

**PRELIMINARY ASSESSMENT OF SOURCES, DISTRIBUTION, AND MOBILITY OF
SELENIUM IN THE SAN JOAQUIN VALLEY, CALIFORNIA**

By Robert J. Gilliom and others

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 88-4186

REGIONAL AQUIFER SYSTEM ANALYSIS

**Prepared in cooperation with the
SAN JOAQUIN VALLEY DRAINAGE PROGRAM**

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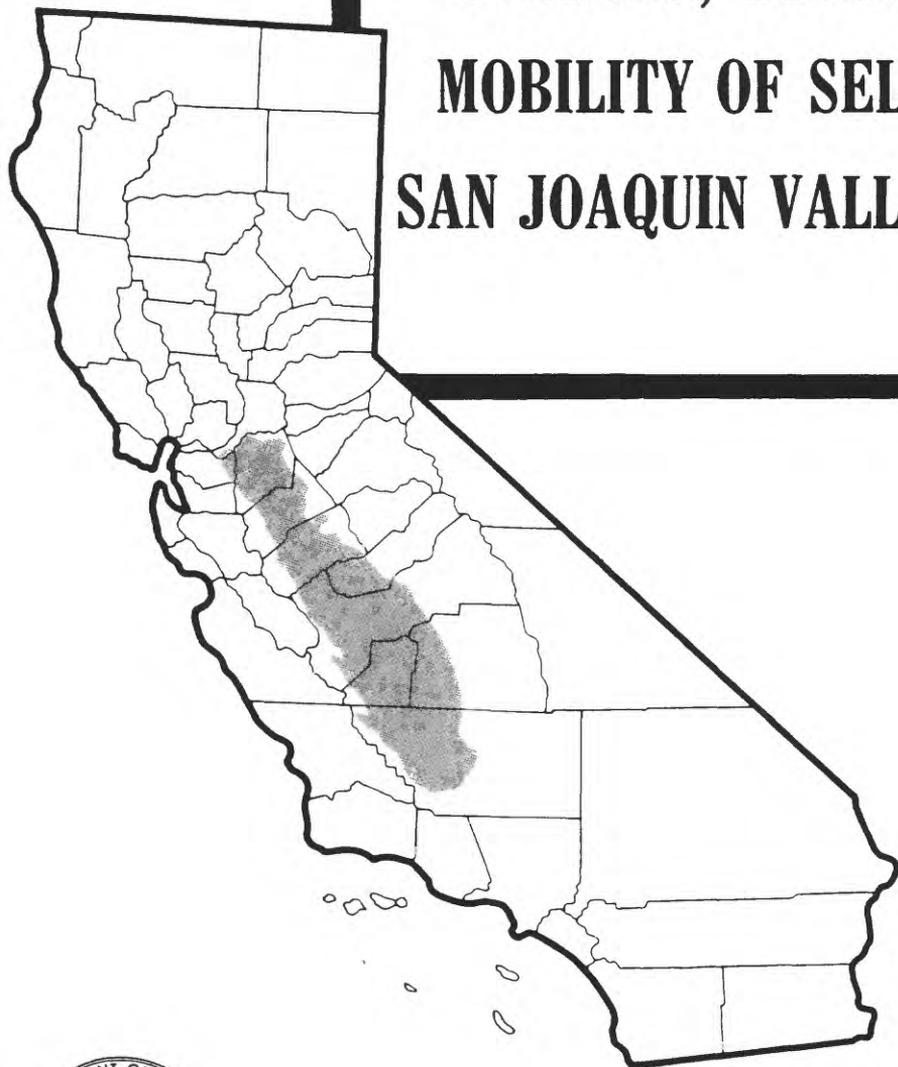
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This report was prepared by the U.S. Geological Survey in cooperation with the San Joaquin Valley Drainage Program and as part of the Regional Aquifer System Analysis Program of the U.S. Geological Survey.

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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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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CONVERSION FACTORS

The inch-pound system of units is used in this report. For those readers who prefer to use metric (International System) units rather than inch-pound units, the conversion factors for the units used in this report are listed below.

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain metric unit</u>
acre	0.4047	square hectometer
acre-ft (acre-foot)	0.001233	cubic hectometer
acre-ft/yr (acre-foot per year)	0.001233	cubic hectometer per year
ft (foot)	0.3048	meter
ft/d (foot per day)	0.3048	meter per day
ft/mi (foot per mile)	0.1894	meter per kilometer
ft/yr (foot per year)	0.3048	meter per year
ft ³ /s (cubic foot per second)	0.0283	cubic meter per second
(ft ³ /yr)/ft ² (cubic foot per year per square foot)	0.3048	cubic meter per year per square meter
in. (inch)	25.4	millimeter
mi (mile)	1.609	kilometer
mi ² (square mile)	2.590	square kilometer
ton/yr (ton per year)	907.2	kilogram per year

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

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

Abbreviations

µg/L	microgram per liter
µm	micrometer
mg/kg	milligram per kilogram
µS/cm	microsiemen per centimeter at 25 degrees Celsius
Tu	tritium unit
mV	millivolt

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."

PRELIMINARY ASSESSMENT OF SOURCES, DISTRIBUTION, AND MOBILITY OF SELENIUM IN THE SAN JOAQUIN VALLEY, CALIFORNIA

By Robert J. Gilliom and others

ABSTRACT

Selenium in tile drain water from parts of the western San Joaquin Valley, California, has adversely affected fish and waterfowl where drain water was impounded. Soils in these drained areas were derived from Coast Range marine sedimentary formations, were naturally saline, and probably contained abundant soluble selenium. Decades of irrigation have redistributed the most soluble forms of selenium from the soil into ground water and have caused the water table to rise 1 to 4 feet per year. Selenium in shallow ground water has been further concentrated because of evapotranspiration. The rising water table has caused a large area of farmland to require artificial drainage of ground water that contains high concentrations of selenium. The present areal distribution of selenium in shallow ground water reflects the natural distribution of saline soils. The depth distribution of selenium in ground water reflects the history of irrigation. The highest concentrations of selenium in ground water (50 to more than 1,000 micrograms per liter) are in a zone of variable thickness located between 20 and 150 feet below the water table. The oxic water in this zone was recharged during the first few decades of irrigation. The large volume of high-selenium ground water makes it desirable to leave this water where it is, rather than bring it to the land surface or allow it to move into parts of the aquifer that may be used for water supply. Selenium concentrations in the San Joaquin River depend on the magnitude of the selenium load from drain water and dilution by water with low concentrations of selenium from all other sources of streamflow. The San Joaquin Valley is a regional-scale example of how manipulation of the hydrologic system can cause water-quality problems if naturally occurring toxic substances are mobilized.

INTRODUCTION

Agricultural drainage problems in the San Joaquin Valley, California, have attracted national attention since 1983, when selenium in water from subsurface tile drainage systems in the central part of the western valley was found to have toxic effects on waterfowl at Kesterson Reservoir (Presser and Barnes, 1985; Ohlendorf and others, 1986). Kesterson Reservoir was then jointly managed by the U.S. Bureau of Reclamation as a drain-water storage facility, and by the U.S. Fish and Wildlife Service as part of the Kesterson National Wildlife Refuge (U.S. Bureau of Reclamation, 1984a). The discovery of selenium in drain water and its toxic effects halted plans by the U.S. Bureau of Reclamation to complete the San Luis Drain, a concrete-lined channel designed to convey drain water from the valley to the delta of the Sacramento and San Joaquin Rivers. The historical chronology of agricultural water management and environmental issues related to agricultural drainage problems in the San Joaquin Valley since the late 1800's has been reviewed by many authors (Kelley and Nye, 1984; U.S. Bureau of Reclamation, 1984a, 1984b, 1984c, 1984d; Bay Institute of San Francisco, 1985; Letey and others, 1986; Tanji and others, 1986; and Water Education Foundation, 1986).

In 1984, the U.S. Department of Interior and the State of California initiated a new study effort, the San Joaquin Valley Drainage Program, aimed at assessing and reevaluating management options for agricultural drainage in the valley. The U.S. Geological Survey is a participating agency in the San Joaquin Valley Drainage Program, with the role of providing a hydrologic and geochemical assessment of the central part of the western San Joaquin Valley, where the most severe drain-water quality problems have occurred.

Purpose and Scope

The purpose of this report is to summarize the results of U.S. Geological Survey studies and related research by others on (1) the sources, distribution, and mobility of selenium in soils and ground water of the San Joaquin Valley, particularly the central part of the western valley, and (2) the sources and concentrations of selenium in the San Joaquin River, where drain water from about 77,000 acres of farmland is discharged. Information presented in this report was compiled during the summer and autumn of 1987 and represents the results of about 2½ years of study--the halfway point of a 5-year effort.

Focus on Selenium

This report focuses on selenium because it is the most severe and widespread constraint on management alternatives for drain water and shallow ground water. However, in the course of this assessment, the basic relations between selenium, hydrology, and saline conditions are examined in a manner

that provides a background on processes likely to affect other potential contaminants as well. Studies are cited that include detailed information on major-ion chemistry, alkalinity, and other characteristics of the types of ground and surface water assessed. The Survey's studies, combined with related work by researchers at the University of California, the Lawrence Berkeley Laboratory, the Agricultural Research Service, and others, address questions of concern to the public and local, State, and Federal water managers:

Where does selenium come from?

Where is selenium now distributed in soils and ground water?

Where and how fast is selenium in ground water moving?

How does selenium get into ground water and drain water?

Will selenium concentrations become lower with time if present management practices continue?

Where and how fast is the water table rising?

Can the water table be controlled by managing irrigation practices and ground-water withdrawals in order to reduce the need for drainage?

How much selenium is reaching the San Joaquin River, and is it having adverse effects on the river, the Sacramento-San Joaquin Delta, or San Francisco Bay?

These and other related questions are partially answered in this report on the basis of presently available information. Careful consideration of present knowledge in relation to these questions provides information and guidance to water managers and aids in modifying and prioritizing goals for future study.

Other Contaminants of Concern

In addition to selenium, other potential contaminants deserve mention and identification for more careful analysis as specific options for managing drainage problems are evaluated. Other trace elements, pesticide residues, and salinity are potential water-quality problems in various parts of the San Joaquin Valley. In general, trace elements are likely to be highest in subsurface drain water and pesticide residues are likely to be highest in agricultural surface runoff. Salinity is highest in subsurface drain water, but also is high in some agricultural surface runoff.

The trace elements boron, molybdenum, manganese, mercury, cadmium, chromium, copper, nickel, and zinc were recently identified by the California State Water Resources Control Board as constituents of primary regulatory concern in the San Joaquin River basin (California State Water Resources Control Board, 1987). Boron and molybdenum usually affect the use of water for agriculture at lower levels than for aquatic life, whereas the other elements have adverse effects on aquatic life at lower levels than for agricultural uses. Cadmium, chromium, copper, mercury, and zinc are all U.S. Environmental Protection Agency priority pollutants and also are potential concerns for drinking-water quality. Arsenic, also a priority pollutant, was not identified as a primary regulatory concern in the San Joaquin River basin. However, arsenic is of concern in some parts of the Tulare Lake drainage basin in the southern San Joaquin Valley, such as the southern Tulare Lake bed and the Goose Lake bed, where arsenic concentrations generally are high, but selenium concentrations are relatively low (Fujii, 1988).

Chromium and mercury were identified as contaminants of concern in the first assessment of trace elements in shallow ground water of the western San Joaquin Valley (Deverel and others, 1984). Although mercury was detected at only a few sites, chromium seems to merit particular concern in some areas. Data collected by the U.S. Bureau of Reclamation from 1984 to 1986 indicate that levels of the hexavalent form of chromium may commonly exceed the U.S. Environmental Protection Agency criterion for protection of aquatic life in shallow ground water in parts of the western valley. The acute criterion is 16 $\mu\text{g/L}$ for 1 hour, and the chronic criterion is 11 $\mu\text{g/L}$ averaged over 4 days (U.S. Environmental Protection Agency, 1986). The Bureau of Reclamation data indicate that hexavalent chromium generally is the most prevalent form of dissolved chromium in the study area, and that concentrations of hexavalent chromium commonly exceeded 16 $\mu\text{g/L}$ at 19 of 30 drain sumps and shallow observation wells.

Many management alternatives developed by Federal, State, and local water managers to address water-quality problems related to high selenium concentrations also may help address problems related to other contaminants. For example, although local geologic sources of chromium may occur in Sierra Nevada foothills, chromium occurs mainly in ground water associated with Coast Range alluvium and is correlated with salinity and selenium. In general, boron and molybdenum also are highest in saline ground water, often where selenium is high as well. Management alternatives that, for example, control the production of high selenium drain water, probably will also help control water-quality problems associated with other contaminants. Nevertheless, as management alternatives designed to address water-quality problems related to selenium are refined, their effectiveness in addressing other contaminants of concern will need to be carefully evaluated.

STUDY AREA

The San Joaquin Valley occupies the southern two-thirds of the Central Valley of California and is bounded by the Sierra Nevada on the east, the Tehachapi Mountains on the south, and the Coast Range on the west. The locations of the San Joaquin Valley and the primary study area of the soil and ground-water studies emphasized in this report are shown in figure 1. The primary study area is in the central part of the western valley and includes the southwest corner of Merced County, western Fresno County, and a small part of western Kings County. Other parts of the San Joaquin Valley are discussed to lesser and varying degrees. The focus of studies of the San Joaquin River is on the perennial-flow part of the river and its major tributaries between Stevinson and Vernalis (fig. 1).

The San Joaquin Valley is a structural trough filled with as much as 3,000 feet of unconsolidated deposits of sediment (Hotchkiss and Balding, 1971). The character of the sediments reflects their geologic origin in adjoining mountains and the hydrologic environments in which they were deposited. The Sierra Nevada are composed largely of pre-Tertiary granitic rocks and metamorphosed sediments and the Tehachapi Mountains are composed largely of pre-Tertiary granitic rocks. The part of the Coast Range adjacent to the primary study area has a core composed chiefly of the Franciscan assemblage of late Jurassic to late Cretaceous or Paleocene age and partly of Mesozoic ultramafic rocks.

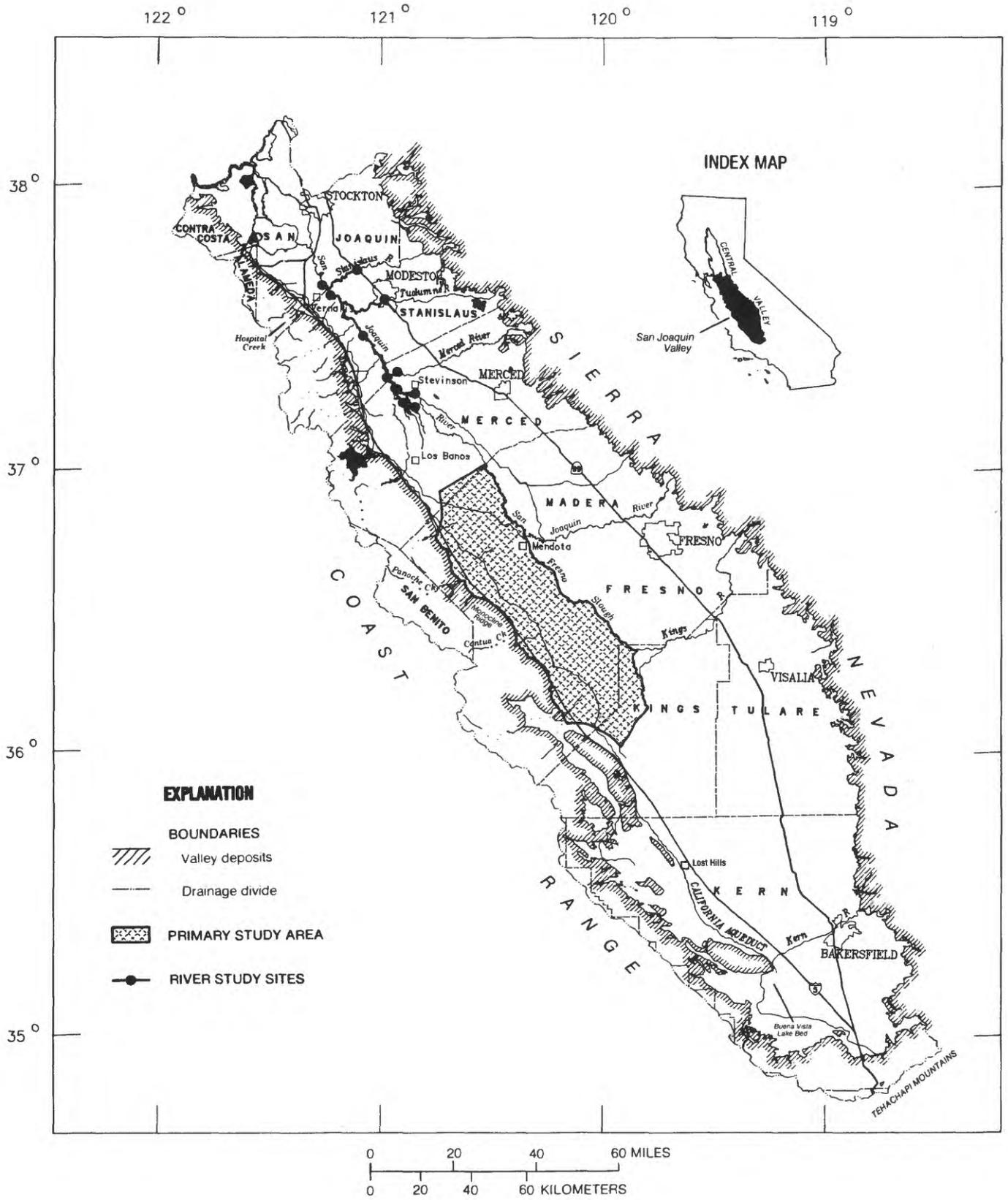


FIGURE 1.— Location of San Joaquin Valley and primary study area in the central part of the western valley.

These rocks are overlain by Cretaceous and Tertiary marine rocks, continental rocks and deposits of Tertiary age, Tertiary volcanic rocks, and, on the extreme western flank, by a mixture of continental rocks and deposits of Tertiary and Quaternary age (Lettis, 1982). The unconsolidated sediments in the valley are mainly composed of alluvial-fan, flood-plain, flood-basin, lacustrine, and marsh deposits. Sediments derived from the Coast Range generally are finer grained than those derived from the Sierra Nevada (Croft, 1972).

The San Joaquin Valley has an arid to semiarid climate that is characterized by hot summers and mild winters. Precipitation on the interior Coast Range, west of the study area, is mostly rainfall and averages 15 to 20 inches annually (Rantz, 1969). Average precipitation is 8 to 15 inches in the foothills of the Coast Range and 6.5 to 8 inches on the valley floor decreasing from north to south. As much as 80 inches of precipitation falls in the Sierra Nevada, mainly as snow. Precipitation occurs mostly in the winter from cyclonic storms. Temperatures in the valley range from an average daily minimum of about 35 °F to an average daily maximum of about 102 °F. Most of the valley is frost free at least 8 months of the year.

The climate and fertile alluvial sediments of the San Joaquin Valley make it one of the world's most productive irrigated agricultural areas. Most of the valley floor is presently irrigated, and more than 200 crops are grown commercially. Cotton is the principal crop in the primary study area in the central part of the western valley. Five counties in the San Joaquin Valley are among the Nation's ten highest producers of agricultural commodities.

GEOLOGIC SOURCE OF SELENIUM AND ITS DISTRIBUTION IN SOIL

by *Robert J. Gilliom*

A general evaluation of geologic sources of selenium and its distribution in soils of the entire San Joaquin Valley provides background information needed for more detailed analysis of the primary study area. Selenium in water, soils, and underlying sediments of the San Joaquin Valley originated from geologic formations exposed in adjacent mountains and was transported to the valley in particulate and dissolved forms derived from the weathering and erosion of source rocks (Barnes, 1985). Source rocks differ in selenium concentrations, in proximity to the valley floor or major stream channels, in resistance to weathering, and thus, in their significance as selenium sources to the valley. The relative significance of different types of source rocks in contributing selenium to the valley can be evaluated from selenium concentrations in soil.

Distribution of Selenium in Soils of the San Joaquin Valley

The distribution of selenium in soil was examined and mapped for the entire San Joaquin Valley by Tidball and others (1986a). Their analysis was based on samples of the top 12 inches of soil collected on an irregular grid, with an approximate spacing of about 6 miles between samples. The areal distribution of estimated total selenium concentrations for the 0- to 12-inch depth interval in soils is shown in figure 2. The dominant influence of Coast Range sources of selenium is evident in the areal distribution shown on this map. Virtually all concentrations greater than the median of 0.13 mg/kg occur in alluvial sediments derived from weathering and erosion of Coast Range rocks. In contrast, soils of the eastern side of the San Joaquin Valley, which consist of sediments derived from rocks in the Sierra Nevada, are low in selenium--generally less than 0.13 mg/kg. For comparison, the median of 912 soil samples from throughout the United States was about 0.3 mg/kg (Shacklette and others, 1974). Only about 10 to 20 percent of the soils in the San Joaquin Valley are estimated to have concentrations of selenium that exceed the national median of 0.3 mg/kg.

The three areas of the valley where selenium in soil commonly exceeds 0.36 mg/kg, the 90th percentile of concentrations in valley soils, are (1) the alluvial fans east of Monocline Ridge, near Panoche and Cantua Creeks, (2) an area west of the town of Lost Hills, and (3) the Buena Vista Lake Bed area, southwest of Bakersfield (fig. 2; Tidball and others, 1986a). All three areas with the highest selenium concentrations in soil are adjacent to parts of the Coast Range where marine sedimentary formations are exposed. These sedimentary formations are sources of sediment from which the soils are derived. Available data indicate the presence of high selenium concentrations in subsurface agricultural drain water from some farmlands near all three areas (Deverel and others, 1984; California Department of Water Resources, 1986).

Geologic maps of the Coast Range to the west of the San Joaquin Valley show the locations and extent of exposed formations (California Division of Mines and Geology, 1959a, 1959b, 1965, 1966, 1969). Eocene marine rock, including the Kreyenhagen Shale, is present in exposures in the Coast Range to the west of all three areas with concentrations of selenium in soil that exceed the 90th percentile for valley soils. Preliminary data reported by Lund and others (1987) for the Cantua Creek drainage indicate that samples of the Kreyenhagen Shale had selenium concentrations ranging from 3.1 to 18.6 mg/kg. The Kreyenhagen Shale is similar in character to the older Moreno Formation, for which 28 mg/kg of selenium was reported in 1941 for a sample collected near Hospital Creek, north of the primary study area (Lakin and Byers, 1941). Lund and others (1987) found that the Moreno Formation in the Cantua Creek drainage had selenium concentrations ranging from 0.2 to 2.4 mg/kg. In other parts of the United States, marine shales generally have the highest concentrations of selenium compared to other rocks (Sharma and Singh, 1983). On a broad scale, the occurrence of soil with high selenium correlates with the presence of geologic formations with high selenium concentrations.

Distribution of Selenium in Soils of the Central Part of the Western Valley

The central part of the western valley has the largest area with concentrations of selenium in soil that exceed the 90th percentile of concentrations for valley soils. The distribution of total selenium in soils in most of this area was examined in detail by Tidball and others (1986a). They collected soil samples from 721 sites on a 1-mi² grid basis in the area of the Panoche Creek and Cantua Creek alluvial fans. Soil samples were collected from the 66- to 72-inch depth and were composited for analyses; total selenium concentrations at this depth were similar to those at shallower depths. The areal distribution of estimated total selenium concentrations for the 66- to 72-inch depth interval in soils is shown in figure 3.

Selenium concentrations are highest between the alluvial fans of Cantua and Panoche Creeks, east of Monocline Ridge. Concentrations in that part of the area generally are greater than 1.14 mg/kg, which is the 90th percentile of all concentrations measured in the central part of the western valley (fig. 3). Selenium concentrations in soils of the alluvial fans of Cantua and Panoche Creeks generally range from 0.80 to 1.14 mg/kg. Concentrations along the eastern margin of the area and to the south of the Cantua Creek fan are lowest--generally less than 0.80 mg/kg, the median for the area.

Tidball and others (1986a, 1986b) were cautious about interpreting the precise geologic sources of selenium in soils. High selenium concentrations in soils of mudflows and other alluvial sediments east of Monocline Ridge, in the area between the alluvial fans of Cantua and Panoche Creeks, may be attributed to high selenium concentrations in the parent geologic formations of the adjoining hills. The Kreyenhagen Shale is exposed on Monocline Ridge (California Division of Mines and Geology, 1959a). Selenium concentrations in soils of the large alluvial fans of Cantua, Little Panoche, and Panoche Creeks are lower than in the interfan area, partly because they are composed of mixtures

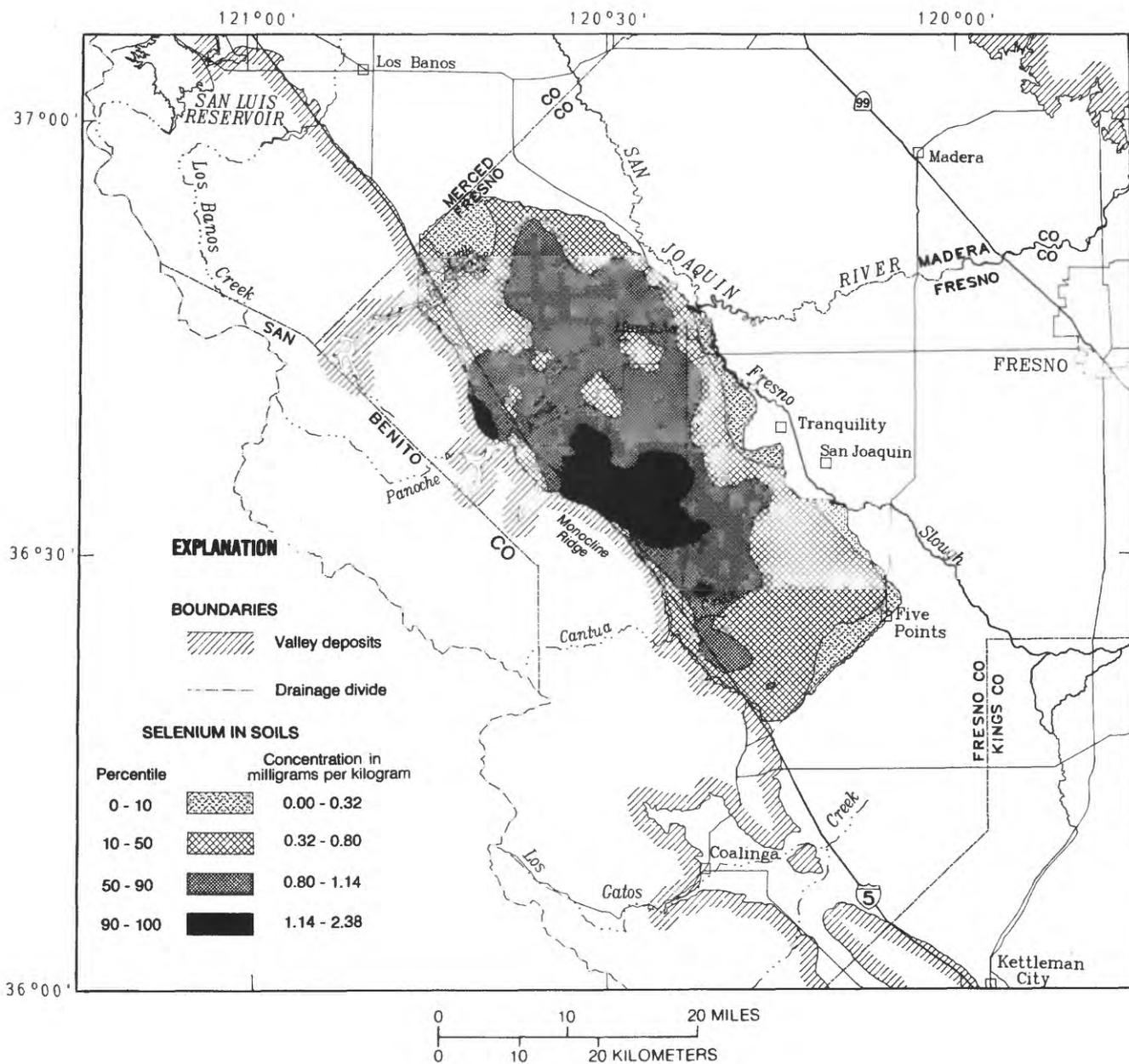


FIGURE 3.— Areal distribution of estimated total selenium concentrations for the 66- to 72-inch depth interval in soils of the central part of the western valley. (Adapted from Tidball and others, 1986a.)

of sediments from large and diverse drainage basins. In the basins of the larger streams, sediments originate from more different types of source materials than in the much smaller drainages associated with the interfan areas. The diversity of sediment sources in the large basins would tend to dilute the effect on soil selenium concentrations of sediment sources with the highest selenium concentrations. In addition, sediments of the fans of the three large streams have been exposed to more natural flushing by runoff water than the sediments deposited by the much smaller streams associated with the areas between the major fans (Belitz, 1988). Although these mechanisms may explain the present distribution of selenium in soil, only direct measurement of geologic source materials at locations where soil sediments originate can determine the geologic sources conclusively.

An exact correlation between the locations of soils and ground water with high selenium concentrations should not be expected. Soluble forms of selenium affect the quality of ground water and the distribution of soluble forms in soil can be different than the distribution of total selenium. The highest concentrations of soluble forms of selenium in soils and ground water can occur in places where hydrologic processes, such as evaporative concentration, contribute to the accumulation of soluble forms of selenium in water or soil. Thus, the highest concentrations of selenium in ground water may occur some distance away from the highest concentrations of total selenium in soil. A key to evaluating the origin and present-day distribution of high selenium concentrations in ground water is to understand the natural distribution of soluble forms of selenium and its redistribution by irrigated agriculture.

GROUND-WATER FLOW SYSTEM OF THE CENTRAL PART OF THE WESTERN VALLEY

by *Kenneth Belitz and Frederick J. Heimes*

Present-day agricultural drainage problems in the central part of the western valley need to be understood in relation to changes in the ground-water system caused by more than 8 decades of irrigated agriculture. Irrigation has been the driving force that has resulted in large and increasing areas with a shallow water table and in the redistribution of readily soluble forms of selenium from soils to ground water. Management of ground water will likely be a key component of strategies used by local, State, and Federal water managers to mitigate subsurface agricultural drainage problems. An understanding of the ground-water flow system is essential for evaluating how present problems occurred and developing possible solutions.

Geohydrologic Framework

The San Joaquin Valley is underlain by several thousand feet of unconsolidated sediments. The upper several hundred to more than a thousand feet of these sediments contain primarily fresh ground water, operationally defined as having a specific conductance of less than 3,000 $\mu\text{S}/\text{cm}$ (Olmsted and Davis, 1961). In much of the western valley, the Corcoran Clay Member of the Tulare Formation divides the flow system of fresh ground water into a lower confined zone and an upper semiconfined zone. The semiconfined zone can be further divided into three geohydrologic units: Coast Range sediments, Sierra Nevada sediments, and flood-basin deposits, which differ in texture, geohydrologic properties, and oxidation state. The primary focus of this report is on ground water in the Coast Range sediments and Sierra Nevada sediments of the semiconfined zone (fig. 4).

The Coast Range alluvial sediments generally are oxidized and range in thickness from 0 feet along the valley trough to more than 800 feet along the Coast Range (fig. 5). Bull (1964b) recognized two types of deposits in the Coast Range alluvial sediments: mudflow and water-laid deposits. The mudflow deposits typically are poorly sorted, are close to the Coast Range or its foothills, and commonly are associated with small ephemeral streams that usually flow only during major storms. The water-laid deposits are better sorted and are more areally extensive than the mudflow deposits. Most water-laid deposits are part of the large alluvial fans of the intermittent streams that flow seasonally.

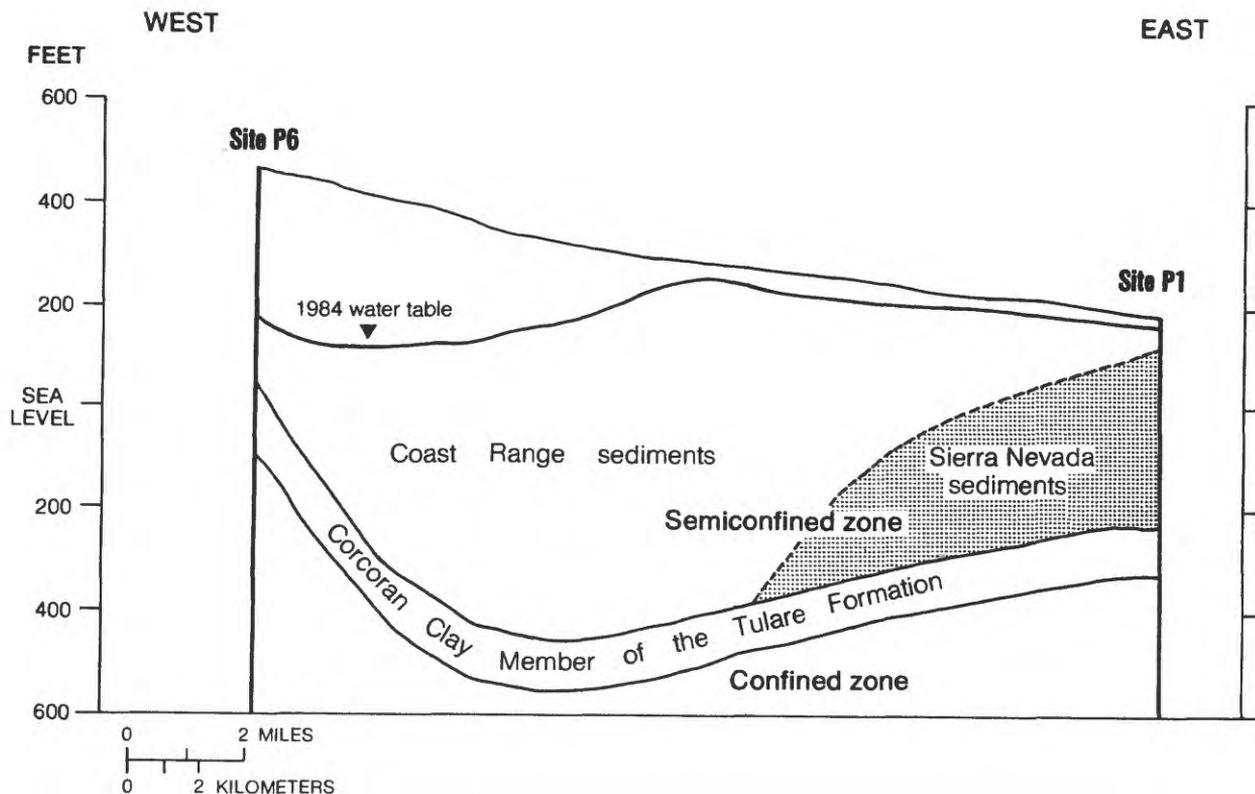


FIGURE 4.— Generalized geohydrologic section of Panoche Creek alluvial fan. (Adapted from Belitz, 1988.)
Location of P6-P1 section shown in figure 6.

