in the agricultural field at the M2 site (fig. 1). Samples collected from wells perforated at 10 and 6 m below land surface are the most evaporated. They also are the most saline and have the highest selenium concentrations (median, 3,500 $\mu g/L$). Samples from wells at the 3-m depth are less evaporated and have lower selenium concentrations (median, 1,600 $\mu g/L$). This water has displaced the enriched water since the mid-1970's, when this area had a water table within 1 m of land surface. The present-day water table fluctuates between 3 and 1.5 m of land surface.

The points plotted in figure 10 represent an evaporative trend that is described by the equation:

$$\delta D = 2.80 \times \delta^{18}O - 40.7 \quad (r=0.92). \quad (8)$$

The slope of this line is significantly ($\alpha=0.01$) lower than the evaporative trend slope of 4.28 reported by Deverel and

Fujii (1988) for shallow ground water collected beneath agricultural fields in the western valley, north of the M2 site. Allison (1982) presented evidence that indicates that this low slope is the result of prolonged evaporation from a dry surface. The slope for six unsaturated-zone isotope values collected from this field is 2.38. This and evidence presented by Allison (1982) indicates that displacement since the mid-1970's of unsaturated-zone water that has been subject to evaporation from a dry surface soil resulted in the present-day pattern of isotopic enrichment in the shallow ground water shown in figure 10.

Samples collected from wells at a depth of 12 m are similar in isotopic composition to the samples collected in wells at a depth of 3 m. Because the isotopic composition of this water is similar to the irrigation water applied prior to 1970, the water at 12 m is probably water that was applied at land surface 25 to 40 years ago. Tritium data indicates that vertical rates of ground-water movement

in this field have been 0.3 to 0.75 m/a during the last 20 years. The high selenium concentrations in this ground water are probably the result of leaching of soluble selenium from the unsaturated zone when this area was initially irrigated. The local well water has less than 10 µg/L of selenium. Tritium is not present in samples collected below 6 m indicating that this water infiltrated prior to 1970. A rise in the water table caused the water now present at the 6 and 10 m depths to become evaporated, increasing its isotopic enrichment and selenium concentration. Installation of drains in 1980 has since lowered the water table so that samples collected at the 3-m depth (near the water-table surface) are less evaporated.

Mineral Controls

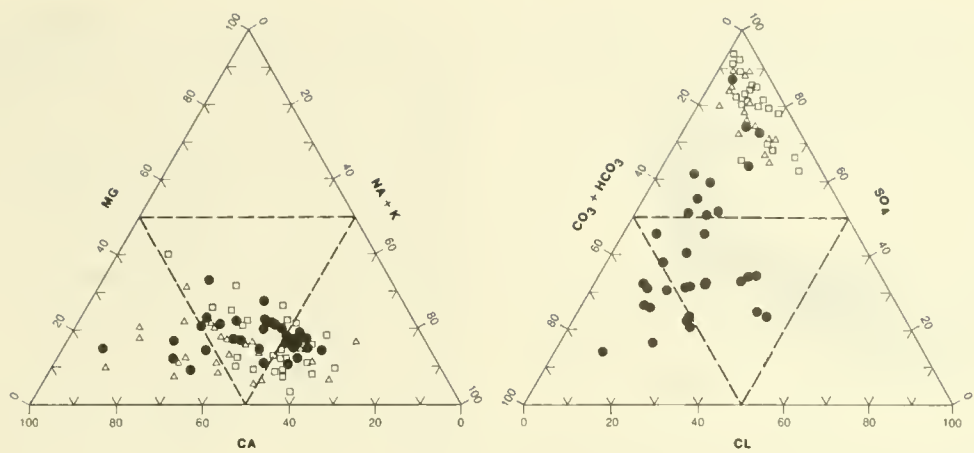
Trends in major-ion composition correspond to differences in ground-water salinity and selenium concentrations (fig. 11). Sodium and sulfate are the predominant ions in the most saline water (those having dissolved solids greater than 6,500 mg/L). The chemistry of ground water that is less saline is more dominated by calcium and bicarbonate. Dissolution and precipitation of gypsum and calcite have probably resulted in less saline calcium sulfate and calcium bicarbonate water.

All the water samples were supersaturated with calcite as determined by WATEQF simulation (Plummer et al., 1976). The increase in bicarbonate percentages with decreasing salinity is probably a manifestation of calcite equilibrium not apparent in water having higher salinities. High partial pressures of carbon

dioxide in the root zone also may lead to higher bicarbonate percentages also not apparent at higher salinities.