Bull (1964a, 1964b, 1972) identified 21 alluvial fans in western Fresno County, ranging in size from less than 1 mi² to more than 250 mi². Coast Range alluvial sediments associated with the four largest fans--Los Gatos Creek fan, Panoche Creek fan, Cantua Creek fan, and Little Panoche Creek fan--occupy most of the total area (fig. 6). Small fans of ephemeral streams, which are of limited areal extent and coalesce with large neighboring fans, are combined in figure 6.

The texture of the Coast Range sediments is largely a function of depth and relative position on the alluvial fans. Alluvial fans are commonly divided into three parts (Blissenbach, 1954; Reineck and Singh, 1980): the apex of the alluvial fan, herein called the upper fan, the area between the fanhead and the outer margin of the fan, herein called the middle fan, and the outer margin of the fan, called the lower fan. Lower-fan areas commonly coalesce with adjacent fans.

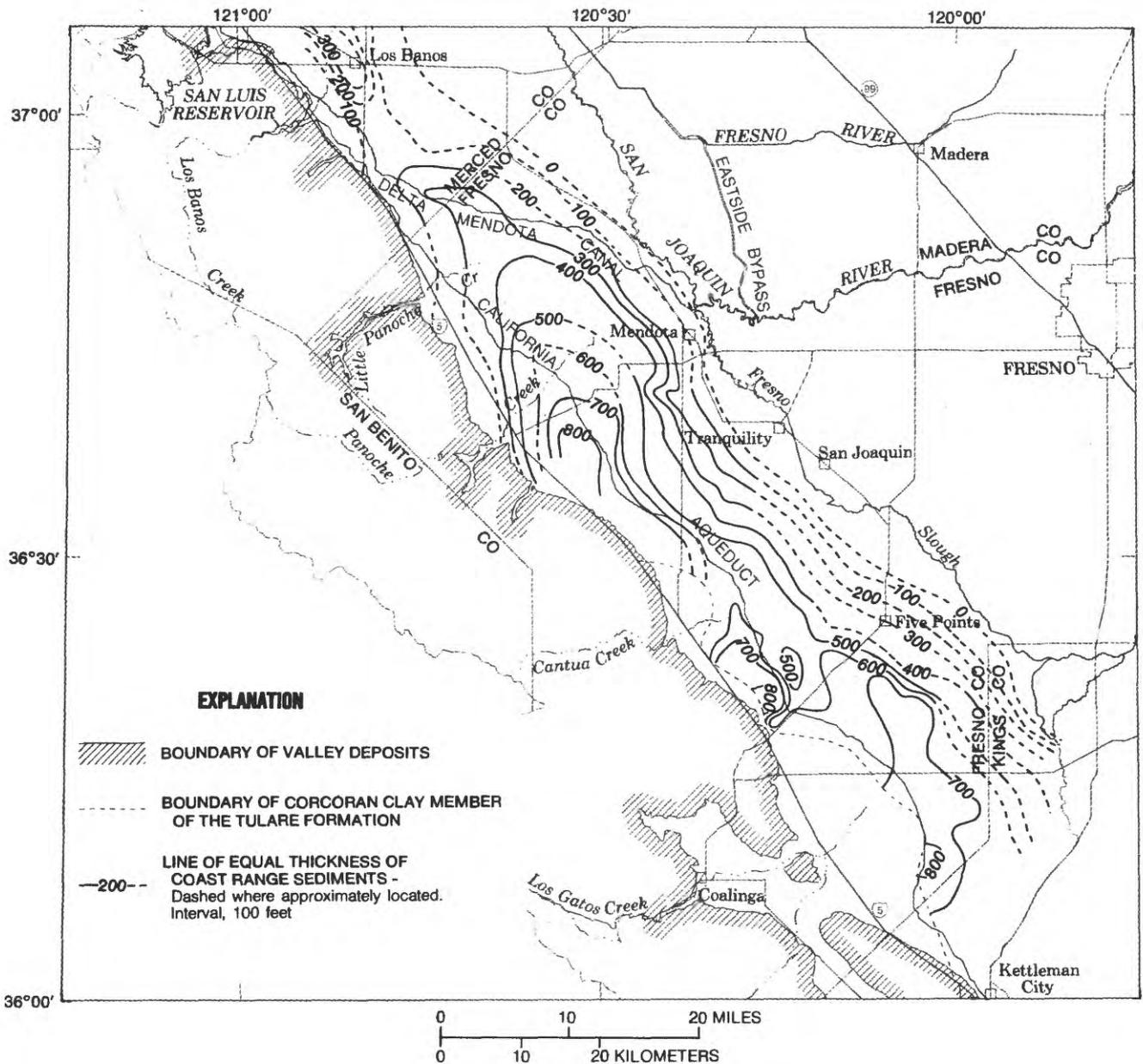


FIGURE 5.— Thickness of Coast Range sediments that overlie the Corcoran Clay Member of the Tulare Formation in the central part of the western valley. (Adapted from Miller and others, 1971.)

Surficial alluvial sediments are coarser at the upper parts of the fans than at middle and lower parts. Textural analysis indicates that the upper-fan surficial sediments are typically 60 to 100 percent sand and gravel and less than 40 percent silt and clay (fig. 7). In contrast, lower-fan surficial sediments typically contain less than 20 percent sand and gravel and more than 80 percent silt and clay. Sediments of the middle fan are mostly fine grained, but are coarse textured along present-day stream channels and older channels. In middle- and lower-fan areas, fine-grained surficial sediments typically are underlain by coarser grained sediments beginning at a depth of about 30 feet (fig. 8).

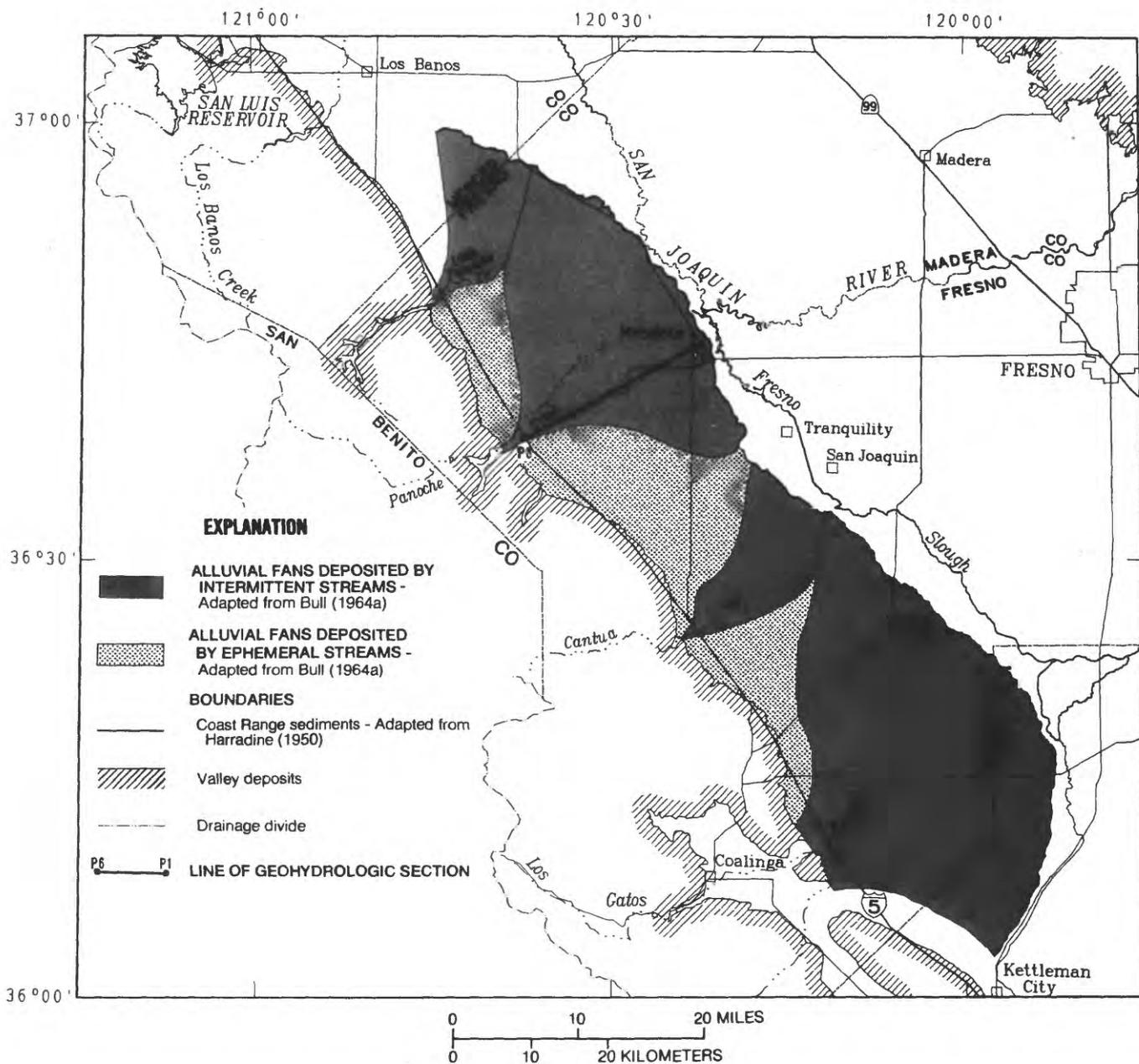


FIGURE 6.— Location and extent of Coast Range alluvial fans in the central part of the western valley.

The relatively coarse-grained alluvial-fan sediments that occur below about 30 feet probably were deposited during a period of greater precipitation and runoff than at present, and sediment transport by streams probably was the dominant mechanism of deposition. The dominance of fine-grained material in the upper 30 feet of the alluvial-fan sediments, and the lack of major stream-channel deposits in these sediments indicate that fluvial deposition decreased with time. The upper parts of the small fans of ephemeral streams have relatively coarse-grained sediments in the upper 30 feet, which are mainly mudflow deposits. The decrease in fluvial deposition and the increase in mudflow deposition indicate that the arid conditions of today probably also existed during the last several thousand years.

The alluvial sediments derived from the Coast Range interfinger in the valley trough with sediments derived from the Sierra Nevada to the east. In the trough of the valley, the sediments derived from the Sierra Nevada are predominantly well-sorted micaceous sands (Miller and others, 1971). The Sierra Nevada sediments are 400 to 500 feet thick in the valley trough and thin eastward and westward (fig. 9). They are highly permeable and have been extensively tapped by wells as a source of water for irrigation and domestic uses. The Sierra Nevada sediments differ from the Coast Range sediments in oxidation state as well as texture. In contrast to Coast Range sediments, the sands from the Sierra Nevada are chemically reduced in the valley trough.

An understanding of the flow system above the Corcoran Clay Member of the Tulare Formation requires, to a certain extent, an understanding of the Corcoran and the sediments below it. The Corcoran is an extensive lacustrine (lakebed) deposit of low permeability (Johnson and others, 1968). The base of the unit ranges in depth from 400 feet in the valley trough to 900 feet along the Coast Range (fig. 10), and most of the unit ranges in thickness from 20 to 120 feet. The upper two-thirds of the Corcoran consists of thin-bedded clayey silt and silty clay and the lower one-third consists of interbedded sand-silt-clay and clayey silt (Bull, 1975). The Corcoran is chemically reduced except in the extreme western part of the study area, where it has been uplifted and partially oxidized. Historically, most of the agricultural production wells in the study area have been perforated below the Corcoran. This confined zone consists of poorly consolidated flood-plain, deltaic, alluvial fan, and lacustrine deposits of the Tulare Formation. The confined zone has been the subject of numerous investigations, many of which focused on land subsidence (Poland and others, 1975).

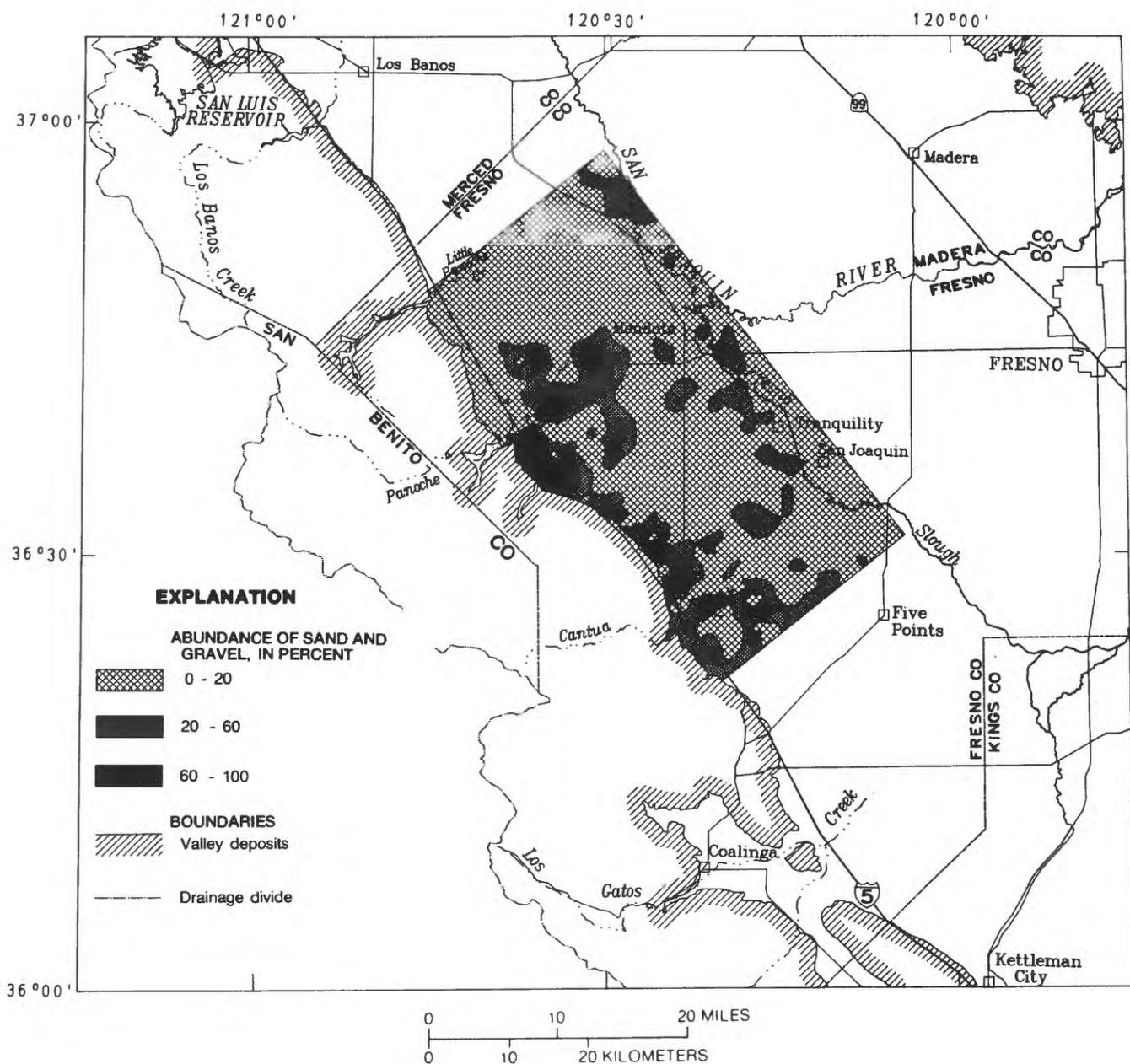


FIGURE 7.— Texture of the 0- to 10-foot depth interval of sediments in the area of the Panoche Creek and Cantua Creek alluvial fans.

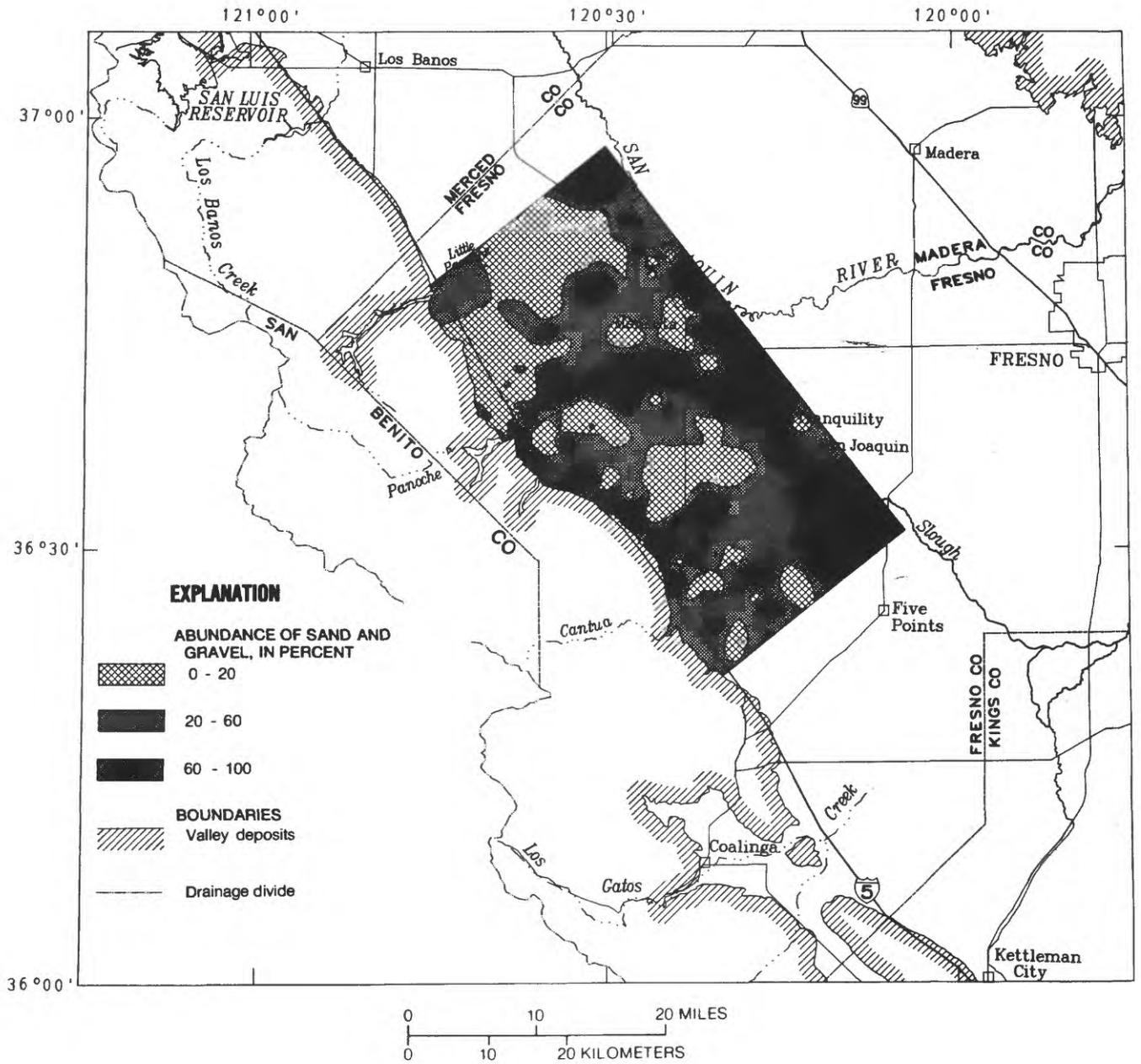


FIGURE 8.— Texture of the 30- to 40-foot depth interval of sediments in the area of the Panoche Creek and Cantua Creek alluvial fans.

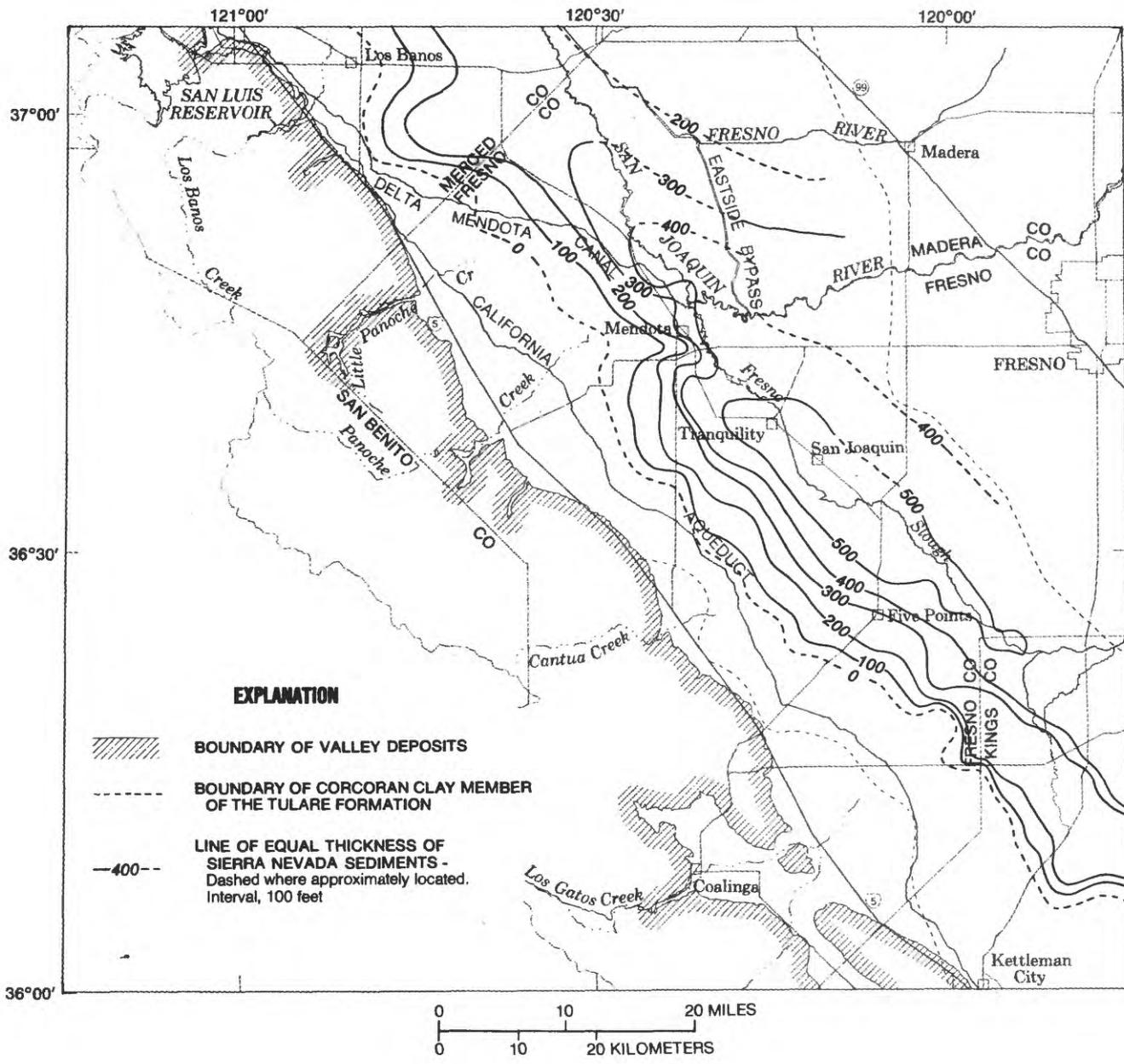


FIGURE 9.— Thickness and extent of Sierra Nevada sediments in the central part of the western valley. (Adapted from Miller and others, 1971.)

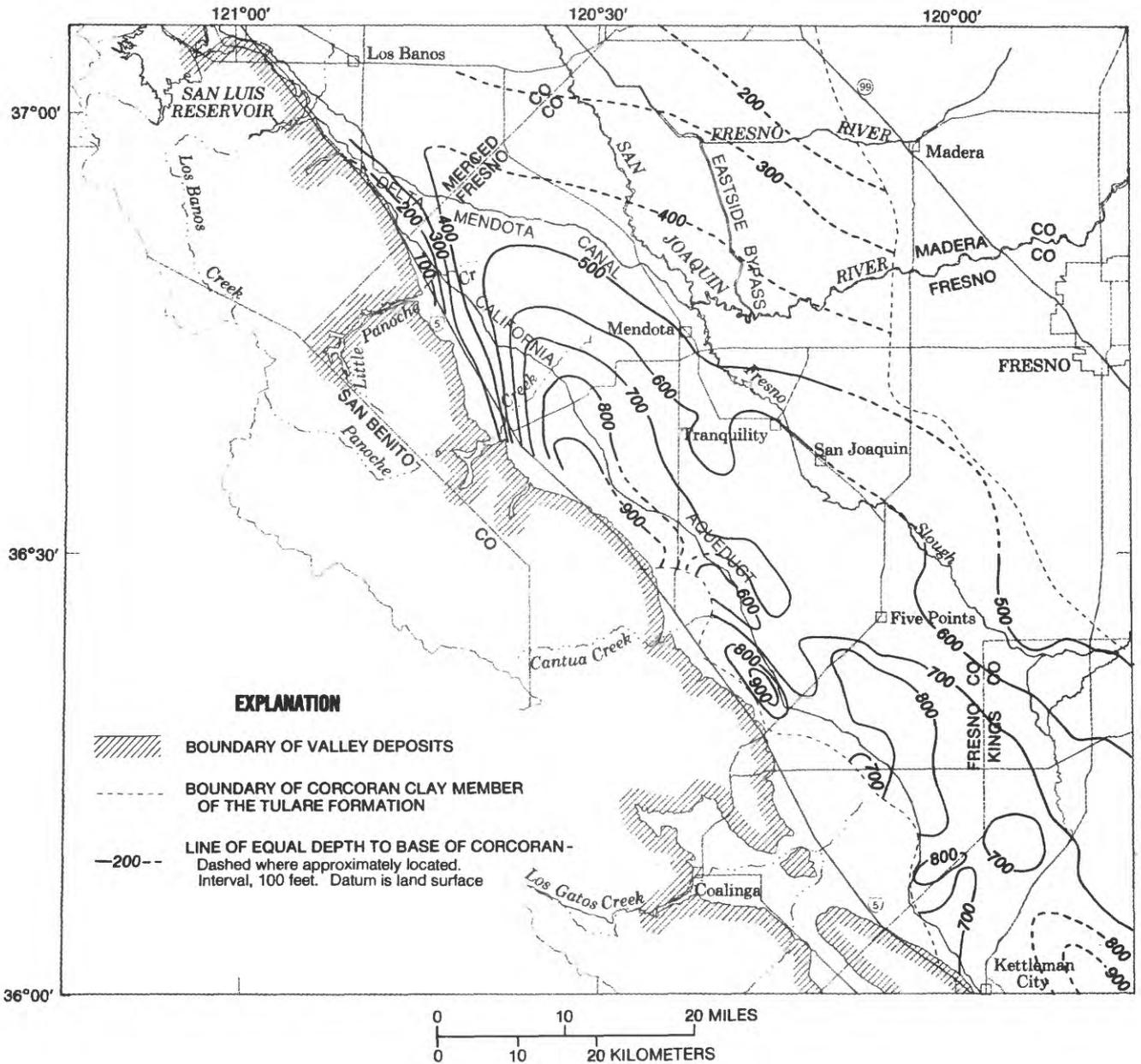


FIGURE 10.— Depth to the base of the Corcoran Clay Member of the Tulare Formation in the central part of the western valley. (Adapted from Bull and Miller, 1975.)

Predevelopment Flow System

Under natural conditions, ground-water recharge was primarily by infiltration of water from intermittent streams (Cantua, Little Panoche, Los Gatos, and Panoche Creeks), which flow seasonally during the winter rainy season (Bull, 1964a). None of the natural stream channels reach the San Joaquin River or Fresno Slough. With the possible exception of extreme storms, all streamflow under natural conditions was lost by evaporation and infiltration before reaching the valley trough. Davis and Poland (1957) estimated that the four intermittent streams typically have a total flow of about 50,000 acre-ft/yr, of which 30,000 to 40,000 acre-ft/yr may infiltrate and recharge the ground water. Davis and Poland (1957) estimated that direct rainfall was an insignificant source of recharge under natural conditions.

Discharge of ground water under natural conditions was primarily by evapotranspiration and streamflow along the valley trough. Early geologic surveys of the valley (Hamilton, 1916) indicate the presence of marshland along most of the valley trough. Mendenhall and others' (1916) map of water levels in early production wells provides an estimate of the water-table configuration before extensive development and indicates that artesian conditions prevailed along a broad stretch of the valley trough (fig. 11). The presence of marshlands and the artesian conditions indicate that the valley trough was a discharge area prior to development.

Mendenhall's map is based on water levels in wells perforated in the semiconfined zone and indicates that ground-water gradients were from the margins to the center of the valley, reflecting the general topographic trend of the area. Gradients typically were only 1 to 3 ft/mi. Mathematical simulation of the natural ground-water flow system (Williamson and others, 1985) indicates that hydraulic head in the confined zone was typically 10 to 20 feet lower than the hydraulic head in the semiconfined zone along the Coast Range and 0 to 10 feet higher along the valley trough.

Agricultural Development and Flow-System Response

Agricultural activity in the central part of the western valley began as early as the 1870's but large-scale farming and irrigation did not occur until World War I (Davis and Poland, 1957; Bull and Miller, 1975). Irrigation with ground water expanded rapidly in the 1920's and steadily increased until World War II (fig. 12). After World War II, the price of commodities stimulated increased agricultural production (Davis and Poland, 1957), and by the early 1950's nearly 1 million acre-ft of water was being pumped from the aquifer system. Most of the water was pumped from the confined zone below the Corcoran Clay Member of the Tulare Formation.

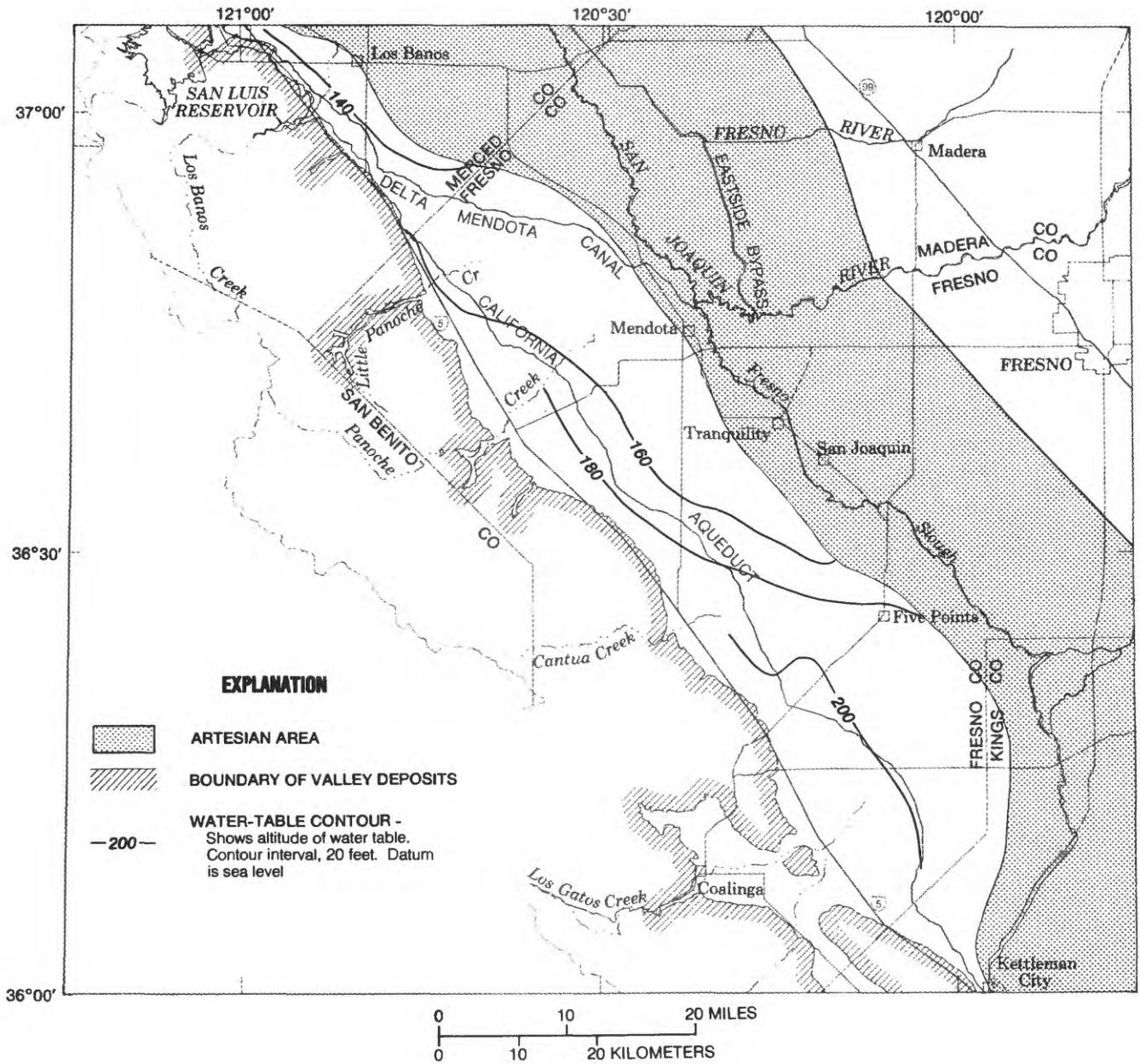


FIGURE 11.— Estimated water-table altitude and extent of artesian areas in the central part of the western valley, 1908. (Adapted from Mendenhall and others, 1916.)

The increase in pumping and in irrigated acreage altered the ground-water flow system. Percolation of irrigation water past crop roots greatly exceeded infiltration of stream water and replaced the latter as the primary mechanism of recharge. Discharge of water through wells and evapotranspiration from crops replaced natural evapotranspiration and streamflow as the primary mechanisms of discharge. Williamson and others (1985) concluded that the postdevelopment rate of recharge during 1961-77 was more than 40 times greater than the estimated predevelopment rate for the Central Valley.