The primary mineral-water interaction in the alluvial shallow aquifer is the dissolution or precipitation of gypsum. As salinity and isotopic enrichment increase, gypsum saturation indices increase (fig. 12). In the ephemeral-stream alluvial fans and the margins of the four major fans, ground water is generally saturated or supersaturated with gypsum. In nonsaline areas of the major fans, ground water is generally undersaturated with gypsum. Gypsum precipitation and dissolution are the major processes controlling sulfate concentrations. Lower salinity values are associated with lower sulfate activities. As salinity increases because of evaporative concentration, gypsum precipitation limits the increase in sulfate concentration.

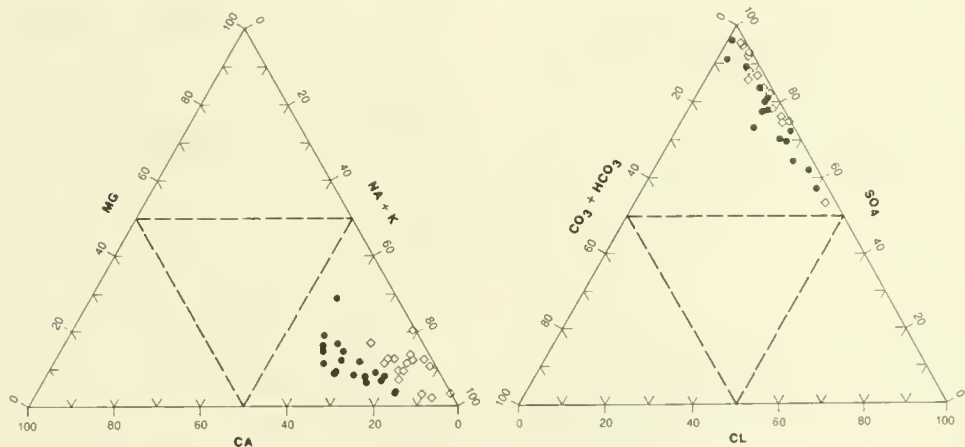
Both sulfate and selenium increase as salinity increases but selenium concentrations increase disproportionately to sulfate concentrations. In saline, selenium-enriched areas, selenium-to-sulfate ratios are higher compared with the low-selenium areas. In the upper and central areas of the alluvial fans deposited by intermittent streams, selenium-to-sulfate ratios are about 0.00001. In more saline and high selenium areas, such as the lower-fan areas of the intermittent-stream fans and middle- and lower-fan areas of the ephemeral-stream fans, ratios range from 0.0001 to 0.001. Similarly, Deverel and Fujii (1988) found that the selenium-to-sulfate ratio increased exponentially with increasing isotopic enrichment of the water sample.



EXPLANATION

DISSOLVED SOLIDS, IN MILLIGRAMS PER LITER

- Less than 2,500
- ▲ 2,501 - 4,000
- 4,001 - 6,500



EXPLANATION

DISSOLVED SOLIDS, IN MILLIGRAMS PER LITER

- 6,501 - 10,500
- ◇ Greater than 10,500

FIGURE 11. Chemical composition of water samples.

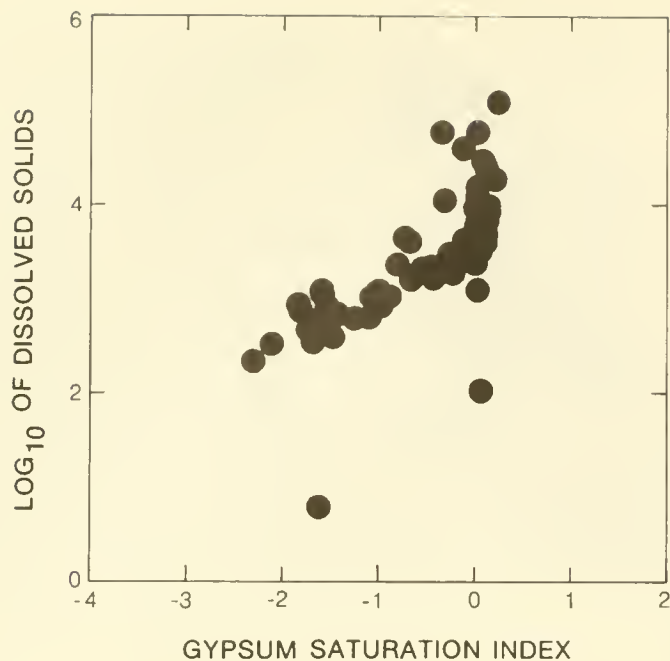


FIGURE 12. Comparison of gypsum saturation indices and dissolved solids.

In water with low-selenium concentrations (less than 200 $\mu\text{g/L}$) and salinities, sulfate and selenium probably behave similarly. In the low range, both sulfate and selenium probably are similarly affected or unaffected by mineral precipitation, dissolution, or other reactions with mineral surfaces. Leckie et al. (1979) and Hingston et al. (1974) demonstrated that selenium in the selenate (+6) oxidation state adsorbs weakly to mineral surfaces such as smectite clays and iron oxyhydroxide surfaces. As ground-water salinity increases because of evaporation, selenium is less affected than sulfate by mineral precipitation or surface phenomena, whereas increases in sulfate activities probably are limited by gypsum precipitation.

Oxidation Reduction

The oxidation-reduction status of the 46 samples collected during spring 1986 is shown in figure 13. The pH and two

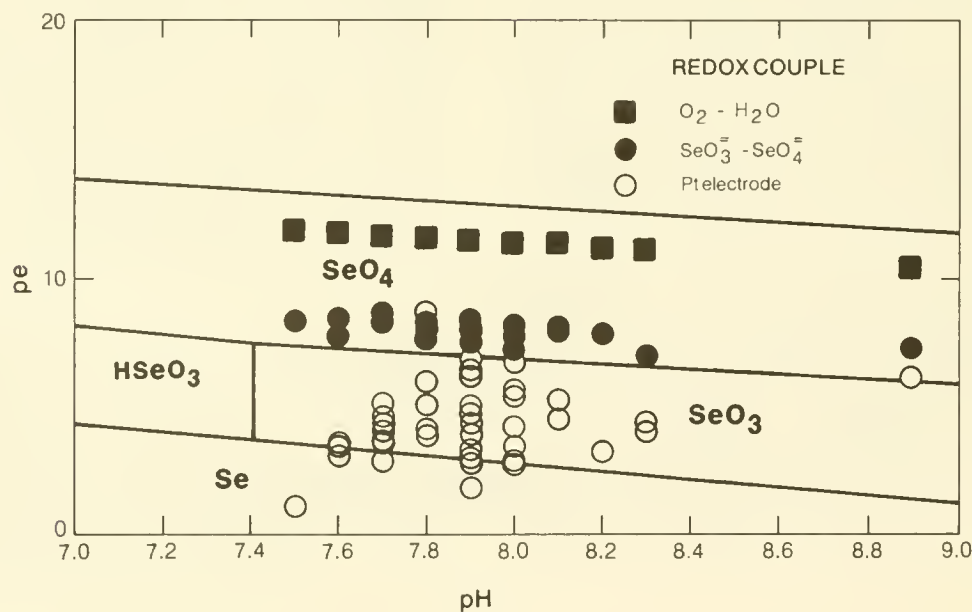


FIGURE 13. Oxidation reduction status of selected samples.

redox indicators', dissolved oxygen and the selenate/selenite couple, indicate oxidized and alkaline conditions. Ferrous iron was not detected at concentrations greater than 10 µg/L, which further indicates oxidized conditions. Ferric-iron concentrations ranged from 60 to 100 µg/L. Dissolved-organic-carbon concentrations were high (Thurman, 1985), with a median of 4.9 mg/L, but organic-matter content of the alluvial materials generally is low (usually less than 0.25 percent). The origin and identity of the dissolved-organic matter is currently being investigated.

The platinum electrode indicates more reducing conditions and is in disequilibrium with the selenium species in solution. This may be indicative of more reducing conditions due to some other redox couple. The oxygen-water couple is typically grossly out of equilibrium (Ball et al., 1979). The presence of some selenite in solution may indicate that nonassimilatory reduction of selenate coupled with the oxidation of organic carbon or another inorganic constituent is taking place. The activity of the selenite species in solution is low because it is rapidly adsorbed onto mineral surfaces. This hypothesis is partly supported by data presented by Fujii et al. (1988). They reported that about 50 percent of the selenium adsorbed on soil samples collected in the study was in the selenite form.

CONCLUSIONS

The results of this study illustrate the processes that have resulted in the regional distribution of salinity and selenium in shallow ground water. The main conclusions are as follows:

- (1) The highest salinity and selenium in shallow ground water occur in alluvium deposited by ephemeral streams and at the margins of the major alluvial fans, where there were naturally saline, fine-grained soils.
- (2) Low-to-moderate salinity and selenium in shallow ground water are associated with upper and middle areas of the major alluvial fans deposited by intermittent streams.
- (3) The history of irrigation in the western valley has affected the distribution of soil and ground-water salinity and selenium. Many areas with the most saline soils have been irrigated only in the last 40 years. These are now the areas of highest dissolved-solids and selenium concentrations in shallow ground water.
- (4) In the area irrigated since 1940, present-day ground-water salinity is significantly correlated with natural soil salinity.
- (5) Oxygen- and hydrogen-isotope data show that the most saline and highest selenium water present at low altitudes resulted from evaporative concentration when the water table was near the land surface.
- (6) Saline and selenium-enriched water is predominately sodium sulfate. Water that is less saline is calcium sulfate and calcium bicarbonate in composition.
- (7) Most dissolved selenium in ground water is in the selenate form and the shallow ground-water samples generally are oxic.

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