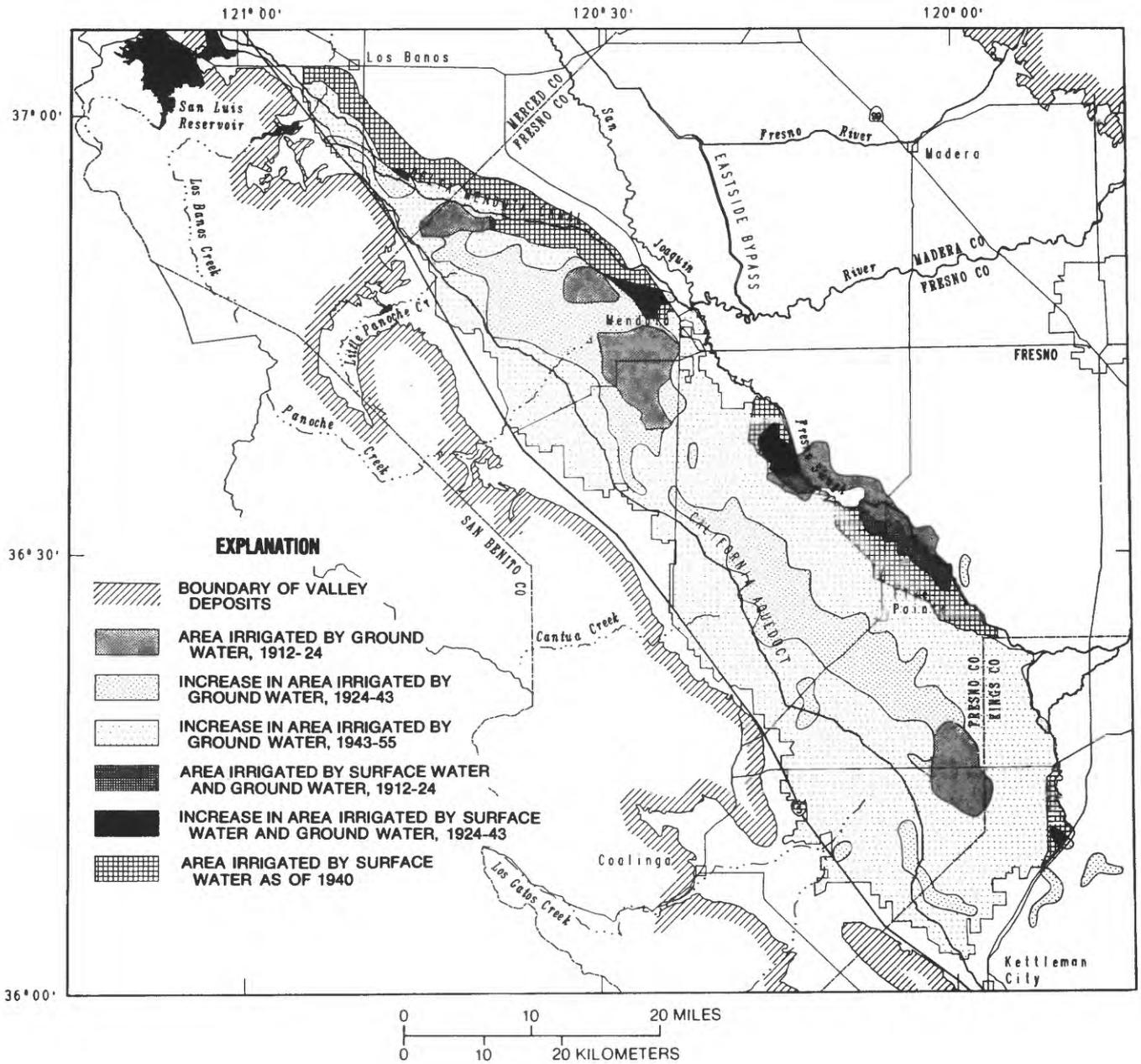


FIGURE 12.— Extent of areas irrigated with ground water and surface water in the central part of the western valley. (Adapted from Bull and Miller, 1975.)

Pumping of ground water in the study area affected the hydraulic head and the direction of flow in the system. The most pronounced changes initially occurred in the confined zone below the Corcoran. By 1952, the potentiometric surface of the confined zone (fig. 13) was drawn down 100 to 200 feet from the estimated predevelopment altitude. The large drawdown in hydraulic head created a reversal in the direction of flow in the lower confined zone from eastward to westward, and also caused a significant component of downward flow from the overlying semiconfined zone.

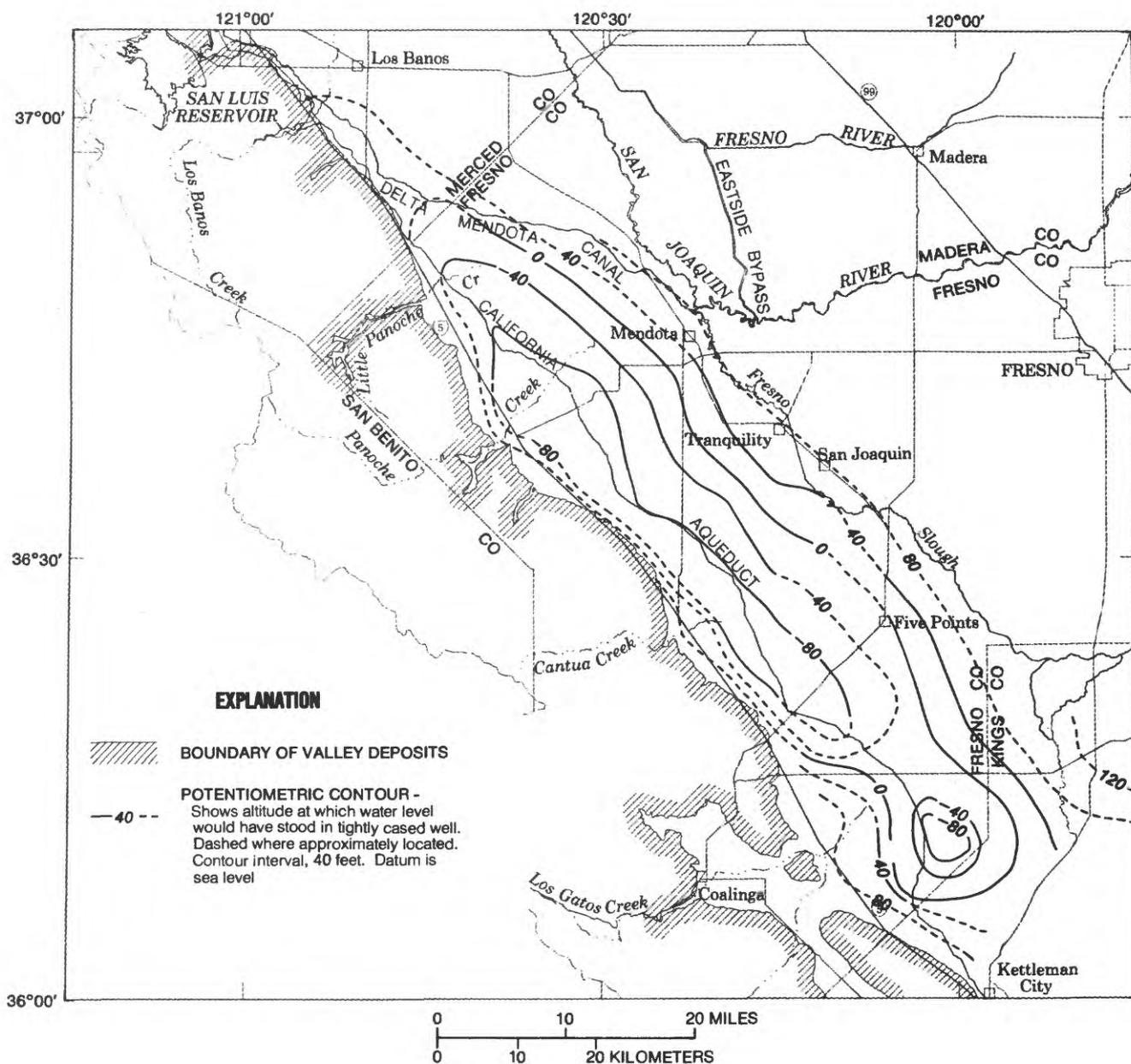


FIGURE 13.— Potentiometric surface of the confined zone of ground water in the central part of the western valley, 1952. (Adapted from Davis and others, 1959.)

Agricultural pumping in excess of recharge continued for more than a decade after 1952 and led to continued lowering of the potentiometric surface of the confined zone. By 1967, the potentiometric surface (fig. 14) had been lowered hundreds of feet over much of the western valley. The large quantities of ground water pumped from the aquifer system had several significant effects, including steepening of westward gradients in the confined zone, substantial increase in pumping lifts, and land subsidence. Pumping lifts exceeded 800 feet over parts of the area and land subsidence of more than 2 feet occurred throughout the study area, with local subsidence reaching as much as 28 feet by 1972 (Poland and others, 1975).

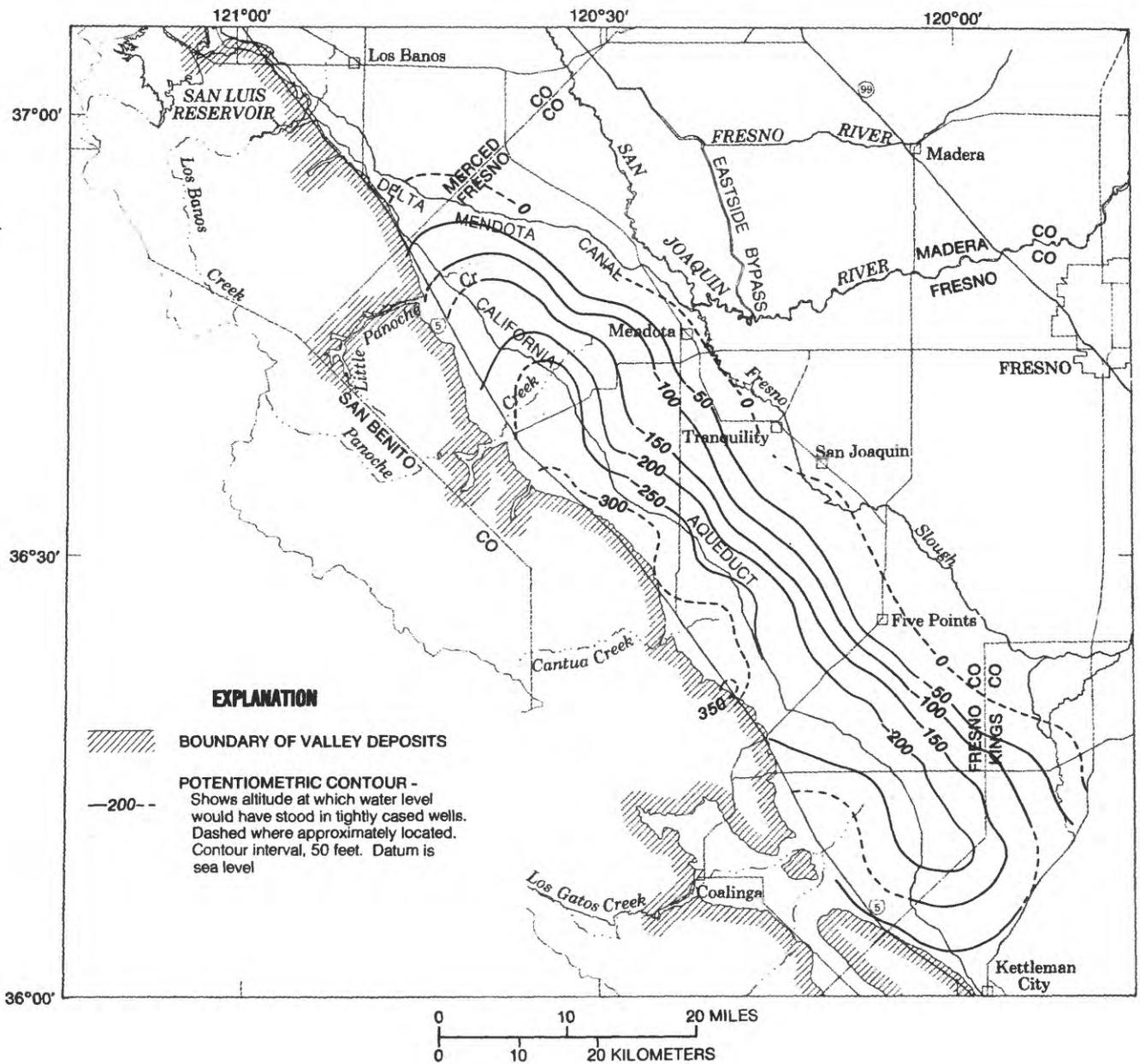


FIGURE 14.— Potentiometric surface of the confined zone of ground water in the central part of the western valley, December 1967. (Adapted from Ireland and others, 1984.)

As a result of land subsidence, increased pumping lifts, and limitations on ground-water use in some areas because of high dissolved solids, surface water was imported to the western valley from the Sacramento-San Joaquin River Delta. Beginning in 1967, surface water imported through the California Aqueduct began to replace ground water as the primary source of irrigation supply in the part of the study area south of Mendota. The availability of imported water led to an increase in the total quantity of water applied, but a decrease in the quantity of water removed from the ground-water system by wells. The marked decrease in pumpage has allowed a recovery in hydraulic head throughout the confined zone. Figures 14 and 15 show the potentiometric

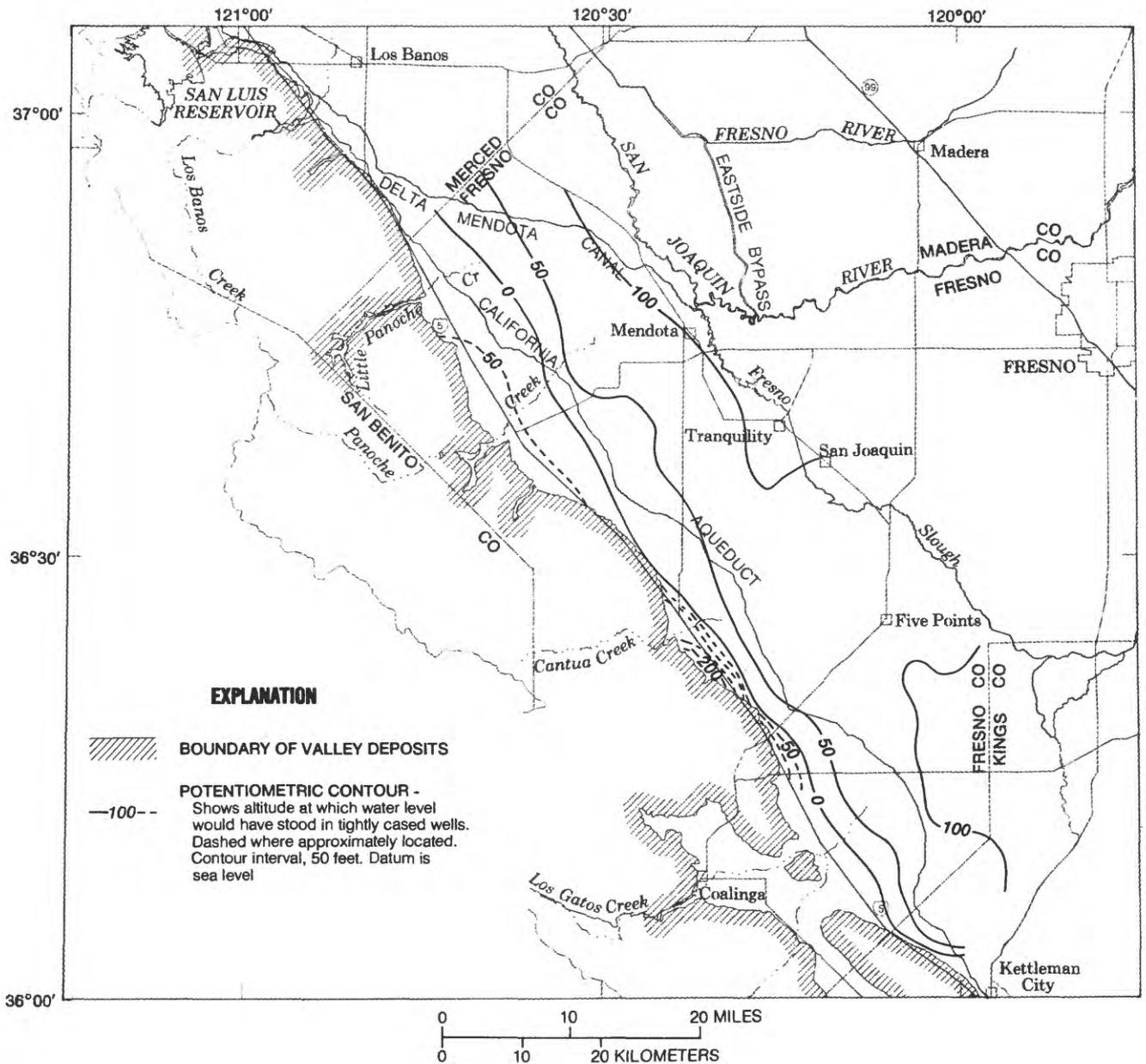


FIGURE 15.— Potentiometric surface of the confined zone of ground water in the central part of the western valley, spring 1984.

surface for the confined zone in 1967 and 1984. Comparison of the 1967 and 1984 maps indicates that hydraulic head in the confined zone has increased 200 to 300 feet from 1967 to 1984 along the western parts of the study area in areas previously characterized by the largest drawdown. Hydraulic head typically has risen 100 feet along the valley trough. Overall, the rise in the potentiometric surface from 1967 to 1984 has been nearly half the drawdown that occurred from predevelopment conditions to 1967. This rise was greater than it would have been if subsidence had not occurred because of the reduction in aquifer storage capacity caused by compaction of sediments (Poland and others, 1975).

The changes in the semiconfined zone were less marked than the changes in the confined zone during the early period of intensive development. Comparison of maps of the altitude of the water table in 1952 (fig. 16) and in 1908 (fig. 11) indicates a lowering of the water table in the lower alluvial fans and along the valley trough. This lowering probably was the result of pumping from the Sierra Nevada sediments above the Corcoran. In contrast, the water table was unchanged to slightly elevated along the western part of the area from 1908 to 1952 (Davis and Poland, 1957).

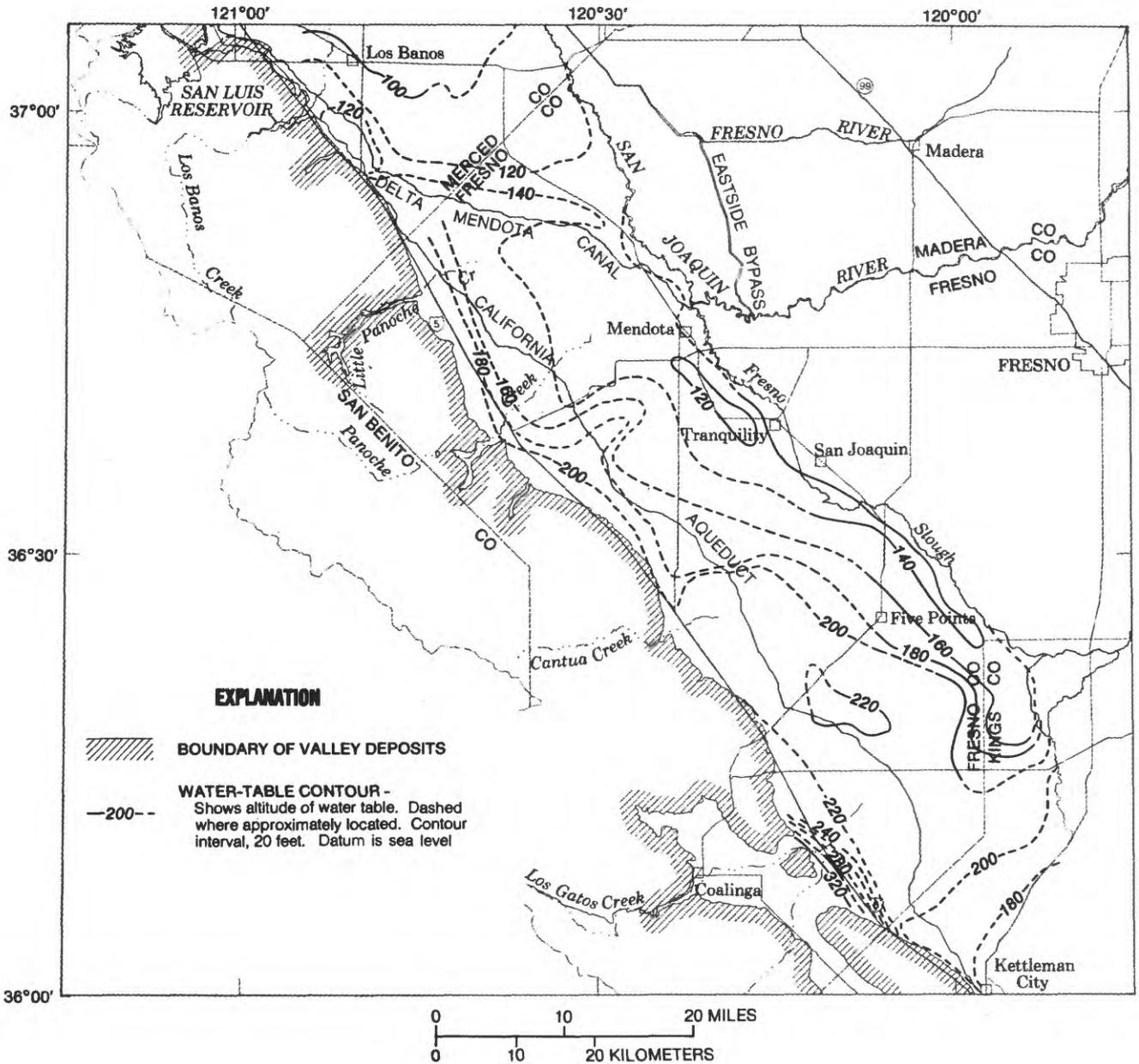


FIGURE 16.— Water-table altitude in the central part of the western valley, spring 1952. (Adapted from Davis and others, 1959.)

Present-Day Flow System

The present-day configuration of the water table is shown in figure 18. The water table demarcates the top of the saturated zone. In many ground-water investigations, flow is assumed to be horizontal and hydraulic head is assumed to be constant with depth. If these assumptions were true, then the altitude of the water table would represent the hydraulic head for the semiconfined zone at all depths. In the western San Joaquin Valley, downward vertical flow is substantial, and thus the altitude of the water table is not representative of

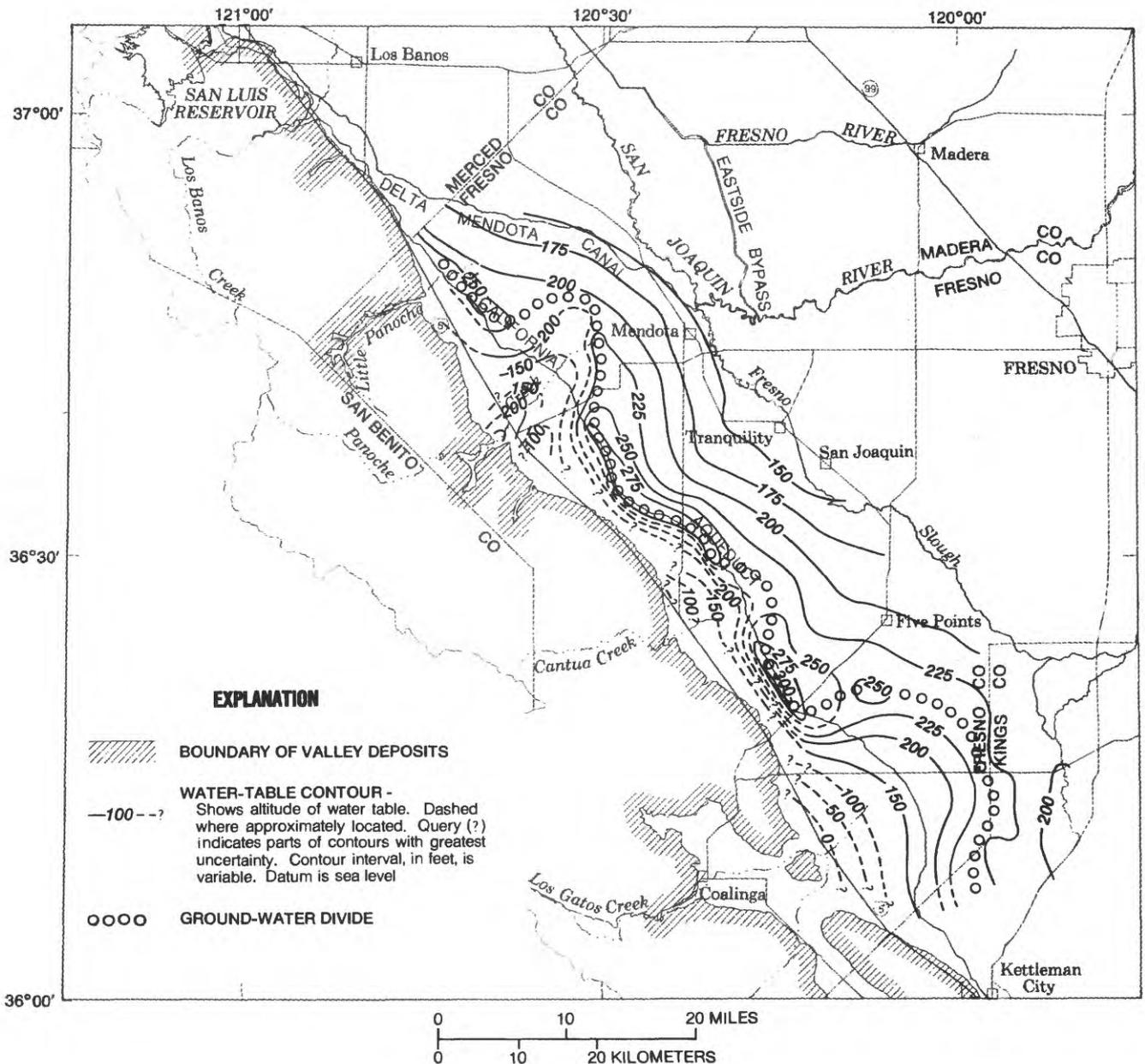


FIGURE 18.— Water-table altitude in the central part of the western valley, October 1984.

the hydraulic head at other depths. However, the map of water-table altitude is useful for indicating the general direction of the lateral component of flow in the semiconfined zone.

One of the most prominent features of the water table is the ground-water divide that parallels the western boundary of the alluvial fans. The ground-water divide shifts westward between the upper parts of the major alluvial fans and shifts eastward near the upper fans. The water table to the east of the ground-water divide lies at shallow depths, is a subdued replica of the topography, and the horizontal component of ground-water flow is eastward and northeastward. Ground-water flow occurs eastward across the valley trough toward active production wells completed above the Corcoran Clay Member of the Tulare Formation in the Sierra Nevada sediments of the eastern valley, and downward toward the confined zone. West of the ground-water divide, the water table slopes steeply to the west, and flow is toward the depression in the water table and downward toward the confined zone (Belitz, 1988).

The existence of the ground-water divide is partly related to historical agricultural activity in the area. Comparison of the present-day altitude of the water table with the altitude in 1952 indicates a lowering of the water table over at least part of the area to the west of the divide (fig. 17) and a rise in the water table over much of the area to the east of the divide. The area of the lowered water table along the western boundary of the alluvial fans corresponds to the area of maximum drawdown in hydraulic head in the confined zone due to historical pumping. The rise in the water table to the east of the divide was caused by increased rates of recharge to the system resulting from irrigation. The location of the ground-water divide also may be affected by the texture of the subsurface sediments (Belitz, 1988). The ground-water divide shifts eastward in the upper-fan areas where the sediments are coarsest, and shifts westward in the middle and lower fan areas where the sediments are finest grained. The altitude of the water table is the lowest, and the ground-water divide farthest to the east, beneath the upper part of the Los Gatos Creek alluvial fan where the poorly permeable Corcoran is absent (fig. 10).

Influence of Tile Drainage Systems

Subsurface tile drainage systems have had substantial effects on the ground-water flow system in some areas. Tile drainage systems consist of perforated pipes that are buried horizontally several feet below the land surface. Ground water that flows into these pipes, which are usually 100 to 400 feet apart, flows through the pipe to a sump or collector drain for further transport or disposal. In 1980-81, tile drainage systems were installed in an area of about 42,000 acres, or 66 mi², west and southwest of Mendota. This area is shown as the drained area in figure 19. During 1981-84, the drains collected an average of 6,900 acre-ft/yr [(0.15 (ft³/yr)/ft²)] of ground water. The drains lowered water levels in most of the drained area from 1 to 3 feet and as much as 5 feet locally. In addition, the drains have decreased seasonal variation in water levels in the drained area.

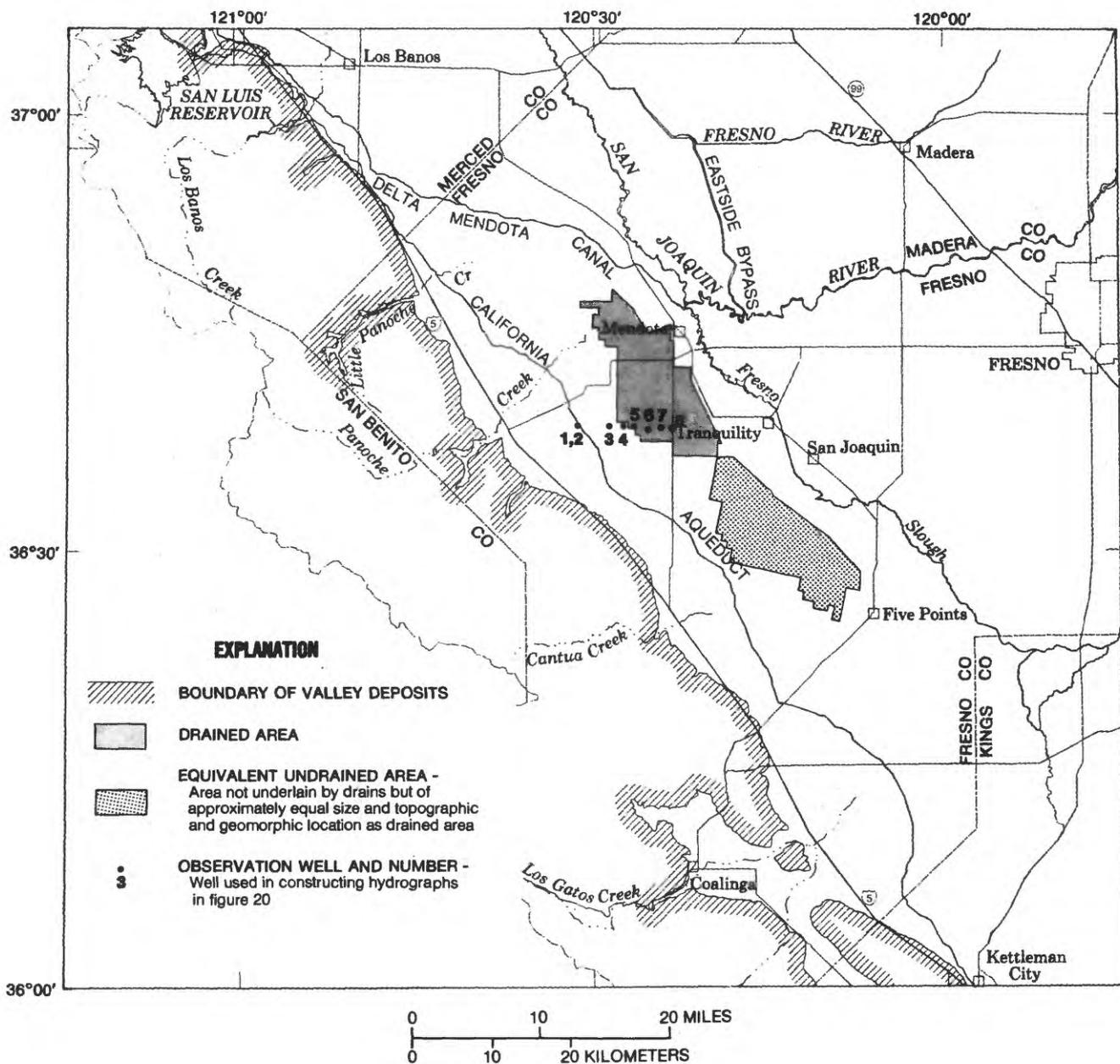


FIGURE 19.— Location of area serviced by tile drainage systems and an undrained area of approximately equivalent size and topographic and geomorphic location.

In the drained area, the total area characterized by a water table within 5 feet of land surface was reduced substantially by artificial drainage. Maps of depth to the water table (Westlands Water District, written commun., 1986) indicate that in April 1976, prior to drain installation, about 27 mi² of the area later serviced by drains had a water table within 5 feet of land surface. In April 1984, after installation of the drains, the area underlain by a water table within 5 feet of land surface had decreased to 4 mi². In contrast, in a similar but undrained area to the south of the drained area, the size of the area underlain by a water table within 5 feet of the land surface increased from 8 mi² in April 1976 to 18 mi² in April 1984. This large increase in area resulted from a rise in the water table of only 1 to 3 feet.

Figure 20 shows water-level hydrographs of eight wells located along a west-to-east line near the southern edge of the Panoche Creek fan (fig. 19). The west-to-east line is nearly perpendicular to the contours of the altitude of the water table and thus corresponds to the lateral component of ground-water flow. The hydrographs illustrate the effects of drainage systems on the ground-water flow system. In general, wells in the drained area have had smaller seasonal variation in water levels since the drains were installed, and smaller seasonal variation than water levels in wells in the undrained area. In addition, water levels in the drained area have been relatively steady since the drains were installed, whereas a rise in water levels is common in wells in the undrained areas. Wells 6, 7, and 8 (fig. 20) are in the drained area and have had relatively constant water levels with reduced seasonal variation since 1981. Although well 5 also is in the drained area, water levels in that well seem unaffected by the installation of the drains in 1980-81. Wells 1, 2, 3, and 4 are in areas not underlain by drains and show rising water levels with time. In addition, wells 2, 3, and 4 show seasonal variations in water levels of 1 to 5 feet. Well 1 is close to the California Aqueduct and does not show seasonal variation in water levels for the period of record. Water-table changes in the study area are variable and many individual wells deviate from the general trends.

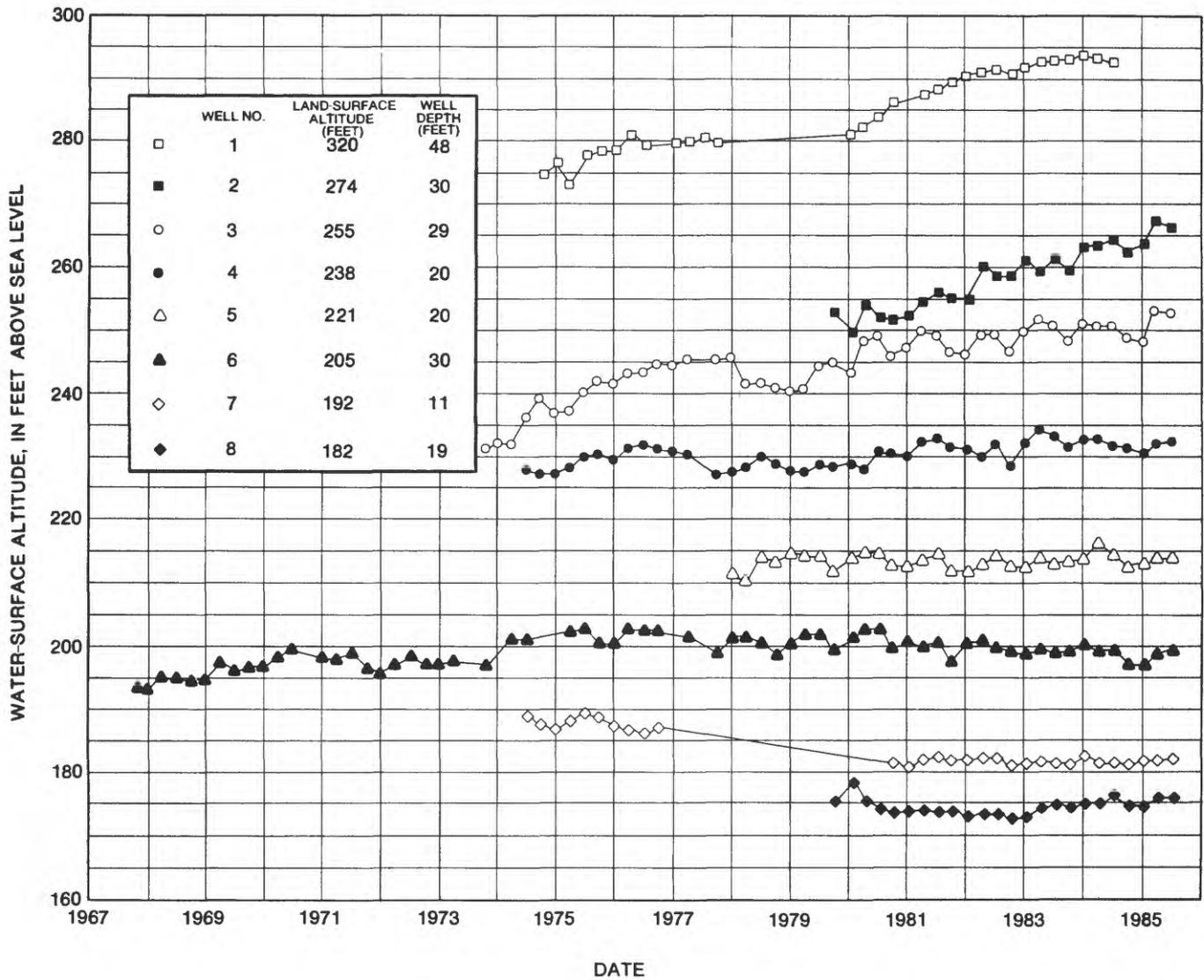


FIGURE 20.— Water levels in eight wells along an approximate flow line through the area drained by tile drainage systems. Drained area and well locations are shown in figure 19.

SELENIUM IN GROUND WATER OF THE CENTRAL PART OF THE WESTERN VALLEY

by Neil M. Dubrovsky and Steven J. Deverel

The present-day distribution of selenium in ground water in relation to the sources and movement of ground water needs to be assessed in order for local, State, and Federal water-resources managers to effectively manage water-quality problems related to irrigation and drainage. The areal and depth distribution of selenium is a key limitation to ground-water management options, such as tile drainage systems, and on present and future ground-water use. In addition, the present distribution provides information about past conditions and about possible future changes. Prior to this study, Davis and Poland (1957) and Bertoldi (1971) assessed the general geochemistry of ground water in the central western valley.

Two types of data have been collected for the present assessment of ground-water quality in the central western valley. Relatively detailed areal water-quality data have been collected for shallow ground water that occurs in the upper 10 to 30 feet of the saturated zone. This ground water is most directly affected by irrigation and drainage and was sampled from existing shallow observation wells. Because of the sparseness of existing wells suitable for sampling and assessing deeper parts of the regional ground-water system, new observation wells also were installed.

New observation wells were placed at multiple depths at several sites along geohydrologic sections through the ground-water flow system of the Panoche Creek alluvial fan. These cluster sites are approximately aligned with the direction of ground-water flow. Data for water samples from wells along two of the three sections are included in this report and are used as the primary basis for examining the age and history of ground water in the system and the depth distribution of selenium concentrations. Data from these sections lack complete areal coverage, but provide detailed information on the relation between the hydrologic system and its chemical properties.

Age and Origin of Ground Water

The relative age and origin of ground water in different parts of the aquifer system can be estimated from data on changes in the flow system over time and its present isotopic composition. These estimates provide the basis for interpreting the present-day depth distribution of selenium in ground water.

Most data used for assessing the age and origin of ground water in the central western valley are from the observation wells installed at cluster sites along two geohydrologic sections, the P6-P1 section from cluster sites P6 to P1, and the P6-M1 section from cluster sites P6 to M1 (fig. 21). The P6-P1 section extends from the upper part of the Panoche Creek alluvial fan to its outer edge near Mendota, and the P6-M1 section extends from the same origin at the upper fan into fine-grained alluvial deposits to the south of the Panoche Creek fan. At each cluster site, individual observation wells were installed at various depths. Figures 22 and 23 show the geohydrologic sections and depths of observation wells at each site.

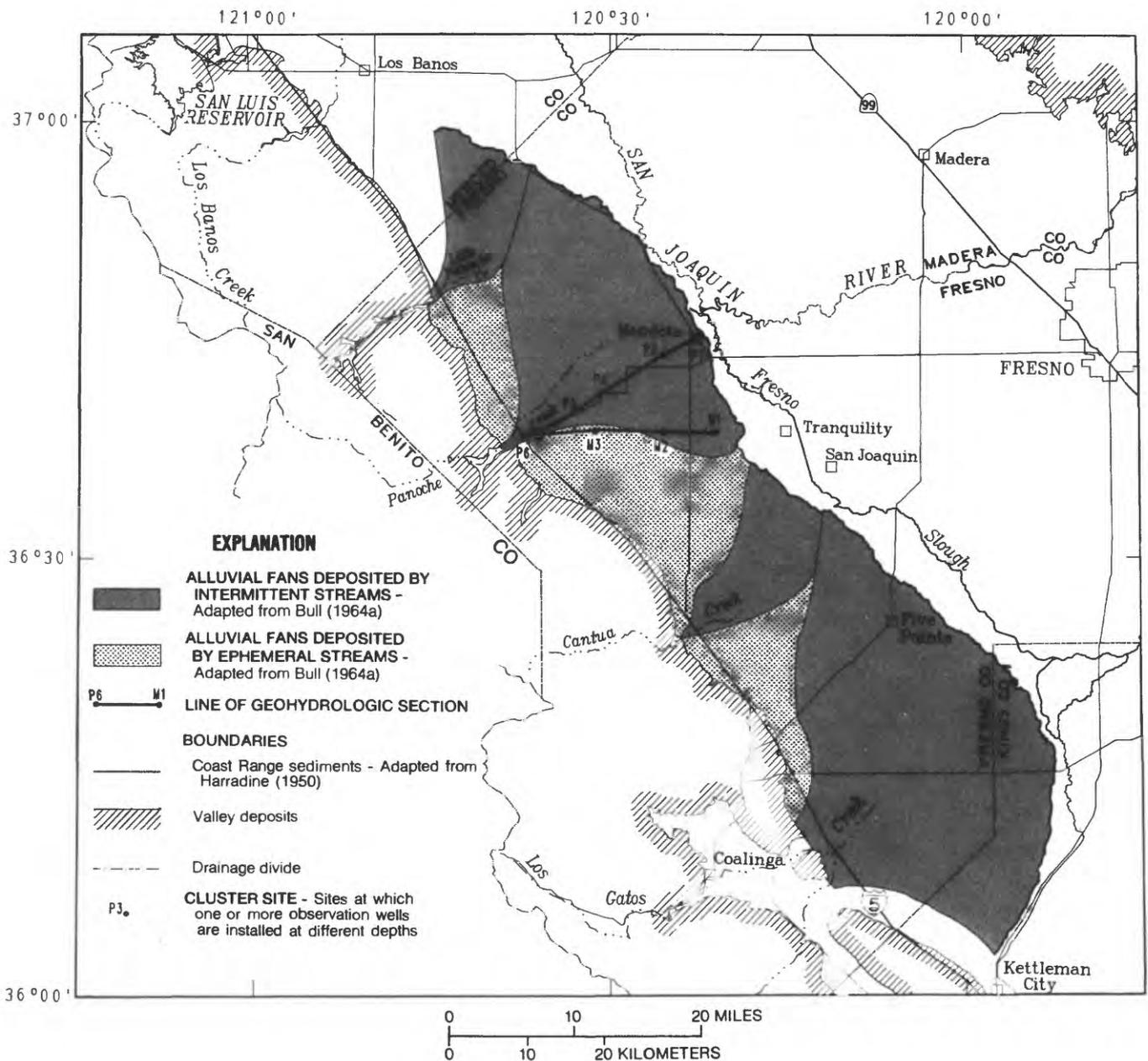


FIGURE 21.— Location of P6-P1 and P6-M1 geohydrologic sections and cluster sites.

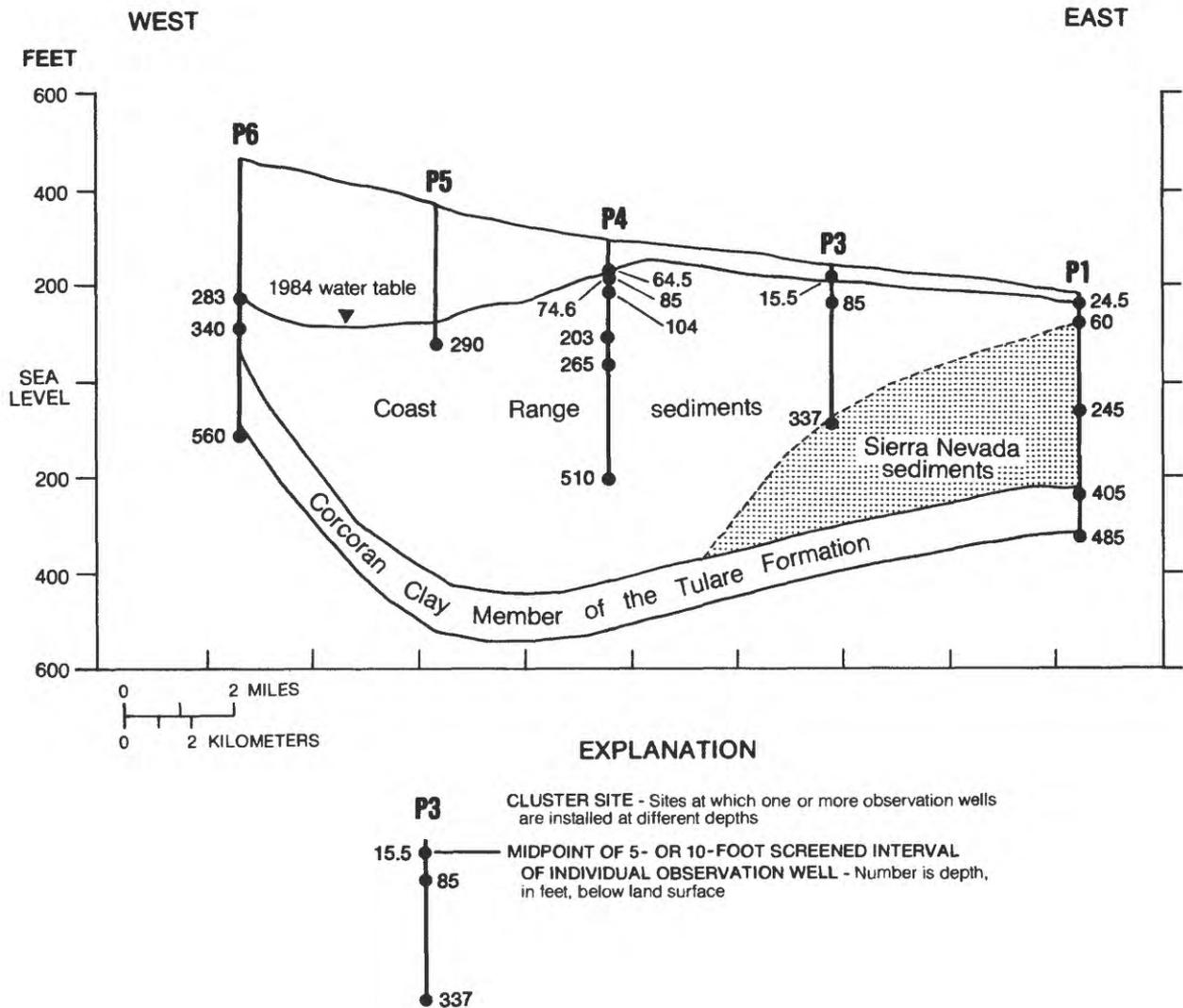


FIGURE 22.— Locations and depths of observation wells at cluster sites along the P6-P1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988).

Most of the water presently used for irrigation in the central part of the western valley originates as runoff from the Sierra Nevada, and it is geochemically different from the native ground water. However, once the applied water comes in contact with soil and aquifer materials, reaction between the solids and solution alter the water chemistry. Dissolution and ion-exchange reactions cause the applied water to resemble the chemistry of the native ground water. In addition, some irrigation water now and in the past was local ground water pumped from wells; therefore, the ground water derived from irrigation may no longer be readily identified by its solute load and ionic composition.

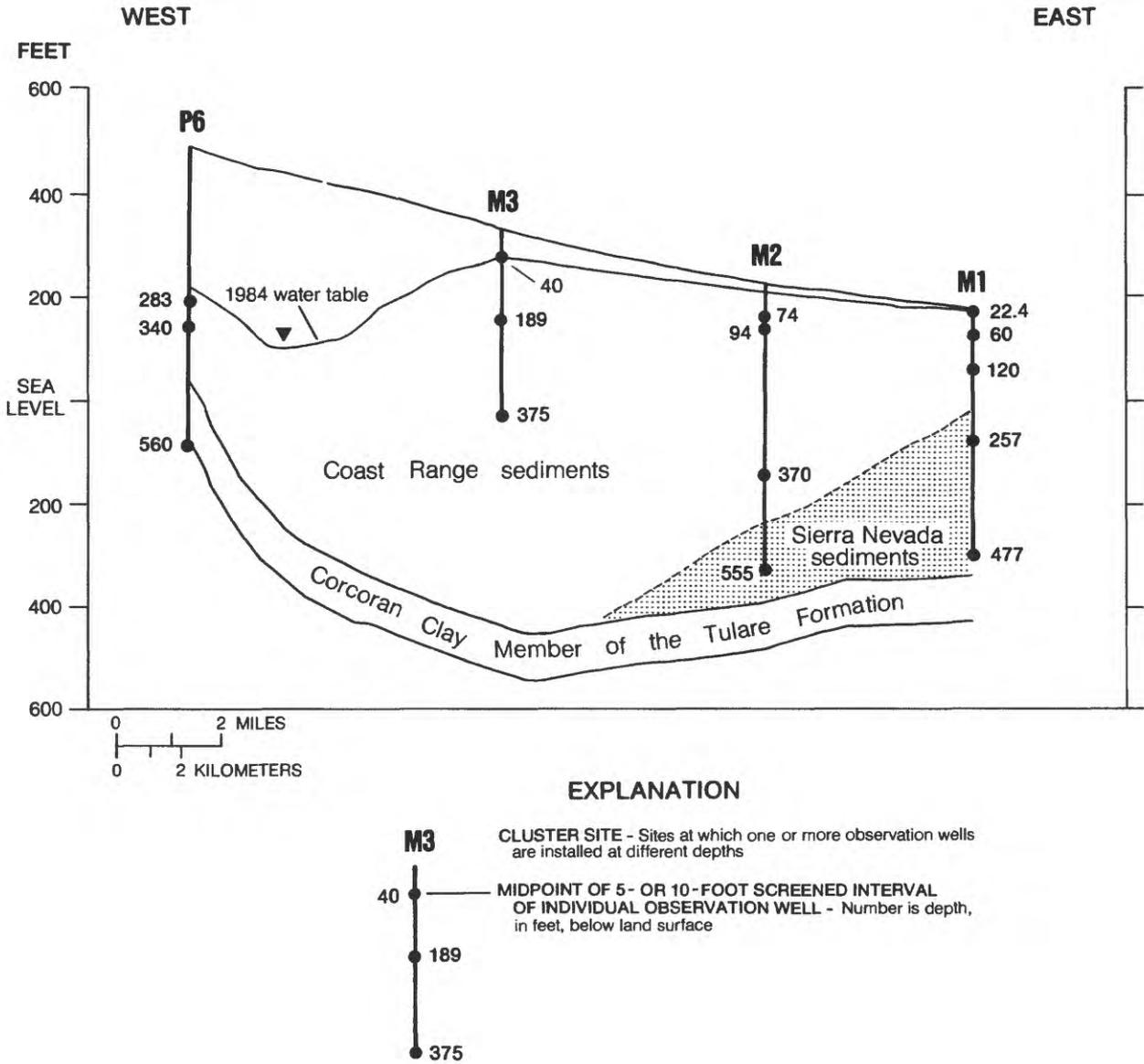


FIGURE 23.— Locations and depths of observation wells at cluster sites along the P6-M1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988).

Tritium

A characteristic of ground water not readily affected by reaction during transport is its tritium concentration. Tritium is a radioactive isotope of hydrogen introduced to the atmosphere, and hence to precipitation and ground water, by atmospheric nuclear testing in the 1950's and 1960's. Prior to 1952, when nuclear testing began, precipitation generally contained less than 5 Tu (tritium units). Because tritium decays over time, with a half life of 12.4 years, ground water that originated as precipitation before 1952 would now have less than 0.5 Tu. In contrast, tritium in precipitation frequently exceeded several hundred tritium units in the 1960's and has been higher than background levels since 1952. The high input of tritium to the atmosphere ceased in the late 1960's with the end of atmospheric testing. The tritium introduced by the testing provides a tracer for distinguishing ground water recharged prior to 1952 from ground water recharged more recently. Generally, ground water that originated solely from precipitation since 1952, including canal water used for irrigation since 1968, commonly would have tritium exceeding 20 Tu.

The large contrast in tritium concentration between pre-1952 and post-1952 precipitation distinguishes between ground water that originated before and after 1952. However, the age of the ground water cannot be estimated precisely because of areal variation in tritium in precipitation, small-scale temporal fluctuations in tritium in precipitation, the natural mixing of ground water of different ages, and the complicated patterns generated by the concurrent irrigation with old local ground water and imported Sierra Nevada runoff.

The analytical method used for tritium analysis in this study has a detection limit of 0.8 ± 0.8 Tu. All ground water with undetectable tritium was either recharged prior to 1952 or may have originated as irrigation water from wells that was applied after 1952. Any ground water with detectable tritium consists at least in part of recharge from irrigation water applied after 1952. Ground water with more than 10 Tu contains a substantial proportion of recharge from canal water applied since 1968.

The distribution of tritium in ground water along the P6-P1 and P6-M1 sections provides the most direct evidence available on the depth to which recent irrigation recharge has moved below the land surface and the water table (figs. 24 and 25). The minimum penetration of water that contains detectable tritium, as determined from the deepest sampling depths where tritium was detected, occurs at variable depths below land surface. Along the P6-P1 section, the minimum depth of penetration ranges from 340 feet below land surface at site P6, to less than 86 feet at site P3. Along the P6-M1 section, excluding site P6, the depth of penetration ranges from 189 feet below land surface at site M3, to 60 feet at site M1, excluding samples from the Sierra Nevada sediments at site M1. Depths to which post-1952 irrigation recharge has moved below the water table are less variable. Minimum depths of tritium

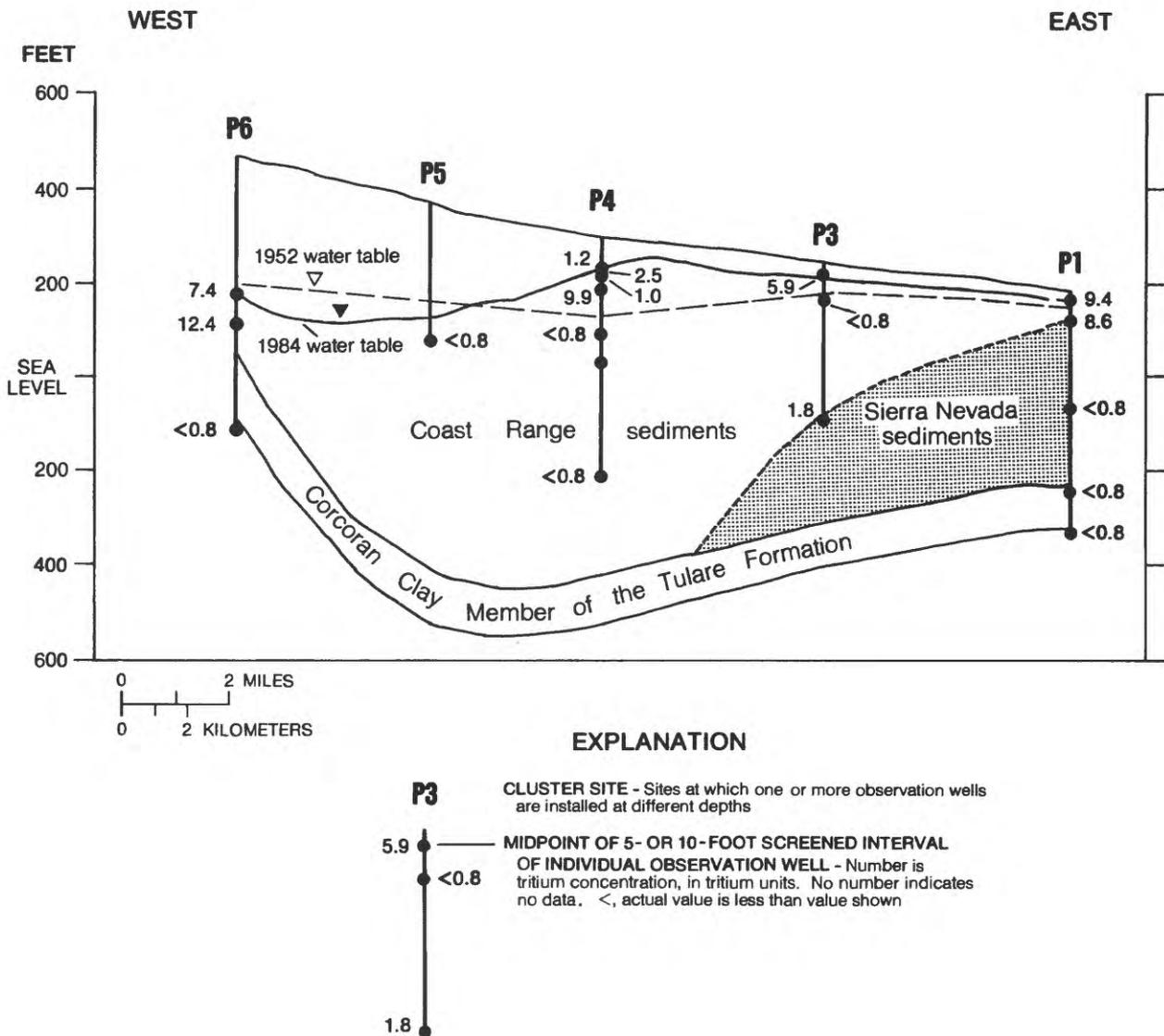


FIGURE 24.— Distribution of tritium in water from observation wells along the P6-P1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.

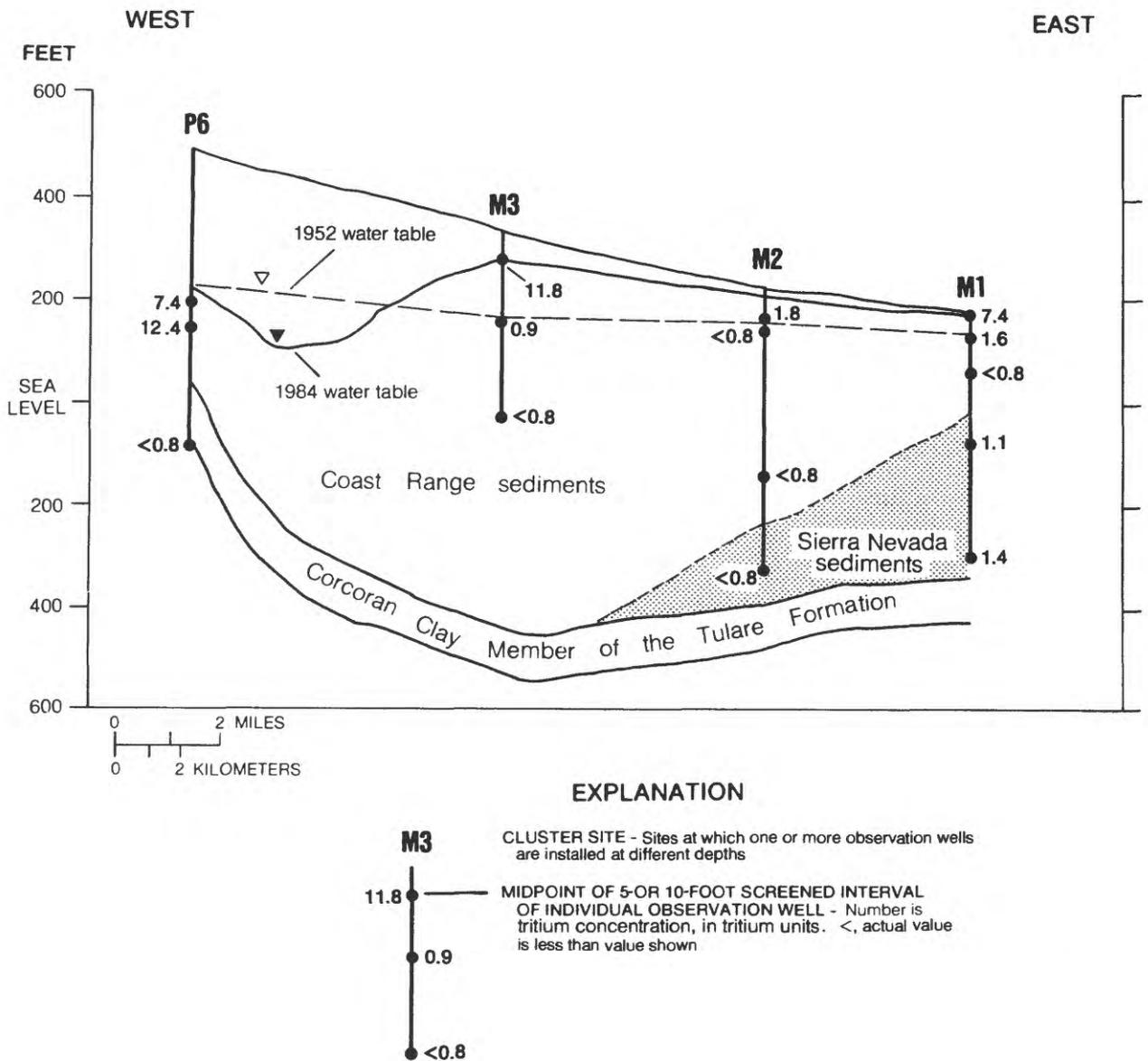


FIGURE 25.— Distribution of tritium in water from observation wells along the P6-M1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.

occurrence for all sites along both sections, again excluding samples from the Sierra Nevada sediments at site M1, range from 6 feet below the water table at site P3 to 161 feet at site M3. The median depth of penetration among all eight sites is 50 feet. In the Coast Range alluvial sediments, irrigation water applied after 1952 thus has reached depths of at least 6 to 161 feet below the water table, with a median of 50 feet.

Three principal factors cause these estimates of the minimum depth of penetration of post-1952 irrigation recharge to be conservatively low. First, there is uncertainty about how much tritiated precipitation mixed with tritium-free ground water that was applied as irrigation water between 1953 and 1968. The volumetric contribution of precipitation to recharge may have been negligible so that detectable tritium actually indicates the presence of post-1968 irrigation water from imported surface-water sources. Second, as water recharges the ground-water system, it mixes with water already in the system and this dilutes tritium concentrations. Third, the ability to define the depth of penetration is limited by the depth distribution of observation wells. The minimum depth of detectable concentration is identified by using the deepest depth at which tritium was detected at a site, because ground water below the sampling depth also may contain detectable tritium.

The range in the depth of the tritium front reflects variation in lithology, position in the flow system, and irrigation history. The greatest depth below land surface occurs in the recharge area at the upper fan, where the sediments are coarse grained, the water table is deep, and ground-water flow is most rapid. The depth of penetration is least at sites M1 and M2, where the sediments are predominantly fine grained. An estimate of the quantity of irrigation that recharges the regional-aquifer system annually can be calculated from the thickness of the zone containing tritiated water. If the thickness of the ground-water zone that has tritium concentrations greater than 2 Tu accumulated during the 19 years between 1968 and 1987, and porosity is 0.25, then 0.35 to 1.06 feet of irrigation recharge occurred annually. This range of estimates is similar to estimates derived from estimated irrigation efficiencies and measured water-table accretion. If irrigation with ground water between 1912 and 1968 resulted in similar rates of recharge, large parts of the study area have a considerable zone of tritium-free irrigation recharge underlying the tritiated ground water. Thus, the depth at which soil salts leached by initial irrigation now occur is likely below the depth at which detectable tritium is found.

Another factor to consider is that irrigation-derived recharge may move downward much more quickly near regularly pumped production wells. Data on tritium in ground water sampled from existing production wells in the central western valley show values greater than the detection limit in the six wells above the Corcoran Clay Member of the Tulare Formation (table 1). Ground water from three deeper wells that are perforated below the Corcoran contained no tritium. The median depth to the top of the screened interval of the wells above the Corcoran is 178 feet, which is greater than the maximum depth at which tritium was detected at all but one cluster site. This implies that recently recharged water is infiltrating the regional aquifers at a greater rate near production wells. The high rate of infiltration near wells probably is caused by high vertical gradients induced by pumpage and by well-construction practices that allow contamination of these wells by shallow water.

TABLE 1. Tritium in ground water sampled from existing production wells in the central part of the western valley

[Tu, tritium units; <, actual value is less than value shown]

State well No.	Screened interval (feet below land surface)	Tritium (Tu)
Perforated above Corcoran Clay Member of the Tulare Formation		
13S/14E-3B1	open at 240	22
15S/15E-9R1	100-200	10
17S/18E-2A2	216-336	21
18S/17E-27F2	40-60	6.5 1.3
13S/15E-34J7	140-220	1.5
17S/18E-35R2	310-350	4.1
Perforated below Corcoran Clay Member of the Tulare Formation		
15S/16E-5J1	663-930	<0.8
16S/14E-16N1	904-1,900	<.8
21S/17E-12E2 ¹	568-1,290	<.8

¹Located where Corcoran is absent.

Water-Table History

The history of water-table changes along the P6-P1 and P6-M1 sections support and enhance conclusions reached from tritium data. The configuration of the water table along the two sections in 1952, as interpolated from the water-table map (fig. 16), is shown in figures 24 and 25 along with the water table in 1984. The 1952 water table was within 20 feet of the ground surface only near the eastern limit of the P6-P1 section. The water table rose substantially between 1952 and 1984 along most parts of both sections, resulting in extensive areas of shallow ground water between sites P1 and P3, and sites M1 and M2. The decline in the water table in the western areas of both sections mainly occurred between 1952 and 1967. Water levels have been increasing since 1967 in these areas, but have not yet recovered to 1952 levels.

The largest increases in water-table altitude occurred at sites P4 and M3, where the depth to water decreased by 117 and 157 feet, respectively. These changes in the depth to water indicate minimum rates of water-table rise of 3.6 to 4.9 ft/yr. Assuming a

porosity of 0.25 and an initial moisture content of 0.15, these rates represent about 0.4 to 0.5 ft/yr of irrigation-derived recharge, which are similar to rates of recharge estimated from the thickness of the zone of tritiated water.

Ground water in the zone above the 1952 water table, in which tritium occurs, represents the minimum quantity of ground-water recharge during this period of time. The actual rate of recharge was higher, as an additional volume of water has moved downward and below the level of the 1952 water table. Estimates by Williamson and others (1985) of the flux of water from the semi-confined zone into the heavily pumped confined zone indicate that an additional downward flux of about 0.5 ft/yr of water occurred. In addition, recharge from irrigation with well water occurred before 1952. Areas near site P4, for example, have been irrigated since about 1943, and if the rate of ground-water recharge was similar during this period, then an additional 30 to 40 feet of aquifer may have been infiltrated by irrigation-derived water. Throughout the central western valley, an interval of about 10 to 50 feet of ground water below the altitude of the 1952 water table probably is attributable to irrigation recharge prior to 1952.

Stable Isotopes

The distribution of stable-isotope concentrations along the P6-P1 and P6-M1 sections helps place the recent hydrologic history estimated from tritium and water-table data into the context of a longer time frame. The stable isotope composition of water is an indicator of its history. The ratios of isotopes of oxygen and hydrogen (oxygen-18 and deuterium) in the vapor derived from seawater, the source of most precipitation, are constant. However, as this vapor mass condenses, the heavier isotopes are removed in a greater proportion than the lighter isotopes, because of the higher vapor pressure of the water containing the lighter isotopes. This process, known as isotopic fractionation, results in isotopically enriched precipitation and a depleted vapor mass. The repetition of this process in successive precipitation events, which occur as a vapor mass moves inland, results in precipitation that is progressively depleted of the heavier isotopes. Isotope fractionation also is temperature dependent, and the combination of these two effects produces areal distributions in the isotopic composition of precipitation that are related to topography as well as proximity to the ocean. Oxygen-18 and deuterium are linearly correlated in precipitation and local linear relations, referred to as local meteoric water lines, vary little in slope from the global average, which is referred to as the global meteoric water line. Biological processes, evaporation, freezing, and melting also contribute to fractionation (Freeze and Cherry, 1979). In particular, partial evaporation of water causes the ratio of deuterium to oxygen-18 to be lower than for precipitation, resulting in departure from the meteoric water line along an evaporative trend line.

Inorganic reactions between stable isotopes and the aquifer matrix are negligible at low temperatures. Once water recharges below the depth to which evaporation occurs, it becomes a stable indicator of the conditions during precipitation and recharge. Isotopic composition is expressed in the delta notation as per mil (‰) differences between oxygen isotope ratios in the sample and a standard. The values are calculated as in the following example for oxygen-18:

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

A comprehensive study of oxygen-18 and deuterium in ground water of the San Joaquin Valley was reported by Coplen and others (1985) and Davis and Coplen (in press). They evaluated data for samples from existing wells in the central western valley. After identifying and discarding results for those samples that represented mixtures of ground water from different zones, they identified 10 separate types of native ground water. The 10 types were then combined into three general groups of native ground water on the basis of similarity in range of oxygen-18 values, which probably reflects a similar origin of the waters.

The first group consists of ground water in Sierra Nevada sediments underlying modern flood plains, which has a delta oxygen-18 ranging from -9.7 to -12.75. This water is similar to present-day runoff from the Sierra Nevada. The second group consists of most of the ground water in the semiconfined zone above the Corcoran Clay Member of the Tulare Formation and ground water in the confined zone in one area in the extreme southwest of the study area where the Corcoran is absent. The second group is the most enriched in the heavier isotope, with delta oxygen-18 ranging from -6.4 to -8.35. This water is believed to have been derived exclusively from streams draining the Coast Range. The third group is ground water that occurs in the confined zone, in the semiconfined zone near the axis of the valley, and locally in the deepest parts of the semiconfined zone. Delta oxygen-18 for this group ranges from -8.0 to -9.65. The origin of water in the third group is uncertain. The water probably is a mixture of Sierra Nevada and Coast Range runoff; however, the mechanism of mixing is unknown.

Results of analyses of water samples from the observation wells along P6-P1 and P6-M1 sections for delta oxygen-18 and delta deuterium are plotted in figure 26. Most of the data follow the same relation found by Davis and Coplen (in press) for local ground water. Few of the samples have been extensively evaporated. Distributions of delta oxygen-18 from water samples from the two sections are shown in figures 27 and 28. The samples most enriched in oxygen-18 are from wells at sites M1 and M2, where the water table is shallow. These oxygen-18 values are shifted slightly to the right of the global meteoric water line (fig. 26), indicating that the ground water has been partially evaporated.

The distribution of oxygen-18 in the profiles generally agrees with the water types defined by Davis and Coplen (in press). Most of the oxygen-18 values for ground-water samples from the semiconfined zone are within the range defined for ground water derived from Coast Range recharge. Oxygen-18 values for samples from wells screened in Sierra Nevada sediments, especially those closer to the valley axis, are within the range defined for ground water recharged predominantly or in part from Sierra Nevada runoff. The oxygen-18 values for the two wells screened below the Corcoran also are within or close to the range defined for this zone. The data from the P6-P1 and P6-M1 sections indicate no major changes in the distribution of oxygen-18 since the sampling of production wells in 1968.

The agreement between the oxygen-18 distribution in 1968 and 1986-87 was unexpected because of the presence of a substantial zone at the top of the aquifer system that is occupied by recently recharged irrigation water. Irrigation water used in the western valley has been from a variety of sources. Prior to the completion of the San Luis Canal in 1967, most irrigation water was pumped from either Sierra Nevada sediments in the semiconfined zone, or from below the Corcoran. Sierra Nevada runoff has provided most of the irrigation water since completion of the canal. All these sources have more depleted oxygen-18 values than naturally recharged west-side ground water in

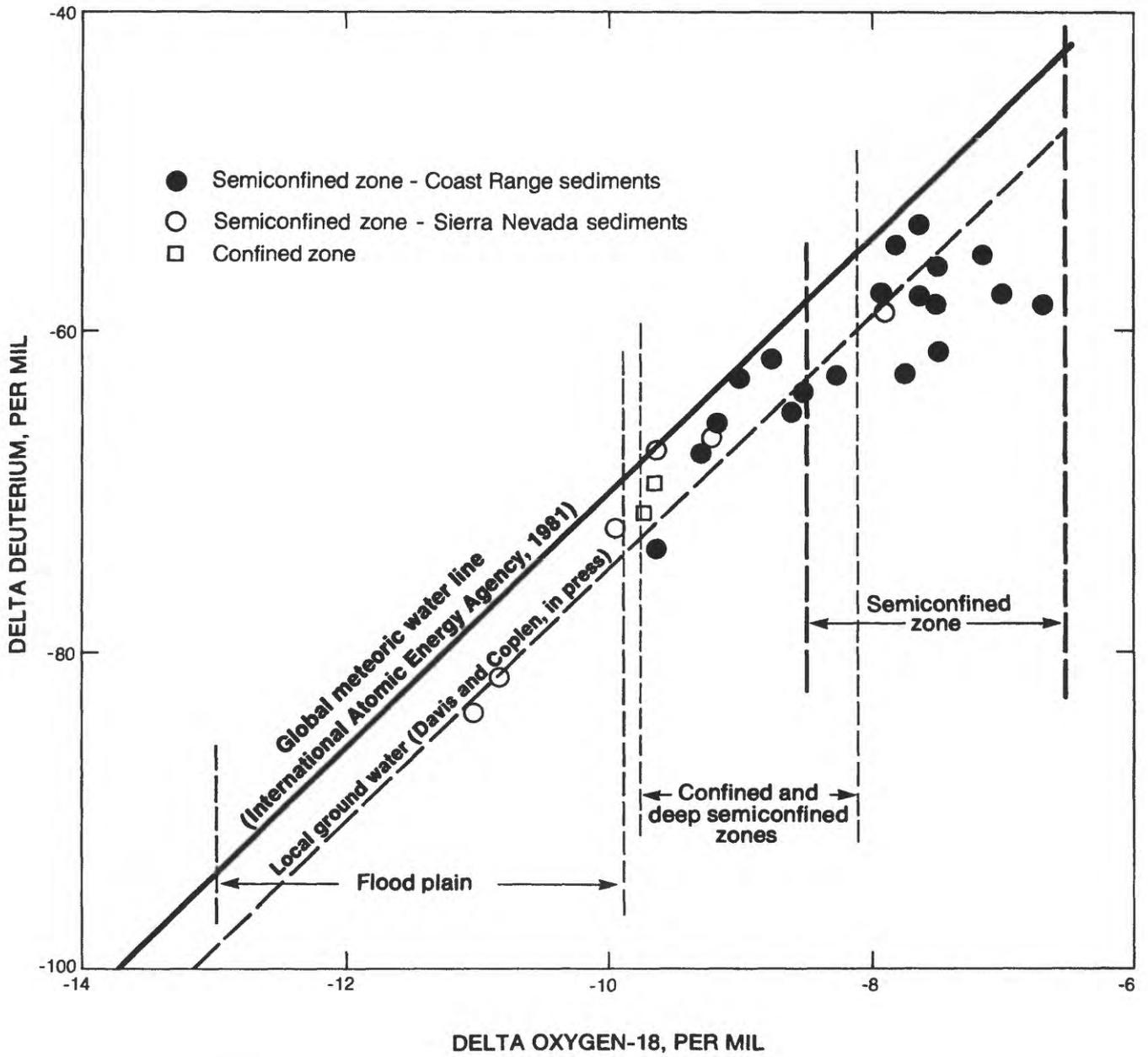


FIGURE 26.— Isotopic composition of samples from observation wells along the P6-P1 and P6-M1 geohydrologic sections. Categories shown are adapted from Davis and Coplen (in press).

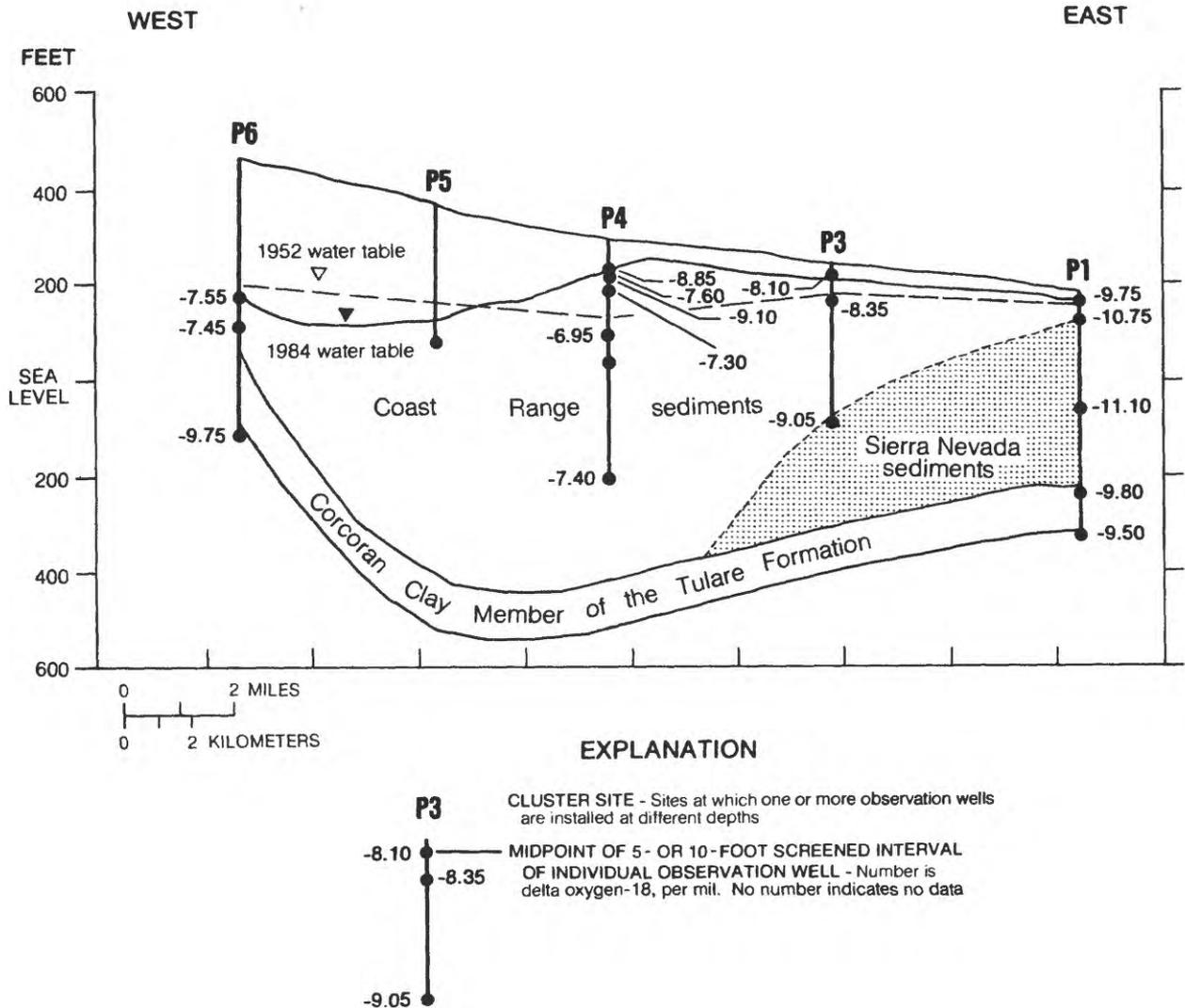


FIGURE 27.— Distribution of delta oxygen-18 in water from observation wells along the P6-P1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.

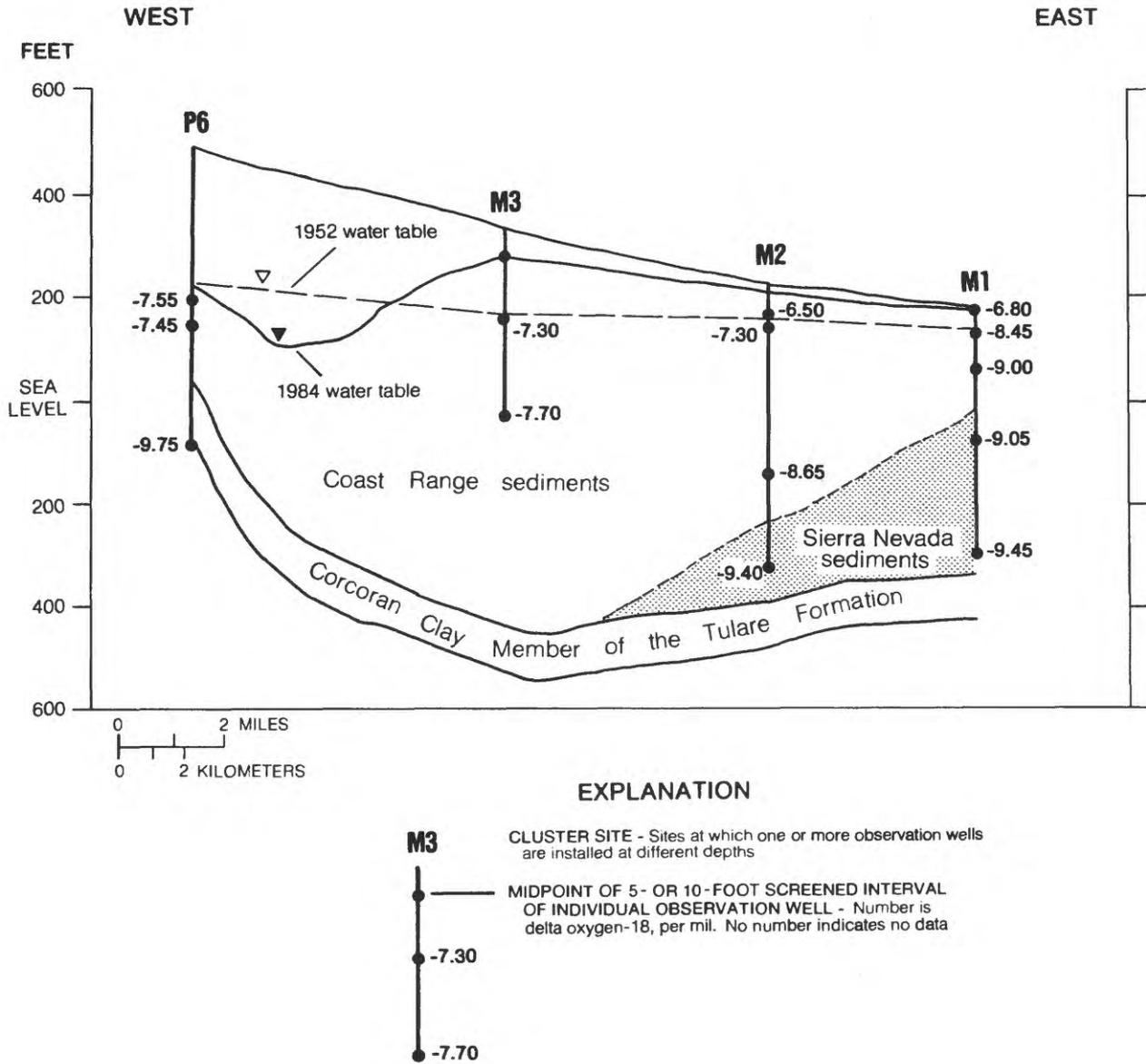


FIGURE 28.— Distribution of delta oxygen-18 in water from observation wells along the P6-M1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.

the semiconfined zone. A comparison was made between semiconfined ground water from wells in Coast Range sediment that had detectable tritium and those that had undetectable tritium to determine whether the younger waters also were more depleted in oxygen-18. A boxplot for ground water in these two categories indicates that the oxygen-18 content of the tritiated water is not significantly different from that of tritium-free ground water (fig. 29). Thus, recent irrigation water cannot be identified by oxygen-18.

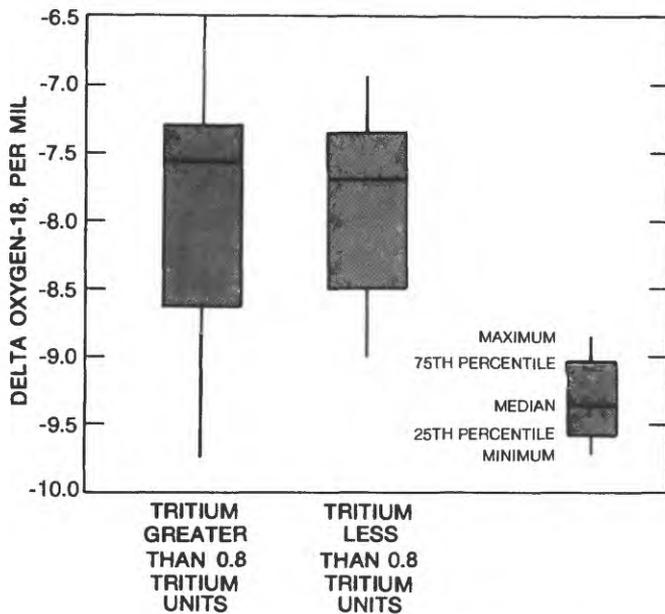


FIGURE 29.— Comparison of delta oxygen-18 in ground water from Coast Range sediments with tritium greater than or less than the detection limit.

Three explanations are possible for the lack of contrast in stable-isotope composition. The lack of contrast may partly result from mixing during irrigation application and recharge. Second, some of the tritium-free ground water may be from irrigation recharge that occurred when well water was used for irrigation. Third, recently recharged ground water has been partially evaporated, particularly at sites where the water table is shallow. These three factors tend to blur the distinctions between water types.

Depth Distribution of Selenium in Ground Water

Concentrations of selenium in ground water along the P6-P1 and P6-M1 sections range from less than the detection limit of 1 µg/L to 2,182 µg/L (figs. 30 and 31). The highest selenium concentrations are associated with high dissolved-solids concentrations in the upper part of both sections. However, at cluster sites P3, P4, and M3, the highest concentrations occur in water that underlies shallower ground water with lower selenium concentrations. The deepest position below the water table of ground water with more than 10 µg/L of selenium is 148 feet at P4. Selenium concentrations are less than or equal to the detection limit of 1 µg/L in samples from all but one of the wells screened in Sierra Nevada sediments or below the Corcoran Clay Member of the Tulare Formation.

Occurrence of the highest selenium concentrations at shallow depths in Coast Range alluvial sediments is the result of its association with irrigation recharge. Most of the wells in which selenium concentrations exceed 10 µg/L are screened at altitudes near or above the 1952 water table (figs. 30 and 31). The four highest selenium concentrations occur in ground water with detectable tritium; however, selenium concentrations in water with and without tritium are not significantly different [$\alpha=0.05$ (fig. 32)]. Concentrations of selenium greater than 10 µg/L occur deeper than detectable tritium at all cluster sites in the middle of the sections (P5, P4, P3, M3, and M2). The deeper occurrence of selenium compared to tritium, combined with the water-table history, indicates that irrigation-derived ground water that recharged the regional aquifers prior to 1952 contained high concentrations of selenium. In addition, these data indicate the possibility that some of the deepest water with high selenium concentrations may be derived from natural processes.

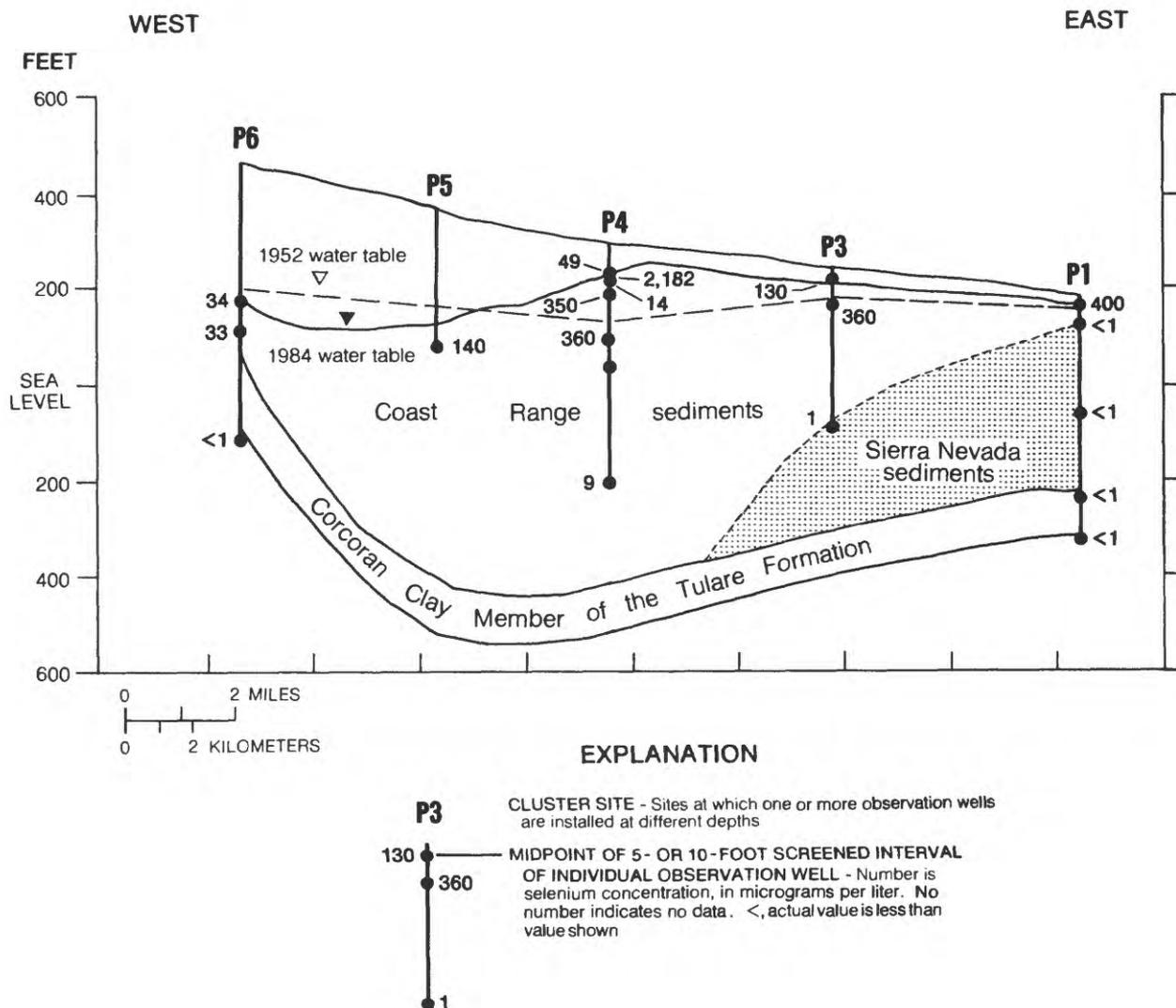
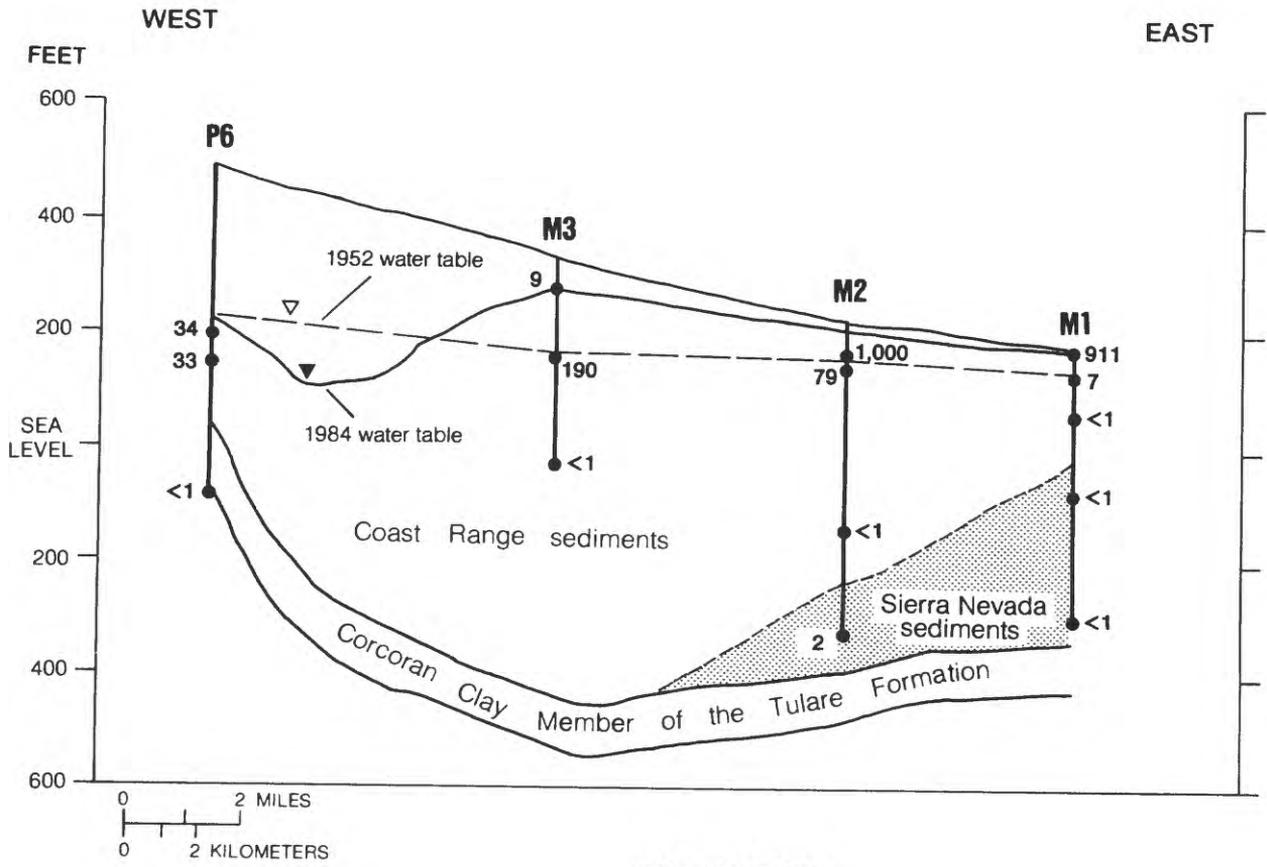


FIGURE 30.— Distribution of selenium concentrations in water from observation wells along the P6-P1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.



EXPLANATION

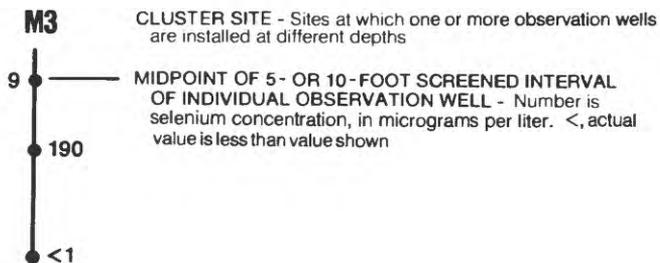


FIGURE 31.— Distribution of selenium concentrations in water from observation wells along the P6-M1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.

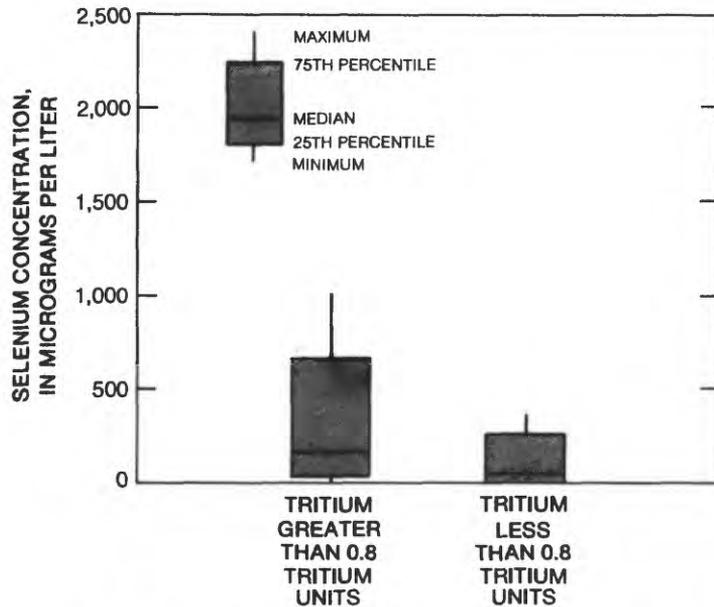


FIGURE 32.— Comparison between selenium concentrations in ground water with and without detectable concentrations of tritium.

Relation to Salinity

Selenium and specific conductance are significantly correlated ($\alpha=0.05$) in ground water in the Coast Range alluvial sediments (fig. 33). This relation is the result of two processes that affect both constituents: leaching of selenium-containing salts during infiltration of irrigation water, and evaporative concentration of selenium along with other soluble salts due to evapotranspiration in areas where the water table is shallow. The primary feature that distinguishes the two processes is that evaporative concentration causes an enrichment in oxygen-18 relative to deuterium.

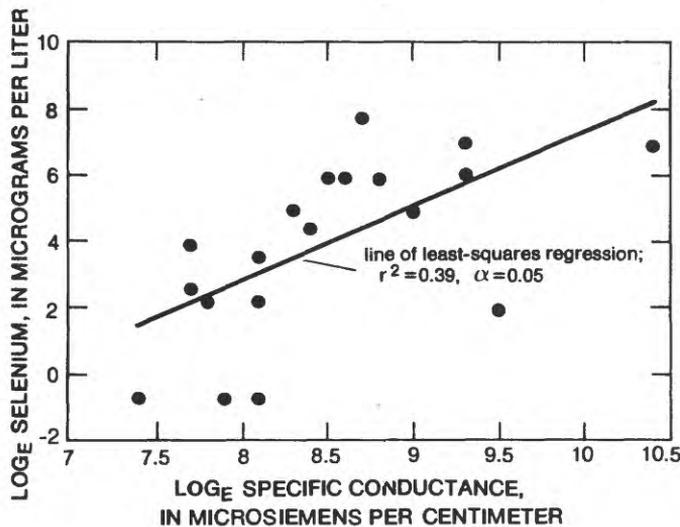


FIGURE 33.— Relation between selenium concentration and specific conductance for ground water in Coast Range sediments.

In areas where the water table is more than 10 feet below land surface, primarily in the middle and upper parts of the alluvial fan, evaporative concentration is minimal and leaching is the primary cause of high selenium concentrations. This is indicated by data from cluster site P4, located in the middle of the Panoche fan, where the water table has been between 55 and 170 feet below land surface since 1952. A plot of the observation-well data from this site, supplemented with data on pore-water samples from cores taken in the intervals of 65 to 176 feet and 200 to 280 feet, shows that specific conductance explains 86 percent of the variability in selenium concentrations (fig. 34), even

though there has not been substantial evaporative concentration. Relatively low selenium concentrations (49 and 14 $\mu\text{g/L}$) that occur near the water table at site P4, and also at sites P3 and M3, probably are the result of recharge of recent irrigation water after most soluble forms of selenium and salts were leached from the soil.

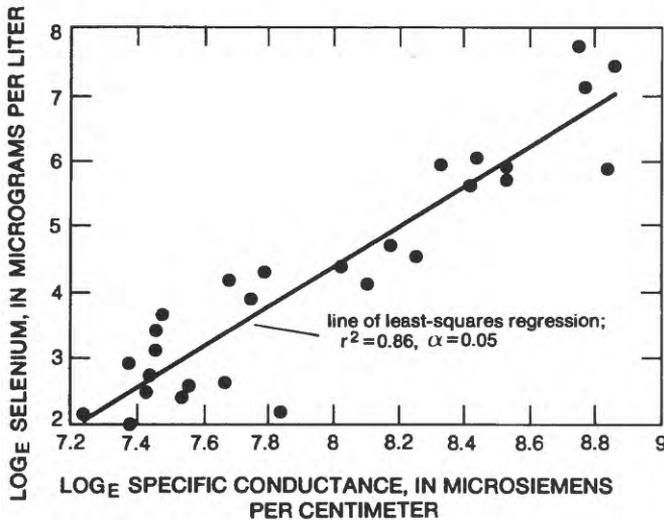


FIGURE 34.— Relation between selenium concentration and specific conductance for ground water at site P4.

Evaporative concentration of salts, including selenium, has been the dominant process in areas where natural ground-water discharge occurred and in areas where a shallow water table developed because of irrigation practices. Soils in the natural discharge areas became highly saline due to precipitation of salts over thousands of years. The effects of evapotranspiration of ground water on salinity and selenium concentrations in ground water are limited to the shallowest ground water in areas where the water table is shallow. Few of the wells along the P6-P1 and P6-M1 sections tap water that shows evidence of direct evapotranspiration of ground water, which causes enrichment of stable isotopes. Ground water sampled from the shallowest wells at sites M2 and M1 shows a moderate amount of oxygen-

18 enrichment (fig. 28). The greatest effects of recent evaporative concentration, described further in following sections, are apparent for ground water in the upper 20 to 30 feet of the saturated zone in agricultural fields that have a history of shallow ground water.

Effect of Redox Potential

Selenium mobility in ground water is dependent on the redox potential of the water. Dissolved selenium is extremely mobile in its most oxidized form, selenate (Goldberg and Glanbig, 1988). More reduced forms are relatively immobile. Selenite is adsorbed under alkaline conditions (Neal and others, 1987a) which prevail in Coast Range and Sierra Nevada sediments (median pH in both zones is 7.5), and selenide forms insoluble solid phases in the presence of metals (Elrashadi and others, 1987). The redox status of ground water can be estimated with a platinum electrode or inferred by the concentrations of redox-sensitive species such as manganese, nitrate, and dissolved oxygen. Evaluation of redox data is necessarily qualitative because many redox reactions are biologically mediated, and because disequilibrium in specific redox couples with respect to independent measures of redox potential is often observed.

Ground-water redox conditions, as indicated by platinum electrode measurements, range from oxidizing [441 mV (millivolts)] in upper parts of the Coast Range alluvial sediments, to reducing (-125 mV) in ground water in Sierra Nevada sediments and below the Corcoran Clay Member of the Tulare Formation (figs. 35 and 36). The redox values generally are highest in shallow wells and

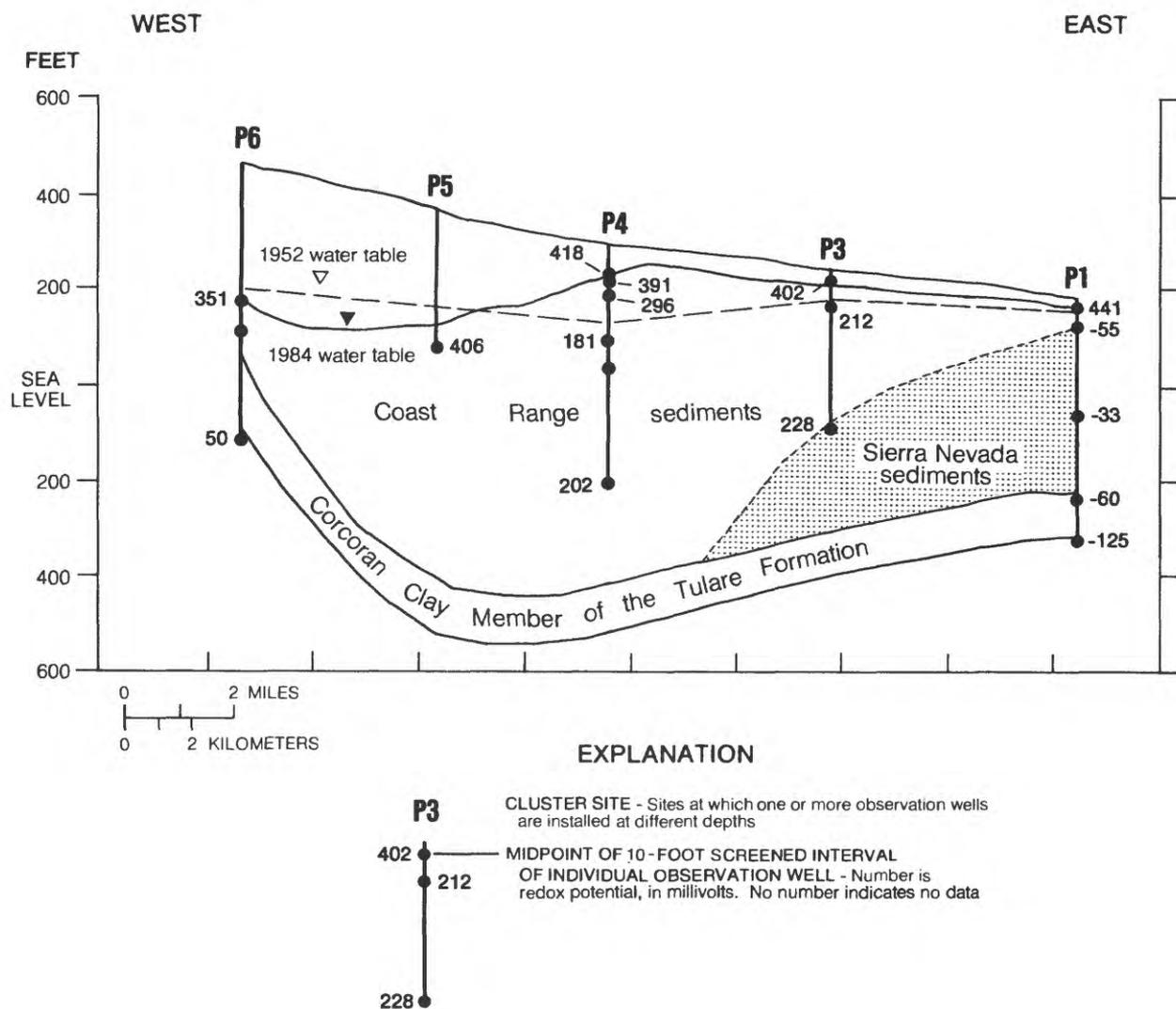


FIGURE 35.— Distribution of redox potential in water from observation wells along the P6-P1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.

decrease with depth. The minimum value measured in ground water from Coast Range sediments is 67 mV, which is moderately reducing. A plot of natural logarithms of selenium in relation to redox potential shows a general tendency for higher selenium in the most oxidized water (fig. 37).

Selenium concentrations and dissolved-oxygen concentrations are not well correlated, but data indicate that the presence of dissolved oxygen is a sufficient, though not necessary, condition for high selenium concentrations in ground water. Selenium concentrations exceeded 10 µg/L, the U.S. Environmental Protection Agency drinking-water standard, in all but 1 of the 12 samples with greater than 1 mg/L of dissolved oxygen. In contrast, the selenium concentration exceeded 10 µg/L in only 2 of the 17 samples with less than 1 mg/L of dissolved oxygen. Selenium is at less than detectable concentrations in water

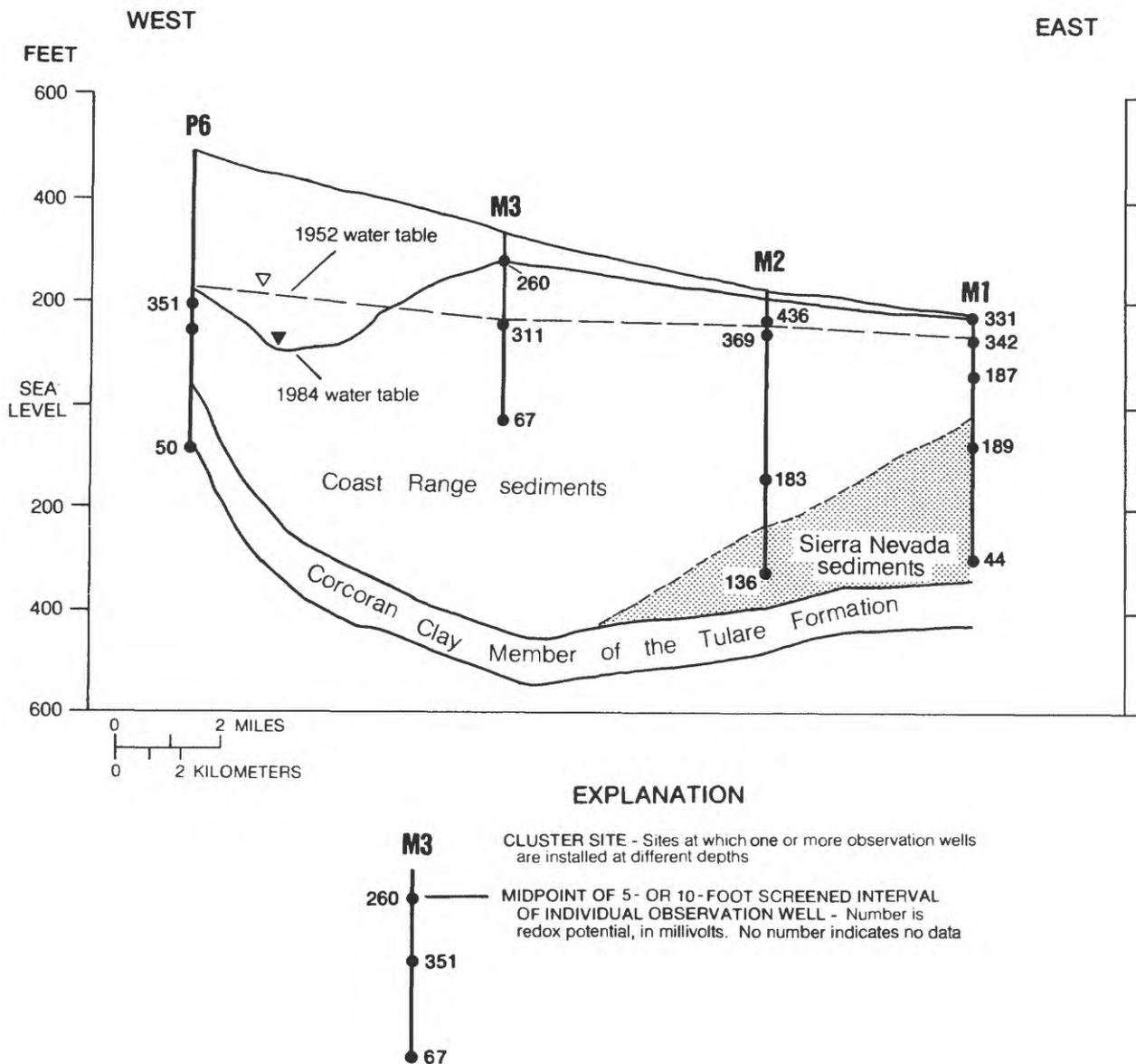


FIGURE 36.— Distribution of redox potential in water from observation wells along the P6-M1 geohydrologic section. Section location is shown in figure 21. Water-table altitudes and locations of geologic boundaries are from Belitz (1988). Samples were collected during 1985-87.

from three of the four deepest wells screened in Coast Range sediments, where dissolved oxygen is near or less than the detection limit, but occurs at 7 and 360 $\mu\text{g/L}$ in ground water from other wells in which dissolved oxygen is less than the detection limit. Selenium and manganese concentrations in ground water from Coast Range sediments also are not significantly correlated, though the highest selenium concentrations occur with low manganese concentrations, which indicate oxic conditions.

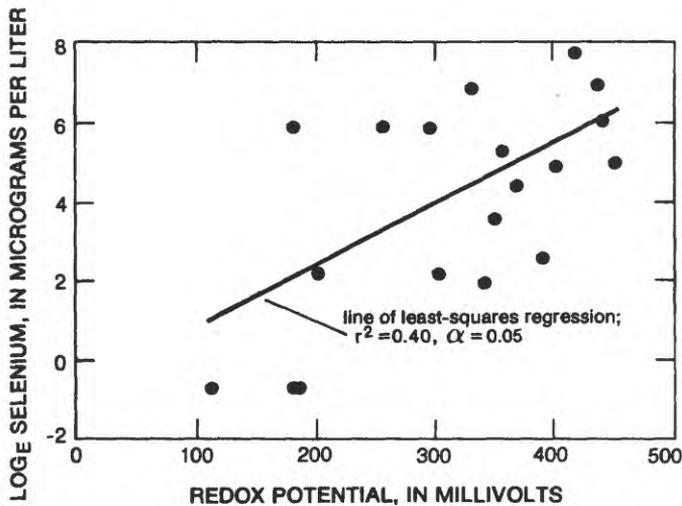


FIGURE 37.— Relation between selenium concentration and platinum electrode measurements of redox potential for water from wells along the P6-P1 and P6-M1 geohydrologic sections.

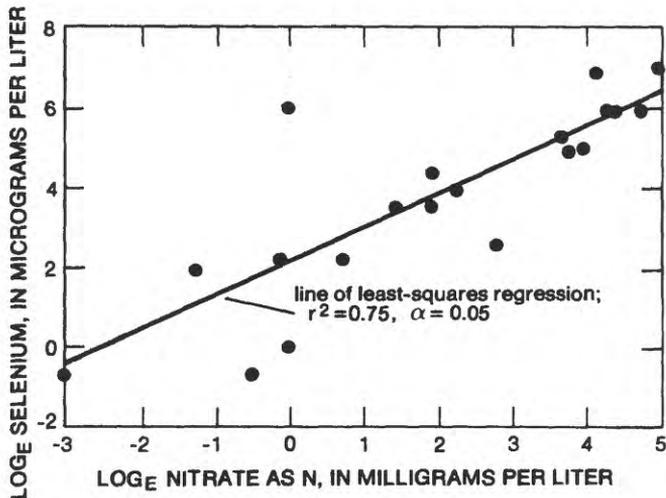


FIGURE 38.— Relation between selenium and nitrate concentrations for water from wells along the P6-P1 and P6-M1 geohydrologic sections.

The strongest relation between selenium and another redox-sensitive constituent is with nitrate (fig. 38). Nitrate concentrations explain 75 percent of the variation in the selenium concentrations for ground water in Coast Range sediments. This correlation indicates that selenium is mobile in the presence of nitrate and immobile where nitrate is absent. A similar relation between selenium and nitrate was noted in ground-water investigations at Kesterson Reservoir by researchers from the Lawrence Berkeley Laboratory. They found that the maximum infiltration of water with high selenium concentrations occurs where the concentration of nitrate also is high, and hypothesized that nitrate oxidizes organic matter in the sediments, thereby preventing the reduction and immobilization of selenium (Lawrence Berkeley Laboratory, 1987). This hypothesis was supported by column experiments in which retardation and coincident breakthrough of selenium and nitrate was observed in organic soils from the western valley (Lawrence Berkeley Laboratory, 1987), though it is not clear whether nitrate actually oxidizes organic matter or is simply present as a result of oxidizing conditions.

The low concentrations of selenium in ground water from wells screened in Sierra Nevada sediments or below the Corcoran Clay Member of the Tulare Formation are attributable to the low redox potential measured in these waters and to the low availability of selenium in these sediments. Immobilization of selenium due to reducing conditions is indicated by the absence of selenium even in highly saline, recently recharged ground water that

occurs in Sierra Nevada and mixed-source sediments in a shallow zone from 32 to 55 feet below land surface at cluster site P1. The immobility of selenium in Sierra Nevada sediments was directly demonstrated in an experiment at Kesterson Reservoir in which water with 1,000 mg/L of selenate was injected into a well screened in Sierra Nevada sediments, and then withdrawn over a period of 25 days (Lawrence Berkeley Laboratory, 1987). Results showed an approximately linear decrease in selenate, with less than 1 percent of the original concentration remaining in solution after 25 days (Lawrence Berkeley Laboratory, 1987).

Data indicate that selenium is mobile in Coast Range sediments under the oxidizing conditions present in the shallow part of the semiconfined zone. Ground water at shallow depths originated primarily as irrigation recharge, and the most oxidizing conditions are associated with ground water that has recharged since 1952. This association indicates that oxidizing conditions may be the result of rapid recharge of irrigation water. However, oxygenated ground water has been found at considerable depth in other alluvial aquifers in a semiarid climate (Rose and Long, 1988). There is no information on the natural redox conditions in the study area.

Areal Distribution of Selenium in Shallow Ground Water

Because tile drainage systems withdraw shallow ground water, the areal distribution of selenium in shallow ground water is a key limitation on alternatives for drainage management. Shallow ground water will herein be defined as water within the upper 20 feet of the saturated zone, in areas where the water table is less than 20 feet below the land surface. This definition restricts the assessment to areas where drainage problems presently occur or may soon develop, and to the upper part of the flow system that is most affected by tile drainage systems. Virtually all shallow ground water encompassed by this definition probably originated as irrigation water applied since 1967, when imported canal water became the primary irrigation supply for most of the primary study area.

The regional distribution of selenium and the general geochemistry of shallow ground water was first described by Deverel and others (1984) and further analyzed by Deverel and Millard (1988). A general conclusion of these studies was that high selenium concentrations in shallow ground water occur only in Coast Range alluvial sediments, which is in agreement with the preceding assessment of selenium concentrations along the P6-P1 and P6-M1 sections. All samples of shallow ground water that occurs in Sierra Nevada sediments contained less than 10 µg/L of selenium. Thus, the focus of this analysis is on evaluating the distribution of selenium in shallow ground water in Coast Range alluvial sediments.

In the central part of the western valley, concentrations of selenium in shallow ground water generally are less than 20 $\mu\text{g/L}$ in the middle fan areas of the alluvial fans deposited by Cantua, Little Panoche, Los Gatos, and Panoche Creeks (fig. 39). In the lower-fan areas, particularly at the northern and southern margins of the Panoche Creek fan, concentrations in ground water are higher and are as much as several hundred micrograms per liter. Patterns of distribution are more difficult to generalize for the ephemeral-stream fans,

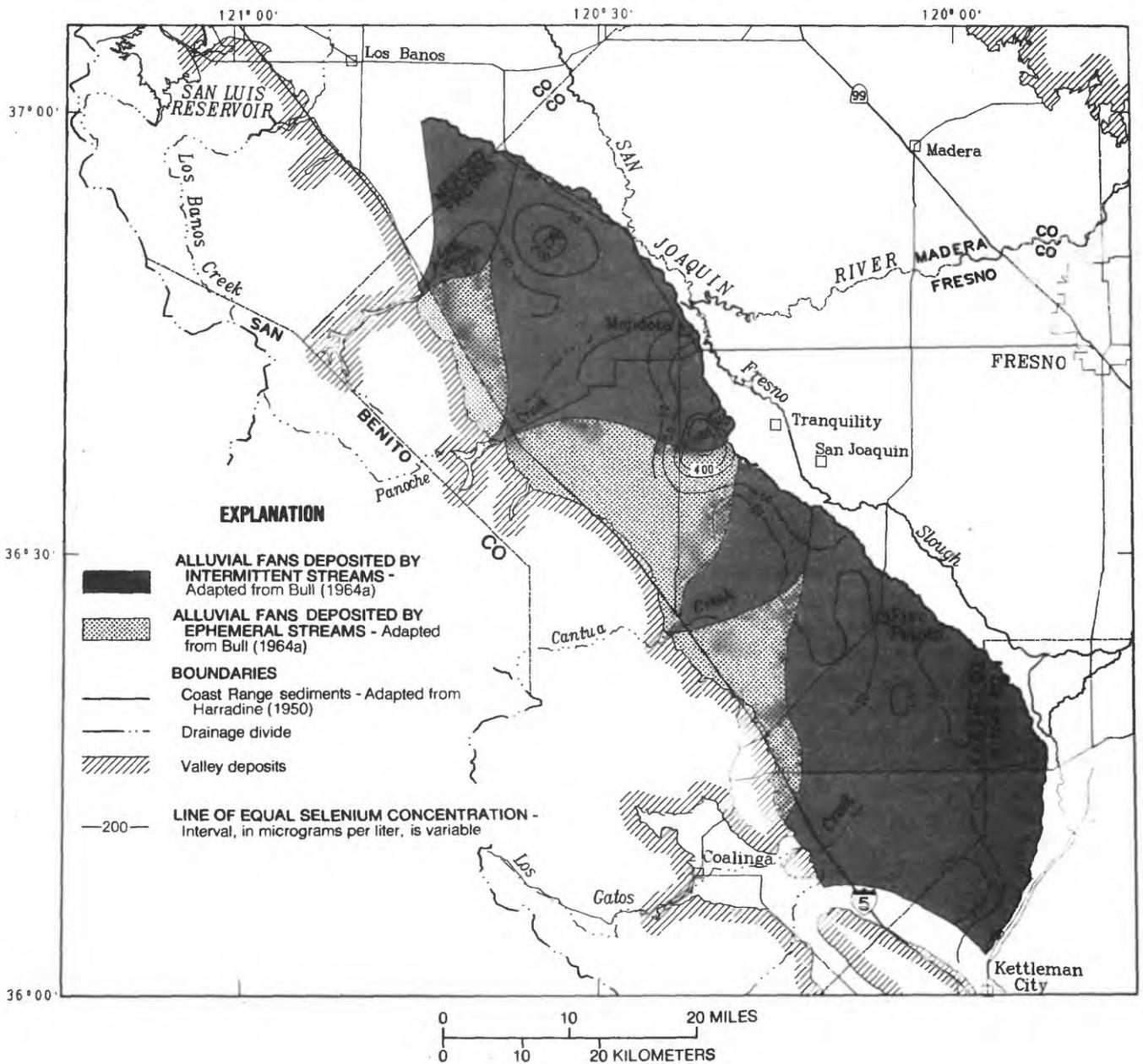


FIGURE 39.— Selenium concentrations in shallow ground water of the central part of the western valley, 1986 (Deverel and Gallanthine, 1988).

largely because only a small area of these fans is underlain by shallow ground water. The exception is the lowest altitudes of the ephemeral-stream fans between the Panoche Creek and Cantua Creek fans. Some of the highest selenium concentrations observed in ground water occur in this part of the study area.

Selenium concentrations are low in the middle-fan areas of Panoche Creek and Cantua Creek alluvial fans because the ground water sampled in those areas mostly consists of only the most recently recharged water near the water table (Deverel and Gallanthine, 1988). The recent recharge has occurred through soils that have been leached by several decades of irrigation. The ground water resulting from this recent recharge has lower selenium concentrations and higher tritium content than underlying ground water derived from earlier irrigation recharge (Deverel and Gallanthine, 1988). The depth distribution of selenium at cluster sites P4, P3, and M3 shows similar evidence of lower selenium concentrations in recent recharge compared to earlier recharge.

Relation to Soil Selenium

The area with the highest concentrations of selenium in shallow ground water (fig. 39), which is in the ephemeral-stream fans between Panoche and Cantua Creeks, occurs about 1 to 5 miles to the northeast of the highest concentrations of total selenium in soil (fig. 3). The proximity of the high ground-water and soil concentrations may partly reflect the common influence of geologic sources of selenium near Monocline Ridge. The proximity also may be coincidental, with total soil concentrations most affected by the geologic sources and the concentrations in shallow ground water most affected by hydrologic processes that have redistributed soluble forms of selenium.

Total soil selenium and selenium in shallow ground water are not clearly correlated within the areas of the Coast Range alluvial fans that are underlain by shallow ground water. The lack of correlation probably is because present-day total selenium in soil does not accurately represent the predevelopment distribution of soluble forms of selenium. Soluble forms of selenium, which directly affect ground-water concentrations, are now only a small fraction of total soil selenium because the most soluble forms already have been leached from present-day soils.

Amundson and others (1986) examined changes in potassium phosphate-extractable selenium concentrations in soil samples from the Panoche Creek alluvial fan collected in 1946 and 1985. Potassium-phosphate extractions are one way to estimate the amount of readily mobile selenium in soil. Soil samples from areas that were irrigated after 1940 were higher in extractable selenium in 1946 than those from areas that were irrigated before 1940. Moreover, soil samples collected from the same locations in 1985 as in 1946 showed substantial decreases in extractable selenium. By 1985, values for extractable selenium had decreased to about 10 percent of the 1946 values. Consistent with this, Fujii and others (1988) found that most selenium in presently irrigated soils is in forms that are resistant to leaching.

An understanding of the relation between soil selenium and present-day ground-water selenium concentrations requires focusing on the distribution of soluble forms before irrigation. Direct measurements of conditions prior to irrigation are not available, except for the few archived samples discussed in the preceding paragraph. However, the close relation between dissolved selenium and salinity in shallow ground water derived from irrigation recharge allows useful inferences regarding the natural distribution of soluble forms of selenium from data on soil and ground-water salinity.

Relation Between Selenium and Salinity

Selenium concentrations in shallow ground water in Coast Range sediments are highly correlated with salinity (Deverel and Millard, 1988; Deverel and Fujii, 1988). The dominant form of dissolved selenium is selenate. The selenium dissolved in this ground water seems to be unaffected by precipitation or sorption on mineral surfaces (Deverel and Fujii, 1988). Compared to sulfate, the major ion that selenate most closely resembles, selenate is less affected by solubility constraints (Deverel and Gallanthine, 1988). As ground-water salinity increases because of evapotranspiration, selenium increases disproportionately to sulfate concentration, which is limited by gypsum precipitation. The selenium dissolved in this oxic ground water is relatively nonreactive for a large range of concentrations, and thus behaves as a nonreactive soluble ion. Therefore, an understanding of the factors that have affected the salinity of ground water also yields useful information about the factors affecting selenium distribution.

The distribution of dissolved solids in shallow ground water is similar to that of selenium (fig. 40). In the middle-fan area of the Panoche Creek alluvial fan, dissolved solids in ground water generally are less than 3,000 mg/L. In the lower-fan area, dissolved solids are commonly greater than 5,000 mg/L; in some areas along the fan margins, concentrations are greater than 10,000 mg/L. Similarly, in the middle-fan areas of the Cantua Creek and Los Gatos Creek alluvial fans, dissolved solids also generally are less than 5,000 mg/L and are 5,000 to 10,000 mg/L at the margins of those fans. As was true for selenium, concentrations of dissolved solids in areas of ephemeral-stream alluvial fans generally are higher than in corresponding topographic locations on adjacent fans of the major streams. In the middle-fan area of the ephemeral-stream deposits between the Panoche Creek and Cantua Creek fans, ground water has dissolved-solids concentrations generally between 3,000 and 5,000 mg/L and are as high as 10,000 mg/L. Dissolved solids commonly are greater than 10,000 mg/L at the lowest altitudes of the ephemeral-stream deposits north of Cantua Creek.

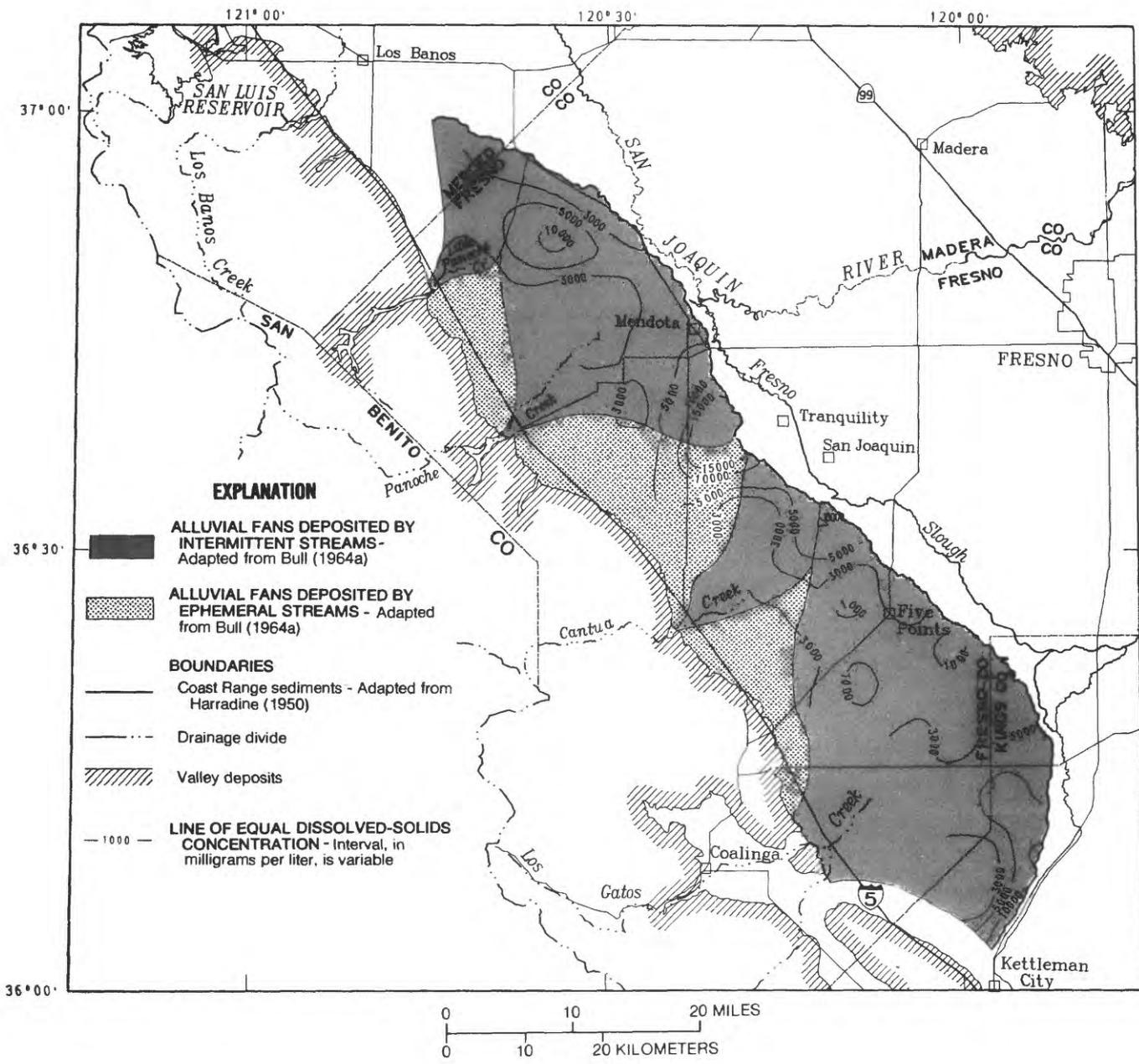


FIGURE 40.— Dissolved-solids concentrations in shallow water of the central part of the western valley, 1986 (Deverel and Gallanthine, 1988).

The distribution of soil salinity before most of the study area was irrigated followed the same relative distribution as dissolved solids and selenium in present-day shallow ground water. Figure 41 shows the distribution of subsurface soil salinity in the mid-1940's (Harradine, 1950) and the area of artesian wells defined by Mendenhall and others (1916), which approximates the natural ground-water discharge area in the valley trough. The highest soil salinity was found along the margins of the alluvial fans, where ground-water

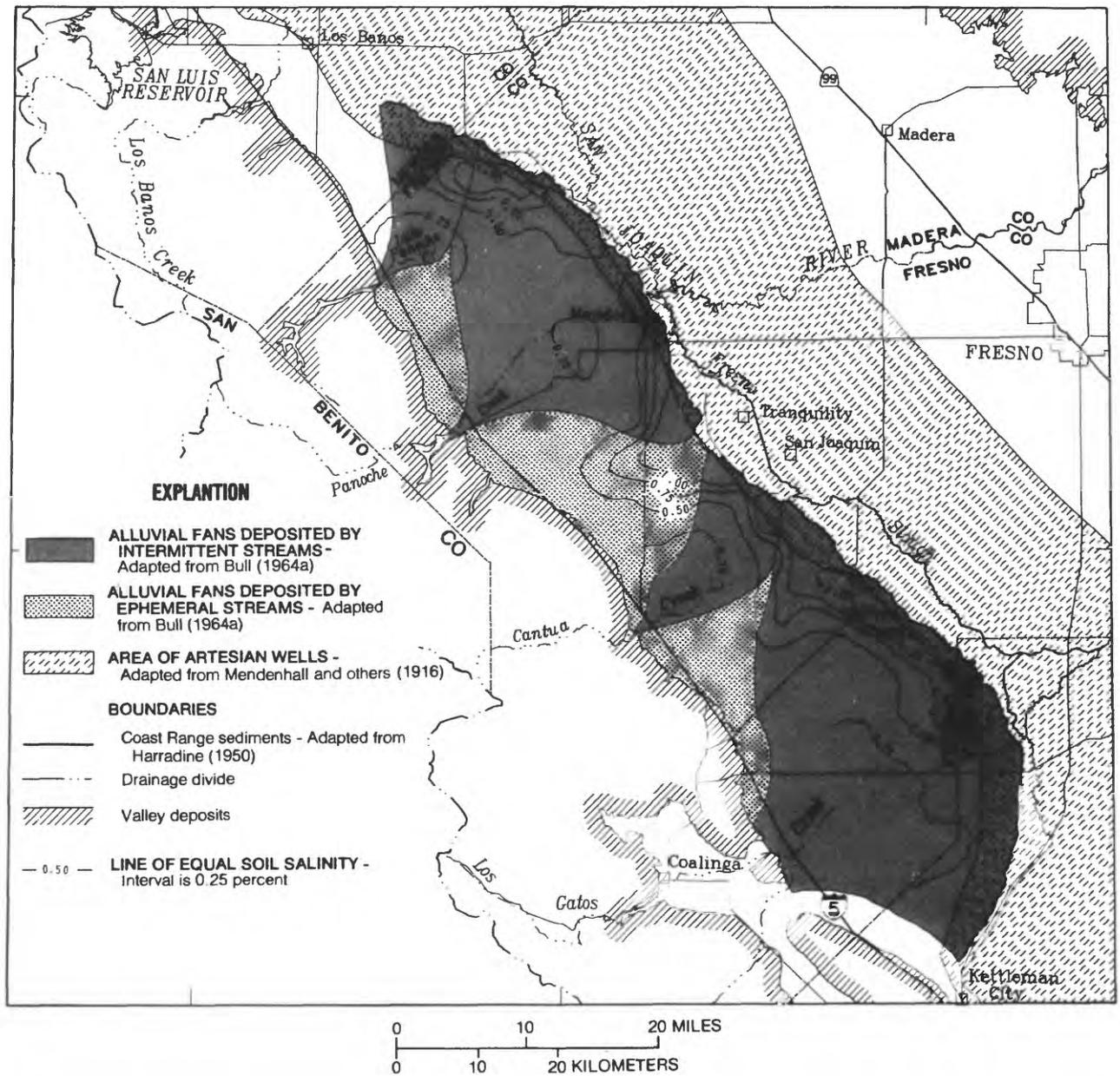


FIGURE 41.— Subsurface-soil salinity in the mid-1940's, and area of artesian wells, 1908, in the central part of the western valley. (Adapted from Harradine, 1950, by Deverel and Gallanthine, 1988.)

discharge by evapotranspiration brought solutes to the surface over several thousand years. The middle and upper parts of the alluvial fans have less saline soils than the lower parts, but the fans of small ephemeral streams generally have more saline soils than the fans of the larger intermittent streams. This pattern probably results from the less frequent flushing of the soils of the ephemeral-stream fans because of their lower and less frequent streamflow.

Similar distributions of salts in soils during the mid-1940's and in present-day shallow ground water indicate that dissolved solids now in shallow ground water were leached from the saline soils by irrigation water. Additional factors have combined with this dominant process, resulting in a complicated distribution of dissolved solids in shallow ground water. As discussed in Deverel and Gallanthine (1988), soil conditions in the mid-1940's did not represent natural conditions in some parts of the area. Figure 42 shows the part of the area that was irrigated with ground water prior to 1940. Present-day ground-water salinity is poorly correlated with mid-1940's soil salinity ($r^2=0.19$) in areas irrigated before 1940. The two are better correlated ($r^2=0.50$) in the part of the area that had not been irrigated before soil samples were collected.

In the mid-1940's, saline soils were reported in the area at the northern margin of the Panoche Creek fan where soils were not found to be saline in 1915 (Nelson and others, 1919). This area was irrigated with surface water beginning in the early 1900's. An irrigation-induced rise in the water table apparently led to saline conditions in the unsaturated zone by the mid-1940's as solutes were concentrated by evapotranspiration. Installation of drainage systems in this area since 1950 has allowed displacement of saline ground water and leaching of saline soils.

The first few decades of irrigation probably leached most of the readily soluble forms of soil selenium and other salts into the shallow ground water. Since irrigation began, there has been relatively little horizontal movement of shallow ground water. Thus, the present-day distribution of selenium in shallow ground water generally follows the distribution of natural soil salinity in the Coast Range alluvial sediments.

Evaporative Concentration

In areas where the water table is shallow, evaporative concentration of dissolved solids in ground water can increase ground-water salinity and selenium concentrations far above the levels resulting from leaching of soil salts by irrigation. Under natural conditions, when little or no recharge of ground water occurred through the lower-fan soils, ground-water discharge by evapotranspiration resulted in accumulation of salts in the soil rather than in the ground water. Under irrigated conditions, loss of water by evapotranspiration tends to concentrate salts in the ground water rather than in the soil because soils regularly are flushed by downward percolating irrigation water, and net ground-water movement generally is downward.

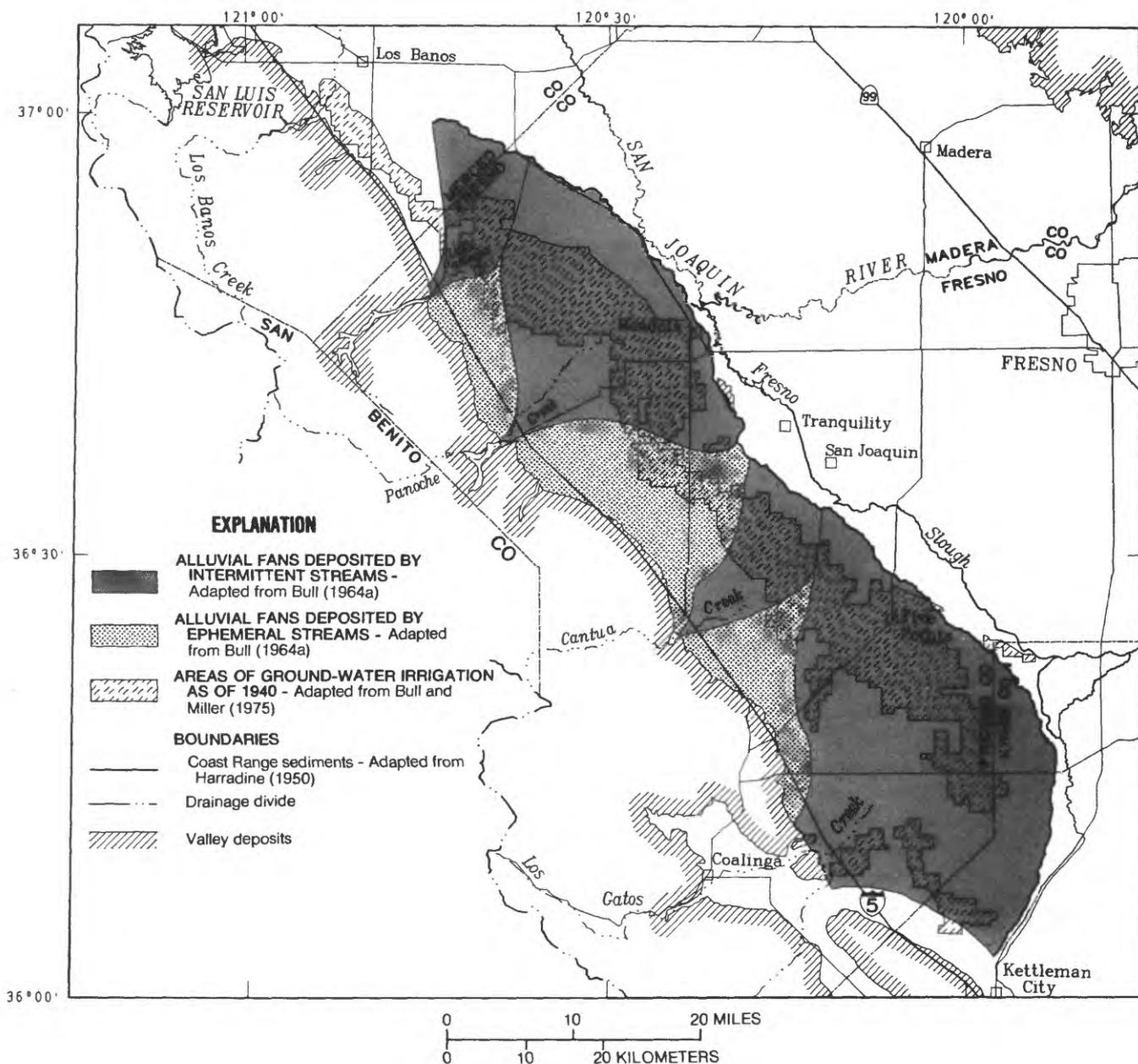


FIGURE 42.— Areas irrigated with ground water prior to 1940 in the central part of the western valley.

Figure 43 shows the composition of stable isotopes in 46 samples of shallow ground water collected from the study area. Samples collected at the lowest land-surface altitudes, where the water table is shallowest or was shallow prior to drainage, are most enriched in the heavy isotopes and follow an evaporative trend line, indicating evaporative concentration. Isotopic data for ground water of three drained agricultural fields fit a similar evaporative trend line (Deverel and Fujii, 1988). Deverel and Fujii (1988) showed that selenium and dissolved-solids concentrations in shallow ground water of the three fields were significantly correlated ($\alpha=0.05$) with delta oxygen-18, and

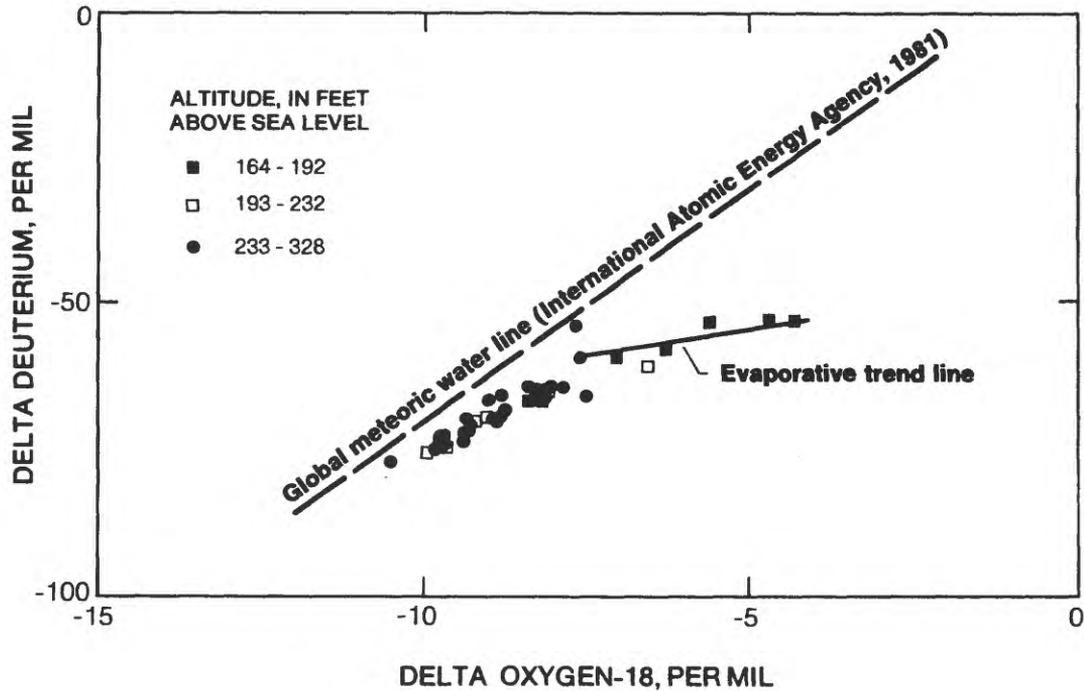


FIGURE 43.— Comparison of delta deuterium and delta oxygen-18 for samples of shallow ground water collected from various land-surface altitudes in the central part of the western valley.

were primarily the result of evaporative concentration. At higher land-surface altitudes, where selenium concentrations generally are low, the shallow ground water is less enriched than at the lower altitudes, indicating little or no evaporation. Most of the shallow ground-water samples collected at the higher land-surface altitudes (233 to 328 feet above sea level) plot close to the meteoric water line and have been subject to little or no evaporation.

General Patterns of Selenium Distribution in Ground Water

Studies of the depth and areal distribution of selenium in ground water of the central western valley lead to some general conclusions. All selenium concentrations that exceeded 10 $\mu\text{g/L}$ occurred in the upper part of the semi-confined zone in Coast Range alluvial sediments. Concentrations of selenium were less than or equal to 2 $\mu\text{g/L}$ in all samples from Sierra Nevada deposits and the confined zone below the Corcoran Clay Member of the Tulare Formation.

The high concentrations of selenium in the upper part of the semiconfined zone occur in oxic ground water derived from irrigation recharge and are correlated with ground-water salinity. Two main processes have affected the

distribution of ground-water salinity and selenium concentrations: (1) leaching of soil salts and soluble selenium during infiltration of irrigation water, and (2) evaporative concentration of dissolved selenium and other soluble salts in areas where the water table has been shallow. The areal distribution of selenium concentrations in shallow ground water generally correlates with soil salinity before agricultural development, reflecting the leaching of natural soil salts by irrigation. In some areas where the water table is near the land surface, the highest concentrations of selenium in shallow ground water have developed as a result of evapotranspiration of ground water. In some irrigated areas where the water table is deep enough that evaporative concentration has not been substantive, recently recharged ground water has lower selenium concentrations than ground water from early irrigation recharge, because most soluble forms of selenium already have been leached from the soil.

Although the natural processes and human influences that govern the distribution of selenium in ground water in the Coast Range sediments vary greatly throughout the central western valley, general patterns are evident. Within about 10 to 20 feet below the water table, selenium concentrations commonly range from 10 to 50 $\mu\text{g/L}$, but are 10 to 100 times higher than this where the water table has been near the land surface for an extended period, and evaporative concentration has occurred. Water in this shallowest interval is derived principally from the most recent irrigation recharge, probably during the past 10 to 20 years. Within the range of 20 to 150 feet below the water table, an interval of variable thickness occurs in which selenium concentrations commonly are 50 to more than 1,000 $\mu\text{g/L}$. Water in this interval is derived principally from recharge of early irrigation water. Selenium concentrations in both of these upper depth intervals that are associated with irrigation recharge generally are in the highest part of the stated concentration ranges where natural soils were most saline, and in the lowest part of the ranges where natural soils were least saline. Native ground water, with selenium concentrations commonly less than 10 $\mu\text{g/L}$, is below the ground water from irrigation recharge.

SELENIUM IN GROUND WATER OF THE NORTHERN PART OF THE WESTERN VALLEY

by *Neil M. Dubrovsky*

The northern part of the western valley, located mainly in the western parts of Merced, San Joaquin, and Stanislaus Counties, provides some interesting contrasts and comparisons to the central part. The ground-water flow system and general geochemistry of the northern part is described by Hotchkiss and Balding (1971). Generally, selenium concentrations in soil and shallow ground water are lower in the northern part. However, the type of data available for assessing the northern part is different from data for the central part, making specific comparisons difficult. Except for the shallowest ground water, only samples from existing production wells were collected. Regular pumping and the presence of gravel-packed well casings result in rapid downward movement of shallow ground water near some wells. Therefore, data from production wells may not be representative of parts of the ground-water system remote from such wells. Nevertheless, general interpretations are possible that provide a useful assessment of the northern area and a perspective on the primary study area to the south.

Age and Origin of Ground Water

Tritium concentrations measured in selected samples of ground water indicate that recent irrigation water probably has reached depths at least as great in the northern part of the western valley as in the central part. Results of the analyses show tritium concentrations ranging from 1.8 to 28.1 Tu in the semiconfined zone. Of the 12 samples analyzed, 9 had more than 10 Tu, indicating a high proportion of ground water that has recharged since 1952 (fig. 44). The three samples with less than 10 Tu are of uncertain age and probably are mixtures. The midpoints of the screened intervals for the 12 wells range from 33 to 141 feet below land surface and average 85 feet. The data indicate that ground water recharged since 1952, most of which was irrigation-derived recharge, has moved at least to the depths of these screened intervals near the wells sampled. The depth of tritiated ground water possibly is exaggerated, however, by high downward gradients induced by pumpage and leakage down casings and gravel packs.

Tritium concentrations in 13 water samples from the confined zone range from less than the detection limit of 0.8 to 18.5 Tu. Five water samples contained more than 10 Tu, indicating a substantial proportion of post-1952 irrigation recharge. Five water samples contained from 0.9 to 6.1 Tu, indicating the presence of post-1952 recharge in a mixture, and only three samples contained undetectable amounts of tritium. The wells average 387 feet in depth to the midpoint of the screens--about 300 feet deeper than the average for the wells completed in the semiconfined zone.

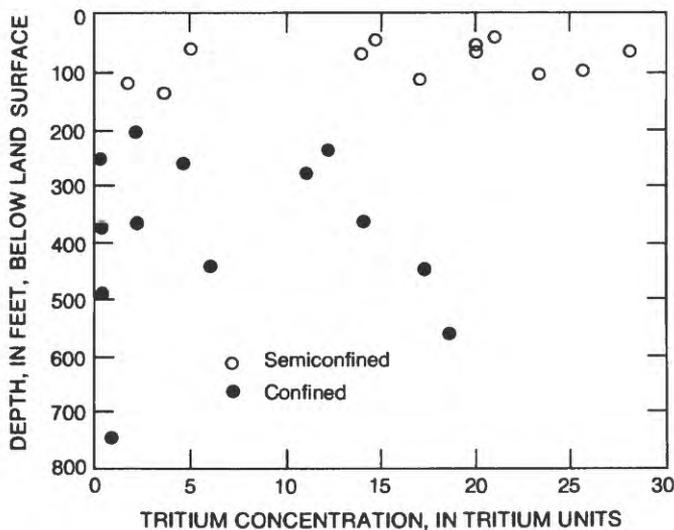


FIGURE 44.— Tritium concentrations in relation to depth in the semiconfined and confined zones of the northern part of the western valley.

In the confined zone, the presence of ground water that originated as post-1952 irrigation water indicates that wells perforating the Corcoran Clay Member of the Tulare Formation have altered the leakage between aquifer zones above and below the clay. Under natural conditions, the Corcoran has a vertical hydraulic conductivity of about 9×10^{-6} ft/d (Page, 1977). With an assumed average gradient of 0.05 (Mandle and Kontis, 1986) and a porosity of 0.25, water would take about 1,500 years to traverse a 100-foot thickness of intact clay. The presence of tritium below the clay indicates that leakage through the clay has been at least locally increased due to perforation by wells. Williamson and others (1985) concluded that the flux of

water across the Corcoran has increased throughout much of the western San Joaquin Valley due to vertical flow through well casings and gravel packs.

An accurate estimate of the amount of ground water in the confined zone that has been affected by vertical flow through well bores cannot be made from existing data. Records indicate more than 450 wells with screened intervals of 250 feet or greater in depth, which is the approximate depth to the top of the Corcoran. The number of unrecorded and abandoned wells probably is equal or greater. The large number of wells, combined with dominantly downward gradients, indicate that leakage of water from the semiconfined zone to the confined zone may be widespread even though the influence probably is limited to parts of the confined zone near individual wells. Parts of the confined zone between wells probably contain unaffected native ground water.

Although only a few existing production wells in the central western valley were sampled, the results for that area are in agreement with the conclusion for the northern area. In both areas, production wells have locally increased downward movement of shallow ground water into deeper parts of the aquifer. Data from the northern area demonstrate that this process occurs not only in the semiconfined zone, but also across the Corcoran.

Distribution of Selenium

The distribution of selenium in shallow ground water is shown in figure 45. In the southwest corner of the area, between the Merced-Fresno County boundary and Los Banos Creek, selenium concentrations commonly are 10 to 100 $\mu\text{g/L}$, and are as high as 260 $\mu\text{g/L}$. In this area, shallow ground water occurs in Coast Range sediments deposited by Little Panoche, Ortigalita, and Los Banos Creeks, and smaller foothill drainages. In all other places, shallow ground water had concentrations of selenium less than 10 $\mu\text{g/L}$.

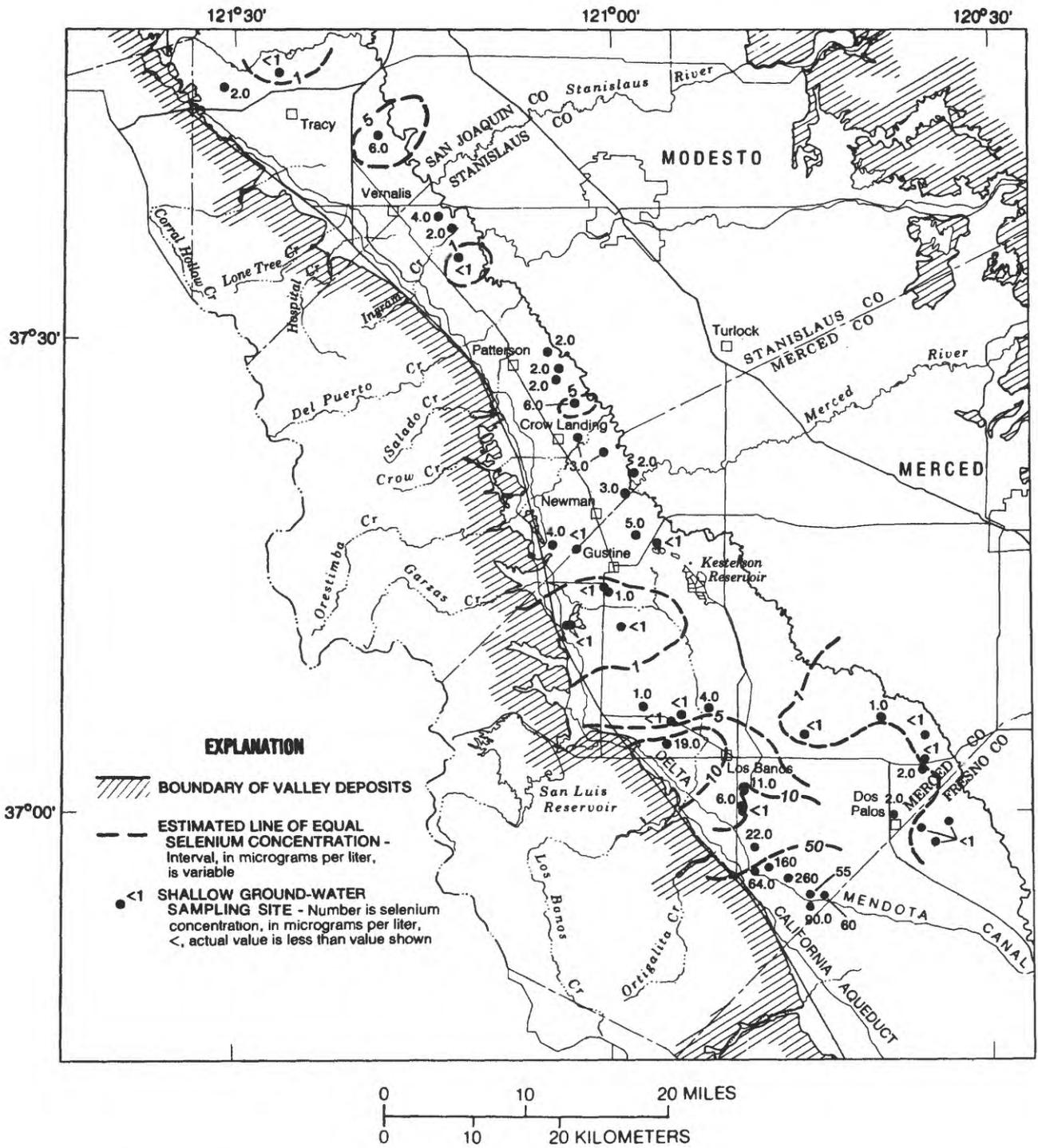


FIGURE 45.— Distribution of selenium concentrations in shallow ground water of the northern part of the western valley, 1984.

Selenium concentrations in the semiconfined and confined zones ranged from less than 1 to 13 $\mu\text{g/L}$, and concentrations and their distribution were generally similar in the semiconfined and confined zones (figs. 46 and 47). In both zones, a narrow area containing the highest selenium concentrations occurs

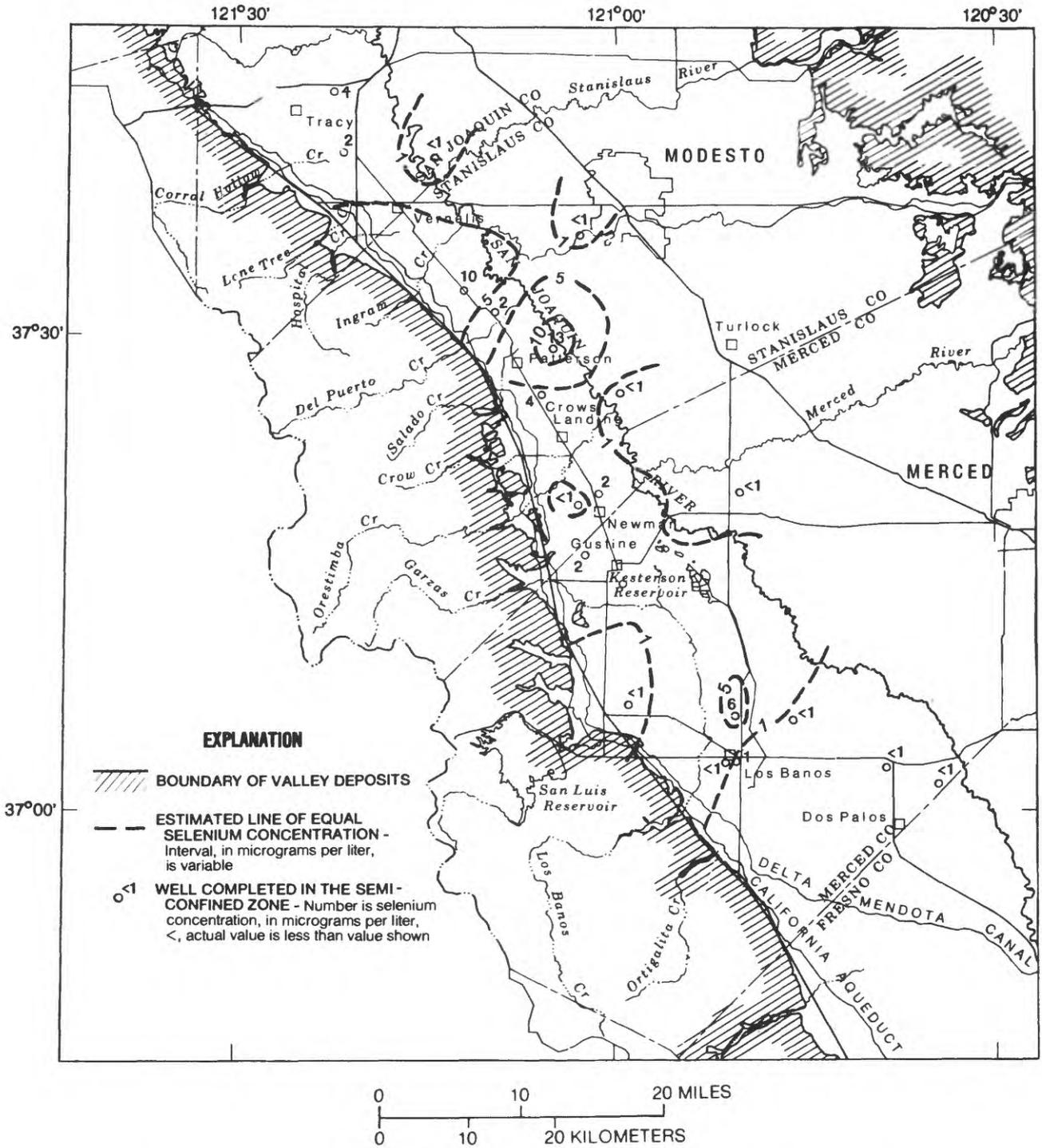


FIGURE 46.— Selenium concentrations in ground water in the semiconfined zone of the northern part of the western valley, 1985.

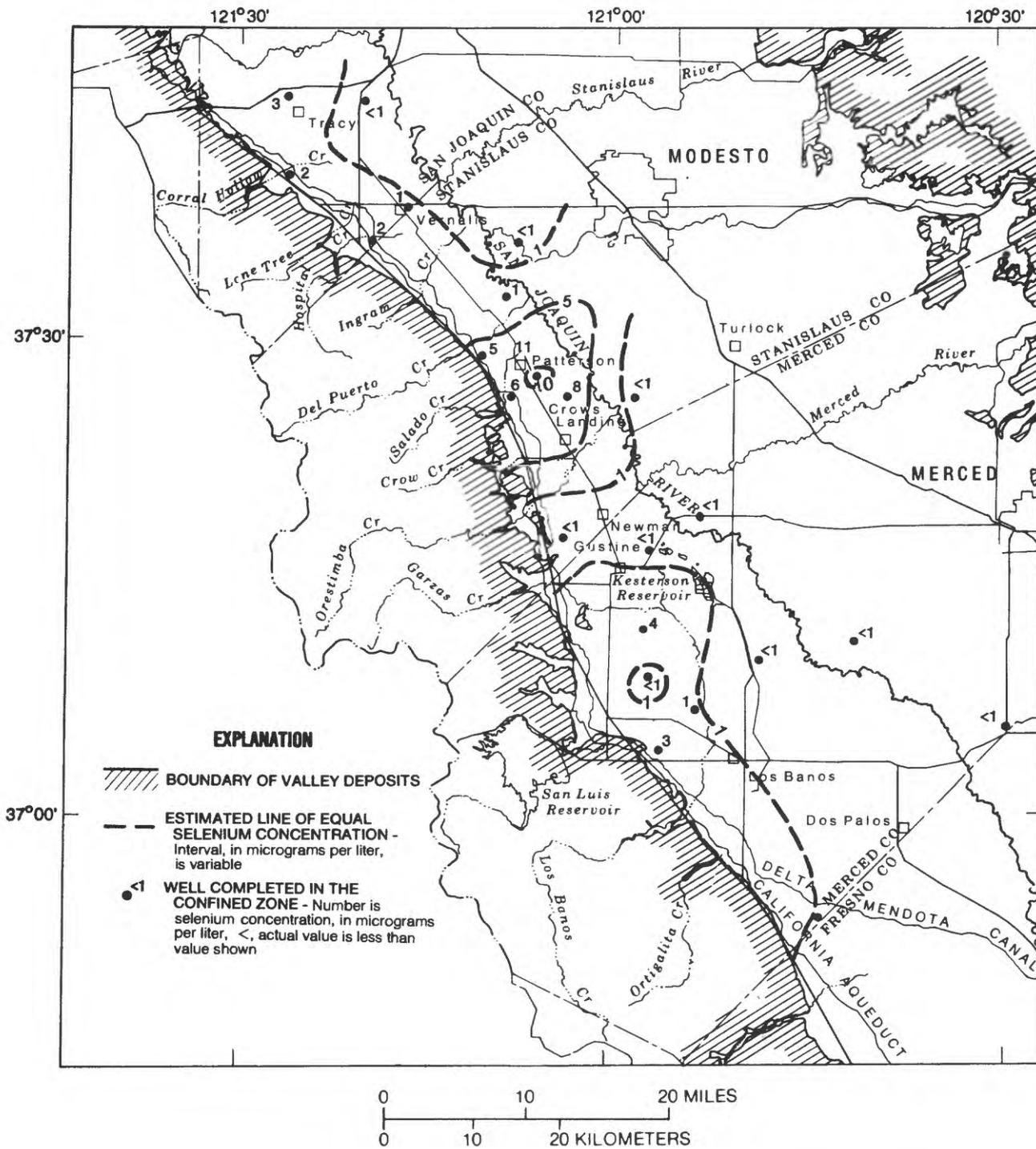


FIGURE 47.— Selenium concentrations in ground water in the confined zone of the northern part of the western valley, 1985.

near Crows Landing. The selenium concentration in this area exceeded the U.S. Environmental Protection Agency drinking water standard of 10 $\mu\text{g/L}$ in one well in the semiconfined zone and one well in the confined zone. Selenium concentrations are lowest along the east side of the study area in the trough of the valley. Available data do not indicate that semiconfined ground water that underlies shallow ground water with high selenium concentrations in the southwest part of the area also has high concentrations. However, data suitable for addressing this issue are sparse.

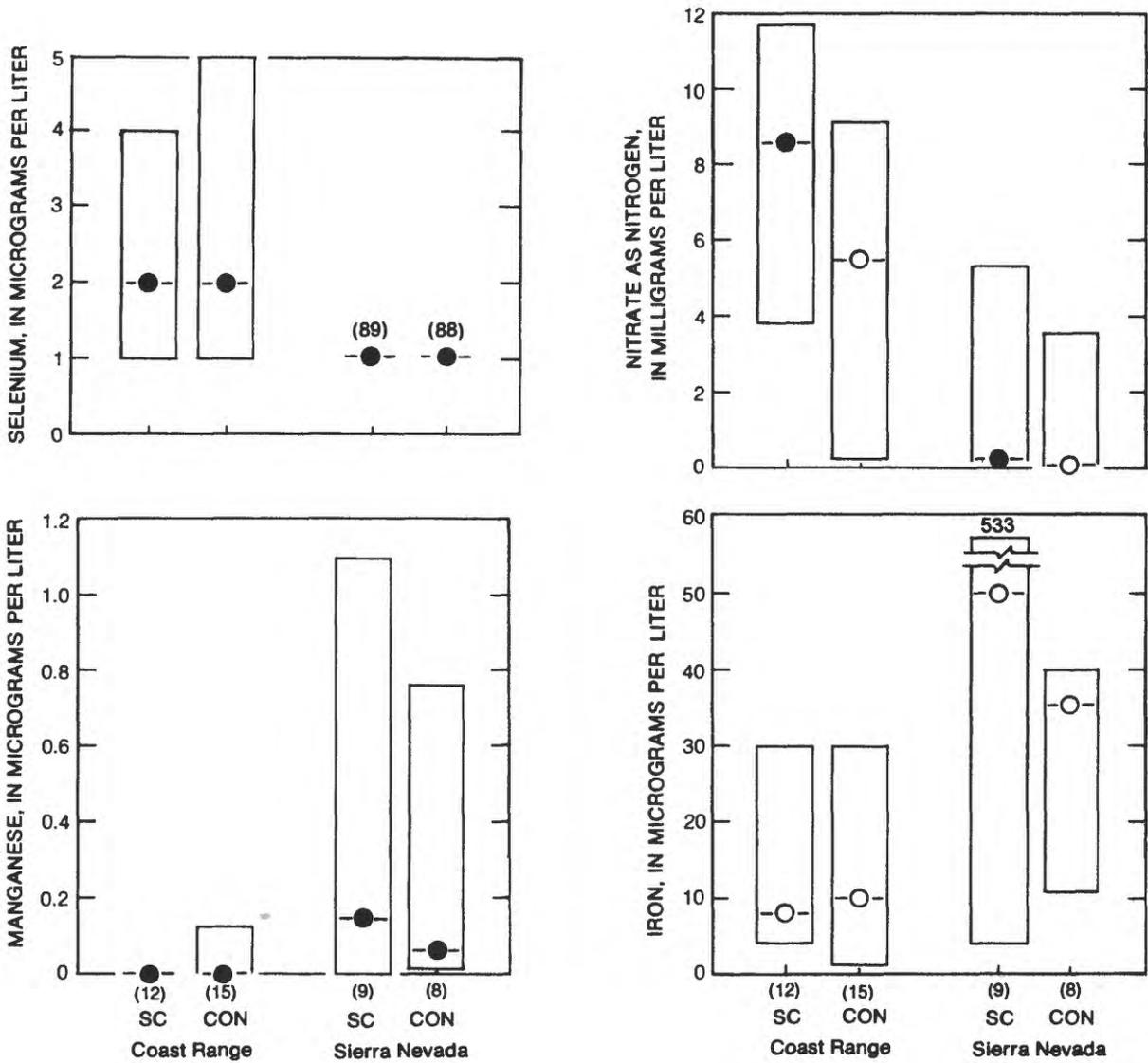
Relation to Geologic Source

Selenium concentrations in the semiconfined and confined zones were significantly higher ($\alpha=0.05$) in Coast Range sediments than in Sierra Nevada sediments (fig. 48). More than 80 percent of all samples of ground water from Sierra Nevada sediments had selenium concentrations less than 1 $\mu\text{g/L}$, whereas more than 80 percent of samples from Coast Range sediments contained 1 $\mu\text{g/L}$ of selenium or more. Selenium analyses of several streams entering the northern study area from the Coast Range indicate high selenium concentrations in Crow and Salado Creeks [(table 2); T.S. Presser, U.S. Geological Survey, written commun., 1987]. These creeks recharge the part of the study area near Crows Landing, where selenium concentrations were highest in ground water. These results indicate that selenium may have been transported to the northern study area under natural conditions by runoff from the Coast Ranges.

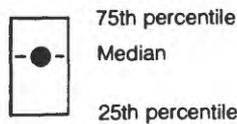
Effect of Redox Potential

As in the central western valley, the relation between selenium concentrations in ground water and the geologic source of aquifer sediments also may be related to the dominance of chemically reduced conditions in Sierra Nevada sediments and more oxidized conditions in most Coast Range sediments. Comparisons of iron and manganese concentrations in ground water in Sierra Nevada and Coast Range sediments for the semiconfined and confined zones show that concentrations of both metals generally are higher in ground water in the Sierra Nevada sediments (fig. 48), though the difference is not significant ($\alpha=0.05$) for iron. This comparison indicates that the Sierra Nevada sediments in this area are more reduced than the Coast Range sediments. Similarly, nitrate concentrations are higher in ground water in Coast Range sediments in both zones (though not significantly different in the confined zone, $\alpha=0.05$), indicating more oxidized conditions in the Coast Range alluvial sediments (fig. 48).

The presence of nitrate indicates oxidized conditions. Reduced conditions cause nitrate to be removed from solution by denitrification, though factors such as insufficient nutrients for bacterial action may prevent denitrification. Naturally high concentrations of nitrate in soils in the western San Joaquin Valley are due in part to the arid conditions and the lack of natural leaching of mudflow deposits (Sullivan, 1978). Conversely, the absence of nitrate in ground water in Sierra Nevada sediments probably is caused partly by flushing during flooding that occurs during deposition of basin deposits, as well as by reducing conditions.



EXPLANATION



- Significant difference between medians of sediment types ($\alpha = 0.05$)
- No significant difference between medians of sediment types ($\alpha = 0.05$)
- (89) Percentage of samples with concentrations below the detection limit (only shown if greater than 50 percent)
- (12) SEMICONFINED ZONE - Number in parenthesis is number of samples
- (15) CONFINED ZONE - Number in parenthesis is number of samples

FIGURE 48. — Comparison of concentrations of selenium with concentrations of nitrate, manganese, and iron in Coast Range and Sierra Nevada sediments for the semiconfined and confined zones in the northern part of the western valley.

TABLE 2. Concentrations of selenium in selected Coast Range streams

[Concentrations are for samples collected in March 1984 and analyzed by T.S. Presser, U.S. Geological Survey, Menlo Park, California. $\mu\text{g/L}$, micrograms per liter. <, actual value is less than value shown]

Stream	Selenium concentration ($\mu\text{g/L}$)
Del Puerto Creek	<1
Corral Hollow Creek	1
Crow Creek	18
Garzas Creek	2
Hospital Creek	1
Ingram Creek	4
Lone Tree Creek	<1
Los Banos Creek	<1
Orestimba Creek	1
Ortigalita Creek	1
Salado Creek	5

Evidence thus indicates that ground water in Sierra Nevada sediments is more reducing than ground water in Coast Range sediments in the northern part of the western valley. The absence of selenium in ground water in Sierra Nevada sediments may be due partly to reduction and immobilization of selenium. Because of the coincidence of the redox boundary with the division between geologic sources of sediments, the relative contributions of these two factors cannot be quantitatively separated on the basis of the data available.

Relation to Salinity

The correlation between selenium and specific conductance in ground water was significant ($\alpha=0.05$) only for the 12 water samples from Coast Range sediments in the semiconfined zone. The natural logarithms of concentrations for those samples are linearly related. One unusual water sample with extremely high chloride and specific conductance was omitted. Excluding this sample, specific conductance explains 78 percent of the variation in selenium concentrations (fig. 49). The slope and intercept of the regression relation for the northern area are not significantly different ($\alpha=0.05$) than the slope and intercept of the similar relation between selenium and specific conductance in the central western valley (figs. 33 and 34).

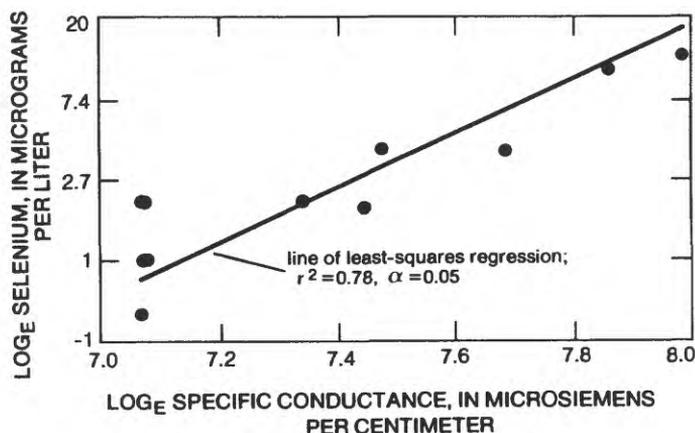


FIGURE 49.— Relation between selenium and specific conductance in ground water from Coast Range sediments in the semiconfined zone of the northern part of the western valley.

As in the central western valley, the positive correlation between selenium and salinity in the Coast Range sediments of the semiconfined aquifer may be explained by either the leaching of soluble salts from soils and aquifer sediments, or by evaporative concentration. However, oxygen-18, an indicator of evaporative enrichment, and selenium are not correlated in ground water from Coast Range sediments in the semiconfined zone. Therefore, the relation between selenium and specific conductance probably results from (1) the leaching of soluble salts from the unsaturated zone, (2) a possible correlation between selenium and salinity in Coast Range runoff, and (3) the generally nonreactive geochemical characteristic of selenium in the Coast Range sediments.

The relation between the natural logarithm of selenium and oxygen-18 in ground water from Coast Range sediments in the confined zone is significant ($\alpha=0.05$), and explains 42 percent of the variation in selenium concentrations (fig. 50), even though selenium and salinity are not correlated. The oxygen-18 values for these samples do not depart from the meteoric water line, as would occur if evaporation had taken place. Thus, the correlation indicates that some of the selenium in the confined zone may be due to infiltration of the confined aquifer by more enriched ground water of the semiconfined zone.

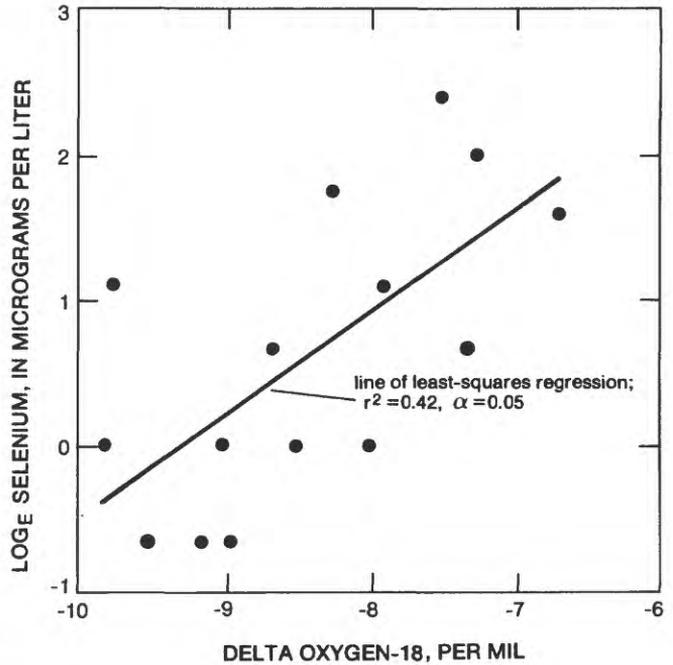


FIGURE 50.— Relation between selenium and delta oxygen-18 in ground water from Coast Range sediments in the confined zone in the northern part of the western valley.

SELENIUM IN TILE DRAIN WATER

by *Steven J. Deverel, John L. Fio, and Robert J. Gilliom*

Effective management of existing tile drainage systems and assessments of the use of tile drains as a management option for the future require an understanding of how tile drains interact with the ground-water flow system and the levels and variability of selenium concentrations likely to occur in drain water. The present understanding is best explained by first reviewing the range of drain-water quality measured in the study area, examining its relation to the regional distribution of selenium in shallow ground water, and then illustrating the complex relation between drain water and ground water with examples from two agricultural fields.

Drain-Water Concentrations

Concentrations of selenium in drain water can be characterized in two main respects: magnitude and variability. These characteristics provide the basis for evaluating relations between drain-water quality, ground-water quality, and irrigation patterns.

The chemistry of drain water has been monitored in 11 farm drain sumps at fields in Coast Range alluvial sediments since March 1984 (U.S. Bureau of Reclamation, 1987). Selenium and specific conductance data for samples collected from these sumps once each month from March 1984 to June 1986 are well-suited to analysis of general patterns in spatial and temporal variability. The locations of the 11 drain sumps are shown in figure 51.

Concentrations of selenium in drain water vary much more widely between sites than they do over time at any particular site. Average concentrations of selenium at each of the 11 drain sumps ranged from 12 to 3,330 $\mu\text{g/L}$. The coefficient of variation (the standard deviation divided by the mean) of the average concentrations for the 11 sites is 2.1, indicating high variability between sumps. In contrast, the coefficients of variation of monthly concentrations of selenium for drain water from individual sumps were much lower, ranging from 0.12 to 0.97, with an average of 0.41. Wichlens and Nelson (1987) reported data for four additional sumps in Broadview Water District, on the northern edge of the study area, which indicate coefficients of variation from 0.17 to 0.38.

The salinity of drain water, as measured by specific conductance, also varied greatly between sites, but was relatively consistent over time at each individual site. Average specific conductances of drain water from the 11 sumps ranged from 4,690 to 25,300 $\mu\text{S/cm}$. The coefficient of variation of the average concentrations is 0.65, considerably lower than the value of 2.1 for selenium. The coefficients of variation for drain water from the individual

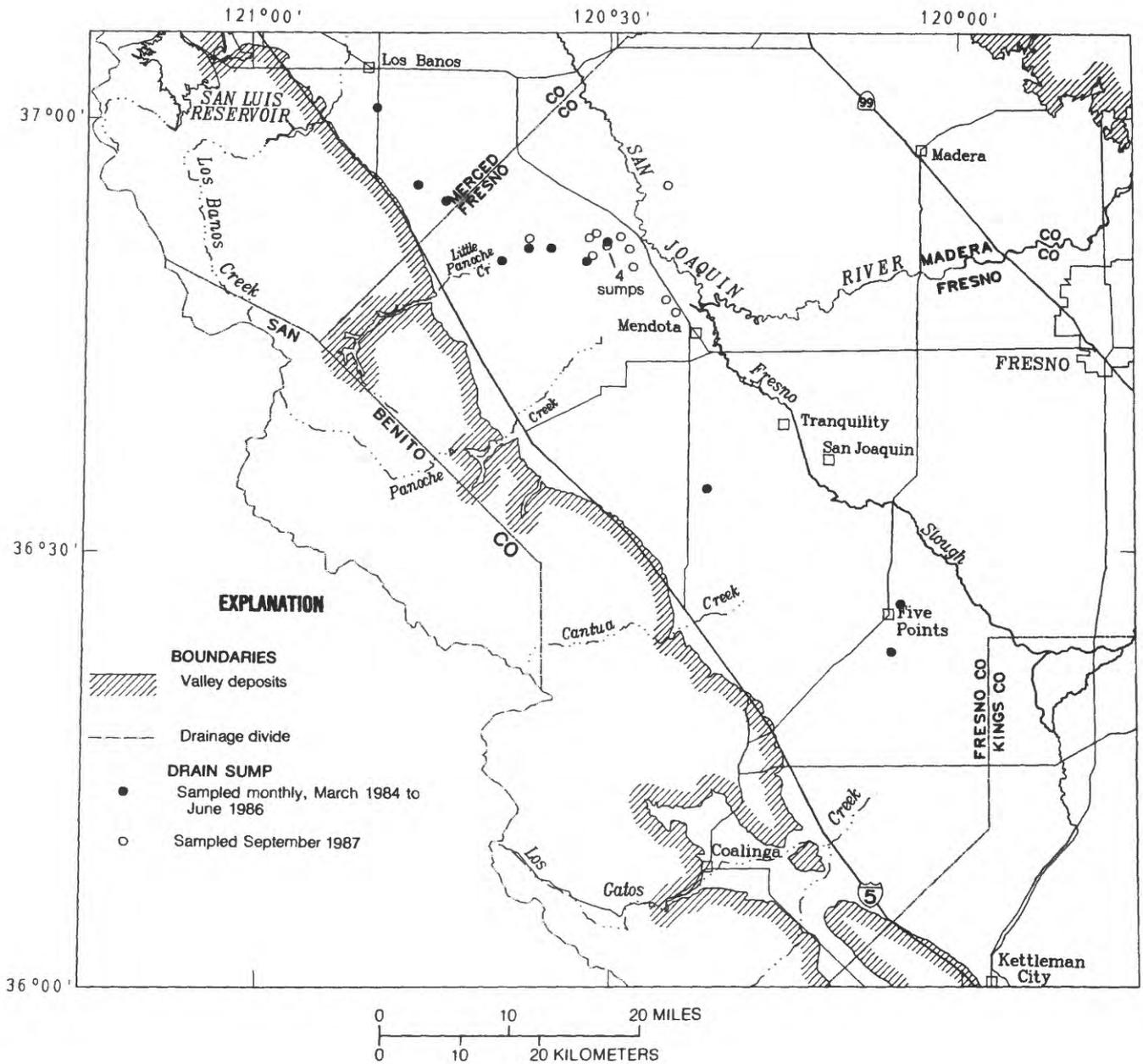


FIGURE 51.— Location of drain sumps where the chemistry of drain water was monitored by U.S. Bureau of Reclamation.

sumps were even lower, ranging from 0.07 to 0.35, with a mean of only 0.16. This is less than one-half the value of 0.41 for selenium. Wichlens and Nelson (1987) reported similar results for 20 drain sumps in the Broadview Water District. Their data indicated coefficients of variation for specific conductance from 0.12 to 0.21.

Selenium and salinity are correlated to varying degrees in drain water from the 11 individual sumps. Values of r^2 for linear-regression models of the relation between selenium and specific conductance in water from individual

sumps range from 0.00 to 0.92. In the four sumps with the narrowest range of salinity--those with coefficients of variation less than 0.10--the correlations were not significant ($\alpha=0.05$) simply because of the low overall variance. Selenium and specific conductance were significantly correlated in drain water from the remaining seven sumps, with values of r^2 ranging from 0.33 to 0.92 after extreme outliers were removed from the data. Thus, for drainage systems with appreciable variability in the salinity of drain water, salinity explains most of the variance in selenium concentrations. For all sumps combined, the 11 pairs of median selenium concentration and median specific conductance were significantly correlated, with a value for r^2 of 0.81. Removal of two data pairs with median specific conductance greater than 10,000 $\mu\text{S}/\text{cm}$ still resulted in an r^2 value of 0.78.

When water from many individual drainage systems over a large area is combined, the relative variability of concentrations over time is reduced in the combined drain water compared to an individual system. Water that was discharged to the San Luis Drain from a combination of regional drain tiles and on-farm drainage systems in a 42,000-acre part of the study area is one example of this effect on variability. The median selenium concentration and specific conductance of San Luis Drain water from March 1984 to June 1985 were 330 $\mu\text{g}/\text{L}$ and 12,100 $\mu\text{S}/\text{cm}$, respectively. The coefficient of variation was 0.19 for selenium and 0.10 for specific conductance, indicating substantially lower variability than in drain water from individual drainage systems. Even with such low variability, selenium concentrations were significantly correlated ($\alpha=0.05$) with specific conductance ($r^2=0.32$).

Only limited data are available to characterize long-term trends in drain-water concentrations. Reliable selenium data are not available for periods prior to spring of 1984. Based on the correlation between selenium and salinity, general conclusions can be inferred from historical data on drain-water salinity. Pillsbury and others (1965) assessed the salinity of drain water from 15 drainage systems during 12 years of operation. The general pattern observed was that the first 1 to 5 years of drainage-system operation yielded drain water of particularly high salinity, with considerable variation between systems. This variation probably resulted from the initial removal of the most saline shallow ground water near the drain tiles. The salinity of drain water during the next several years was lower, much less variable, and showed no clear trend over time.

Data suitable for assessing seasonal patterns also are sparse. Available data indicate variable seasonal patterns for individual drainage systems, chiefly related to seasonal variations in the flow of drain water resulting from irrigation patterns. Figure 52, which was adapted from Wichlens and Nelson (1987), shows dissolved solids in drain water in relation to drain-water flow for a 2-year period for one drainage system. Combined data for the 11 drainage systems show no seasonal pattern common to all systems. Figure 53 shows standardized selenium concentrations (concentration in each sample was divided by the mean for the system) for all 11 drainage systems. The lack of clear and general seasonal patterns in drain-water salinity or selenium concentrations, despite distinct seasonal patterns in irrigation and drain flow, underscores the fact that drains collect ground water, which tends to be of relatively constant character over time at a particular location.

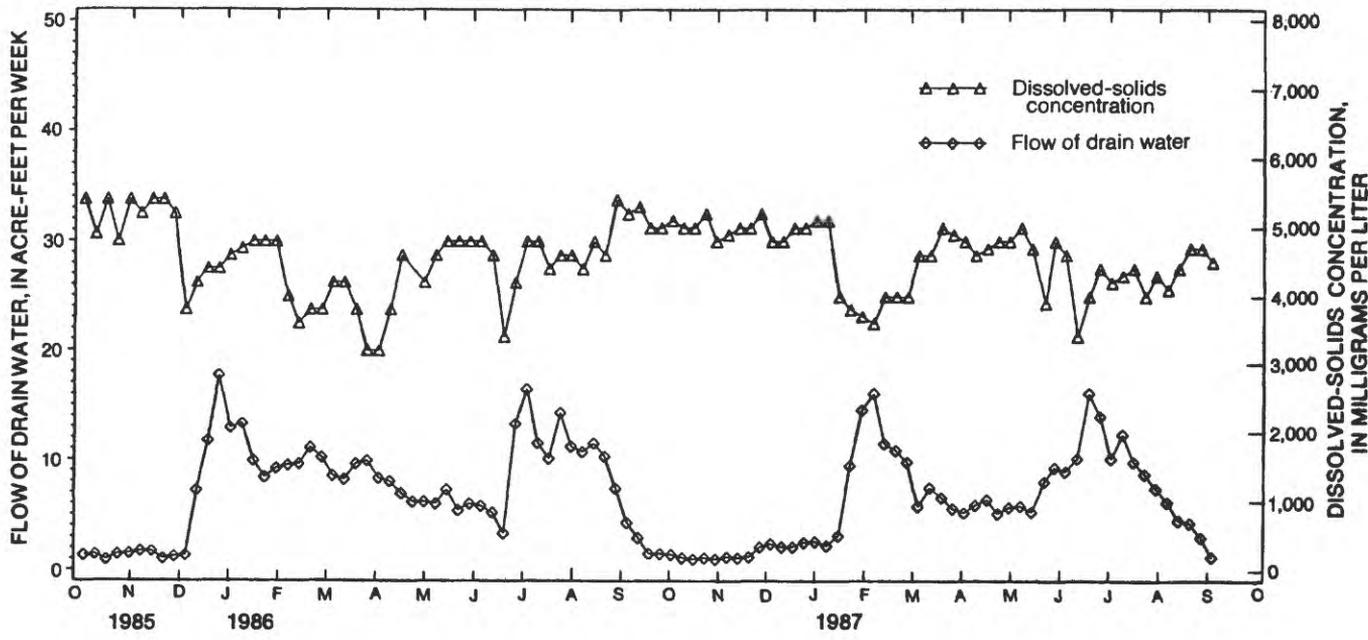


FIGURE 52.— Drain-water flow and dissolved solids for a drain sump in Broadview Water District, October 1985 to October 1987. (Adapted from Wichlens and Nelson, 1987.)

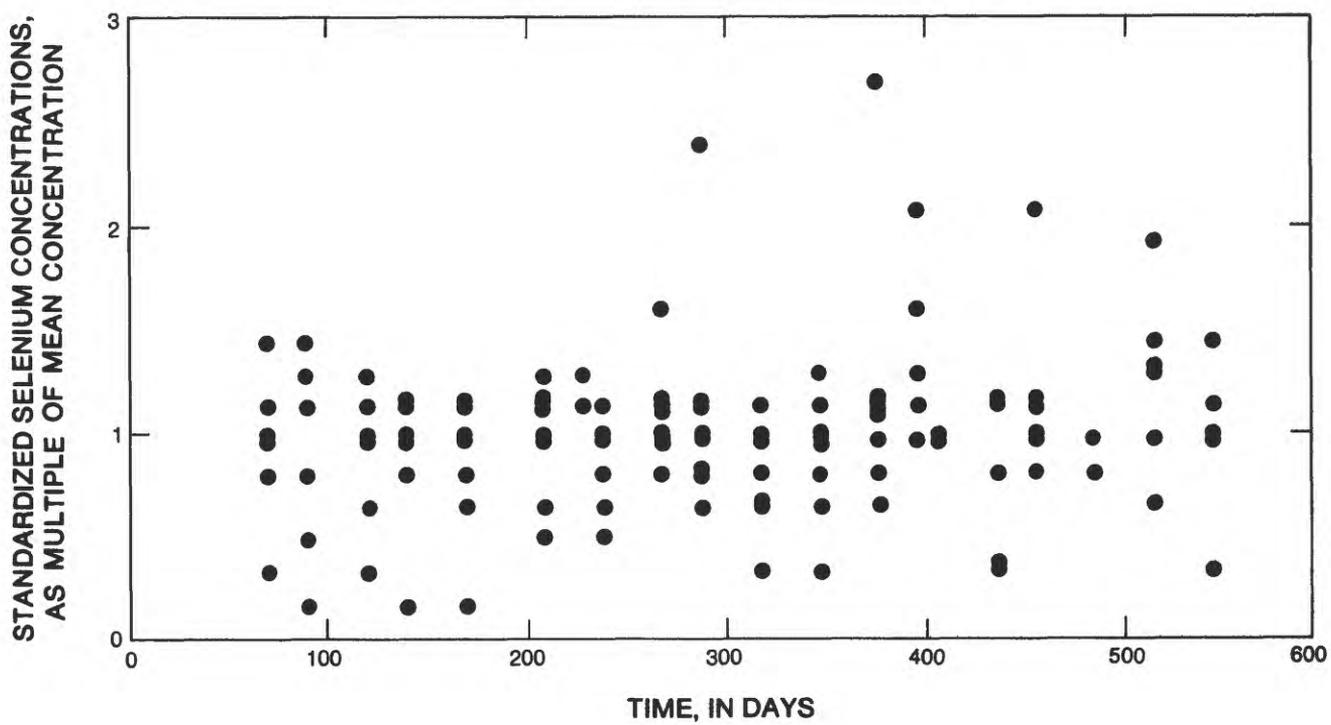


FIGURE 53.— Standardized selenium concentrations for samples of drain water collected approximately once each month from 11 drainage systems, March 1984 to June 1986. The concentration in each sample was divided by the mean concentration measured in water from the drainage system.

The relatively low temporal variability in concentrations of selenium in drain water after the first few years of system operation make estimation of the present and near-future selenium concentration for an existing drainage system possible from only a few direct measurements. On the average, a single measurement of the selenium concentration in drain water will be within 50 percent of the annual mean for about 70 percent of drainage systems. In general, four measurements taken quarterly during a year would reduce this uncertainty in half. In addition, the correlation between specific conductance and selenium is evident in all sumps with drain water that has variable salinity (coefficient of variation for specific conductance greater than 0.10). Thus, field measurements of specific conductance are an easy and effective way to detect potential changes in selenium concentration.

Estimation of Selenium Concentrations in Water from Future Drainage Systems

A key need of water managers and landowners is to estimate selenium concentrations that are likely to occur in drain water from new drainage systems if they are installed to alleviate shallow ground-water problems in presently undrained areas. The high areal variability of salinity and selenium concentrations of soil and ground water in Coast Range alluvial sediments, combined with the variable depth distribution of concentrations, make it very difficult to estimate selenium concentrations in water from future drainage systems. One way to estimate the selenium concentrations in water from a future drainage system is to use the selenium concentration estimate for shallow ground water from the statistical model used to map the distribution of selenium concentrations in shallow ground water (fig. 39). This approach was tested using data from 24 drainage systems in Coast Range sediments that were sampled by the U.S. Bureau of Reclamation. The 24 systems include the 11 drainage systems that were sampled monthly from March 1984 to June 1986, and 13 additional systems that were sampled once during 1987 (fig. 51). A comparison of measured selenium concentrations in drain water to selenium concentrations estimated for the same sites from observation-well data is shown in figure 54. The two are not significantly correlated ($\alpha=0.05$), indicating the absence of a useful predictive relation.

Data for 23 of the same 24 drainage systems, for which installation dates were available, indicate that the age of the drainage system explains 29 percent of the variance between systems in selenium concentration (fig. 55). This is partly due to the high selenium concentrations that often occur in drain water during the first few years of operation. Because each of the 23 drainage systems had different, but unknown, initial conditions, detailed interpretation of the apparent pattern is not warranted. The general indication is that, after the first few years, selenium concentrations in drain water may have gradually declined. Of the 14 drainage systems more than 20 years old, selenium concentrations in drain water from 7 of them still have selenium concentrations of 140 to 800 $\mu\text{g/L}$, and drain water from the other 7 systems have concentrations less than 50 $\mu\text{g/L}$. At present, it cannot be determined into which of these two general groups a new drainage system may fall after 20 years of operation.

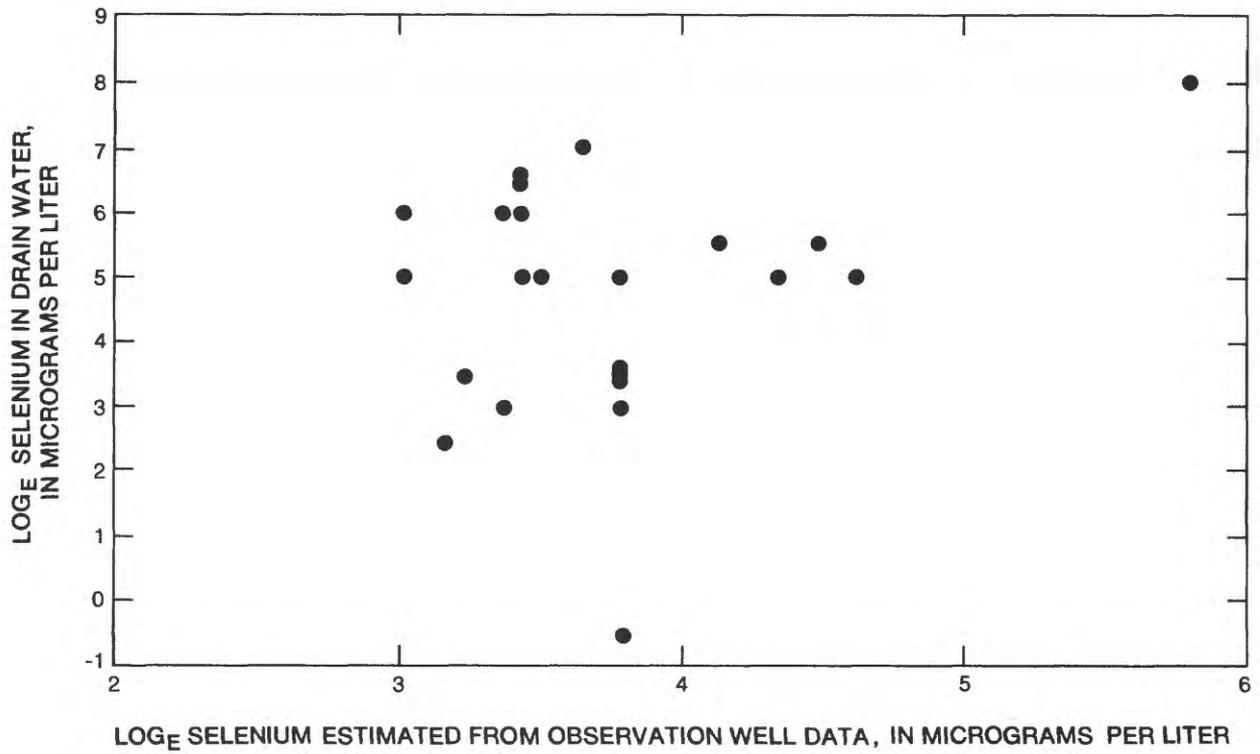


FIGURE 54.— Comparison of measured selenium concentrations in drain water to concentrations estimated from observation well data.

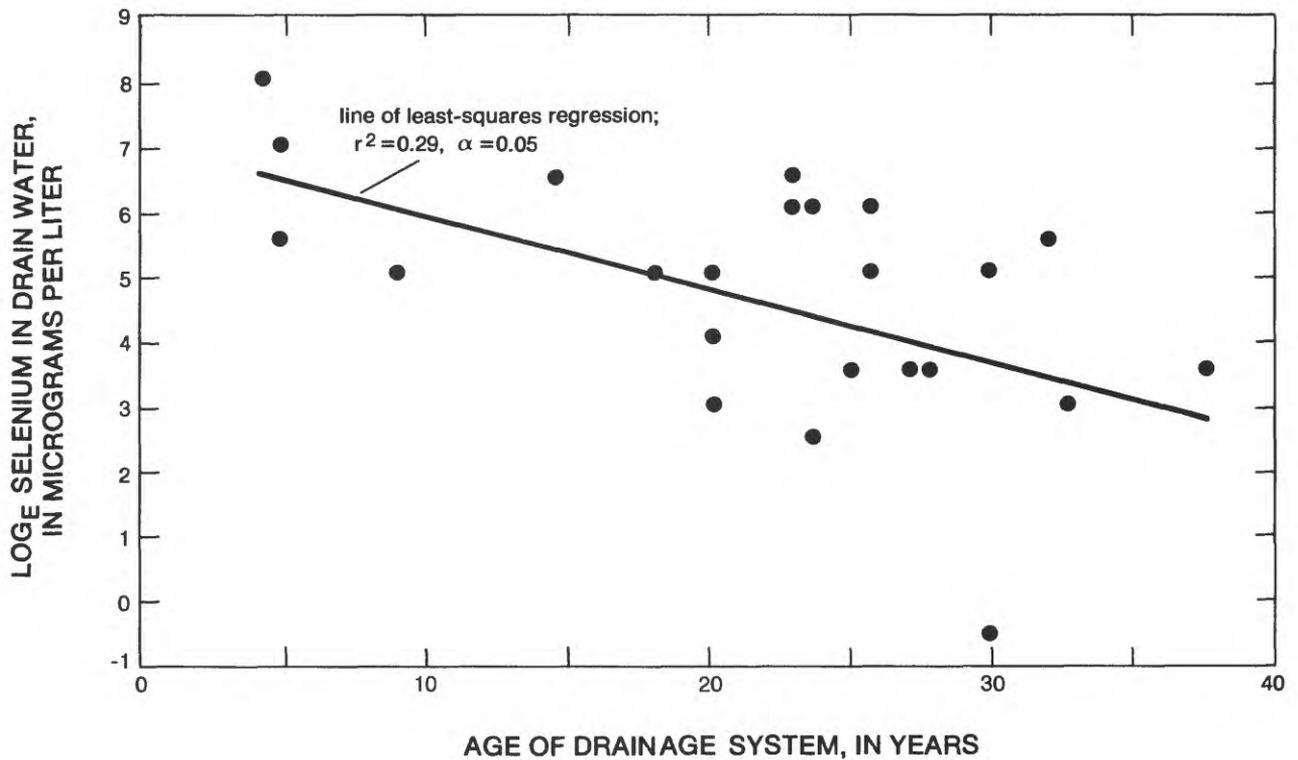


FIGURE 55.— Relation between selenium concentrations in drain water and ages of drainage system.

Two factors that contribute to the high degree of uncertainty in estimating selenium concentrations for future drainage systems are high areal variability and the complex manner in which ground-water flow induced by drainage systems moves selenium in ground water into drain tiles from different depths. The highest selenium concentrations in ground water occur at varying depths in areas that may require drainage in the future. Depending on the design of the drainage system and the local geohydrologic conditions, contributions of ground water from different depths may be dominant in different locations. The interaction of these factors is illustrated by results of studies in progress at two individual agricultural fields.

Interaction of Drainage Systems with Shallow Ground Water in Two Fields

Studies of the interaction of drainage systems with shallow ground water in individual agricultural fields help to explain the unpredictability of selenium concentrations in drain water from a regional assessment of concentrations in shallow ground water. Initial studies of three agricultural fields (fig. 56) drained for 1 year (1-year field), 6 years (6-year field), and 15 years (15-year field), indicated that changes in selenium concentrations in agricultural drain water over time are dependent on the process of slow displacement of high-selenium ground water to drain laterals (Deverel and Fujii, 1988). The highest selenium concentrations were the result of evapotranspiration of shallow ground water that occurred prior to installation of drainage systems. Subsequent investigation at the 1 and 15-year fields demonstrated that this partially evaporated water with high selenium concentrations has been displaced furthest along flow paths to the drain laterals in the field drained for 15 years. In the field drained for only 1 year, little displacement has taken place.

These processes are being investigated in greater detail at two fields--the 15-year field and a fourth field called the Murietta field (fig. 56). The investigations at these fields include (1) rates and direction of ground-water flow, (2) temporal variability of selenium concentrations in drain laterals, and (3) drain-water chemistry in relation to ground-water chemistry. Preliminary results illustrate the complexity and variability of field-scale conditions.

15-Year Field

The 15-year field has been irrigated since about 1952 with surface water, and with ground water from 1940 to 1952. The field has been drained for about 19 years and the selenium concentration in the drain water was about 400 $\mu\text{g/L}$ in 1985. Figure 57 shows a schematic of part of the drainage system in the 15-year field. Observation wells ranging from 10 to 50 feet deep were installed at several locations (Deverel and Fujii, 1988), including three cluster sites along or near section A-A', which is perpendicular to the drain laterals and approximately aligned with flow to the drains.

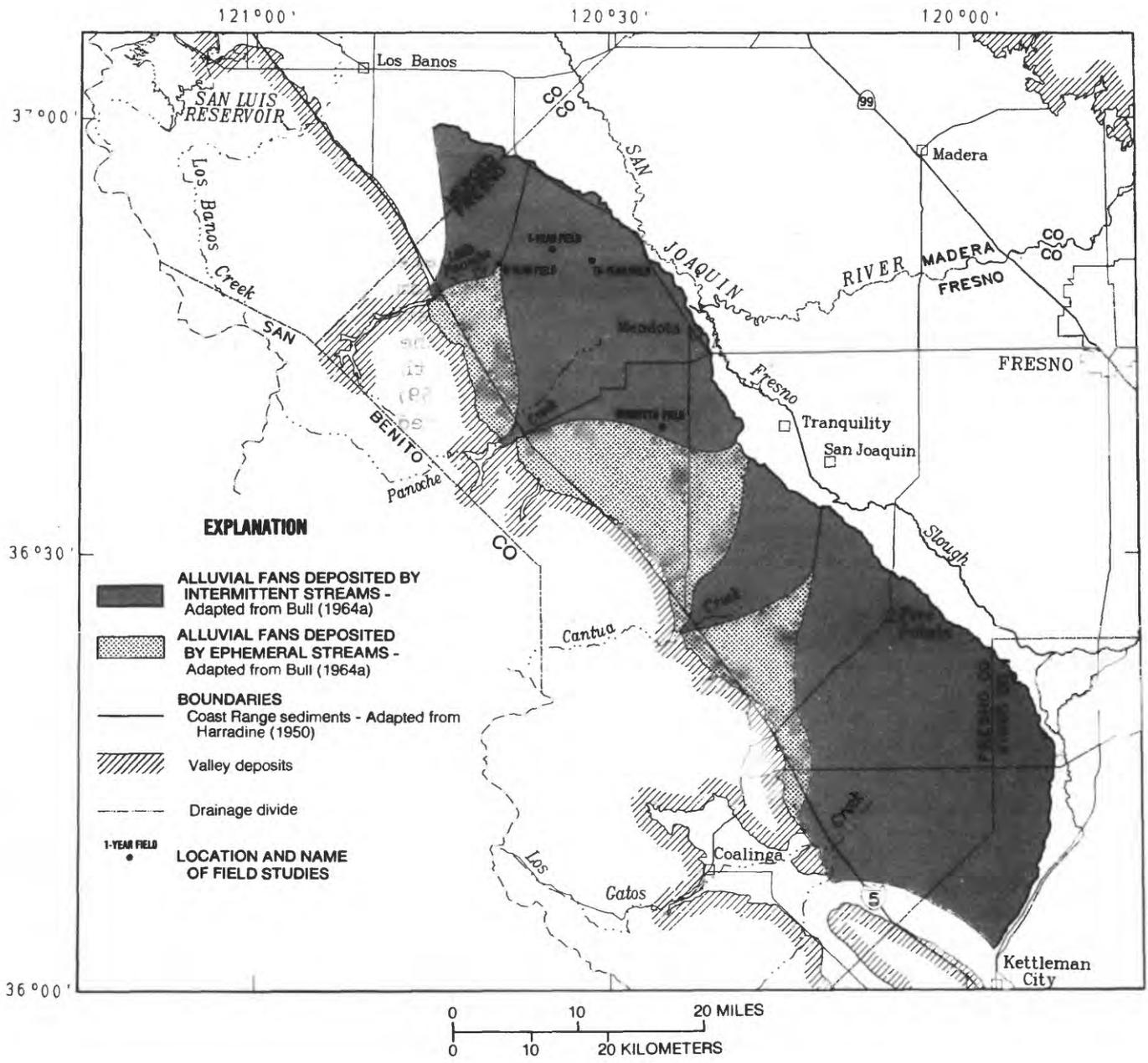


FIGURE 56.— Locations of agricultural fields where intensive soil and groundwater studies have been conducted.

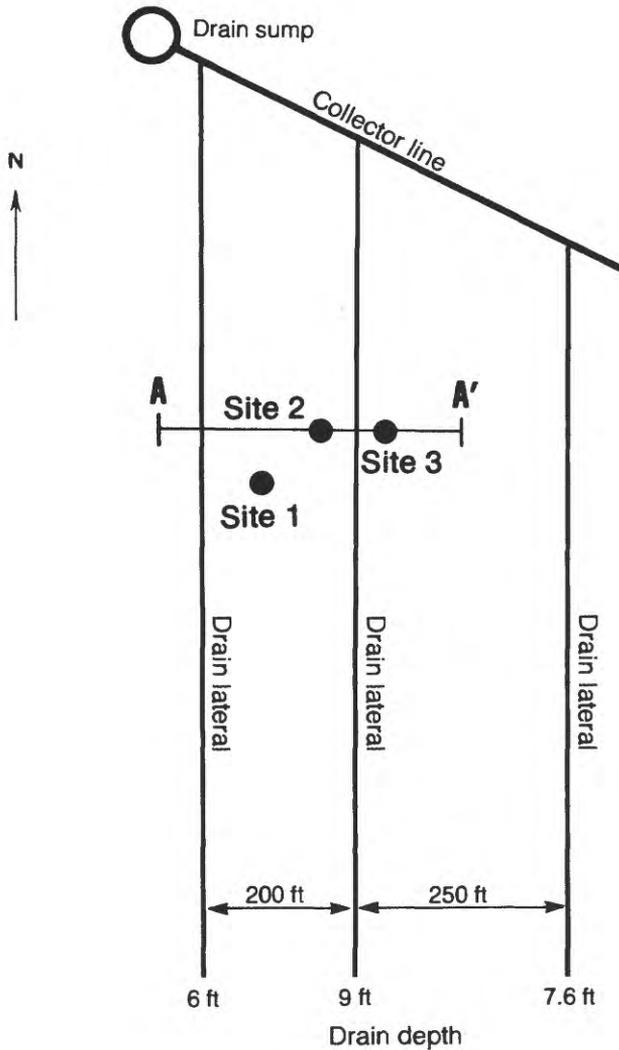


FIGURE 57.— Drainage system for the 15-year field showing sites of observation wells and location of A-A' geohydrologic section.

Figure 58 shows the isotopic composition of all samples collected in the 15-year field. Two distinct isotopic compositions are apparent. Samples of ground water collected within about 20 feet of land surface (group 1) plot on a line with a slope similar to the global meteoric water line and are not significantly evaporated. Tritium data for samples from the 10- and 20-foot depths at cluster sites 1 and 2 indicate that they are mainly composed of water that infiltrated after 1952 (fig. 59). Samples of ground water collected from more than 20 feet below land surface, and next to or immediately below the central drain lateral, plot farthest from the meteoric water line on an evaporative trend line (group 2), indicating partial evaporation. These water samples generally have low to moderate, but usually detectable tritium, and probably represent mixtures of irrigation water that infiltrated before and after 1952 (fig. 59). The group 2 water probably was near the land surface during early irrigation and before drains were installed. This water contains soluble salts leached from the soil during early irrigation, which were then concentrated because of evapotranspiration.

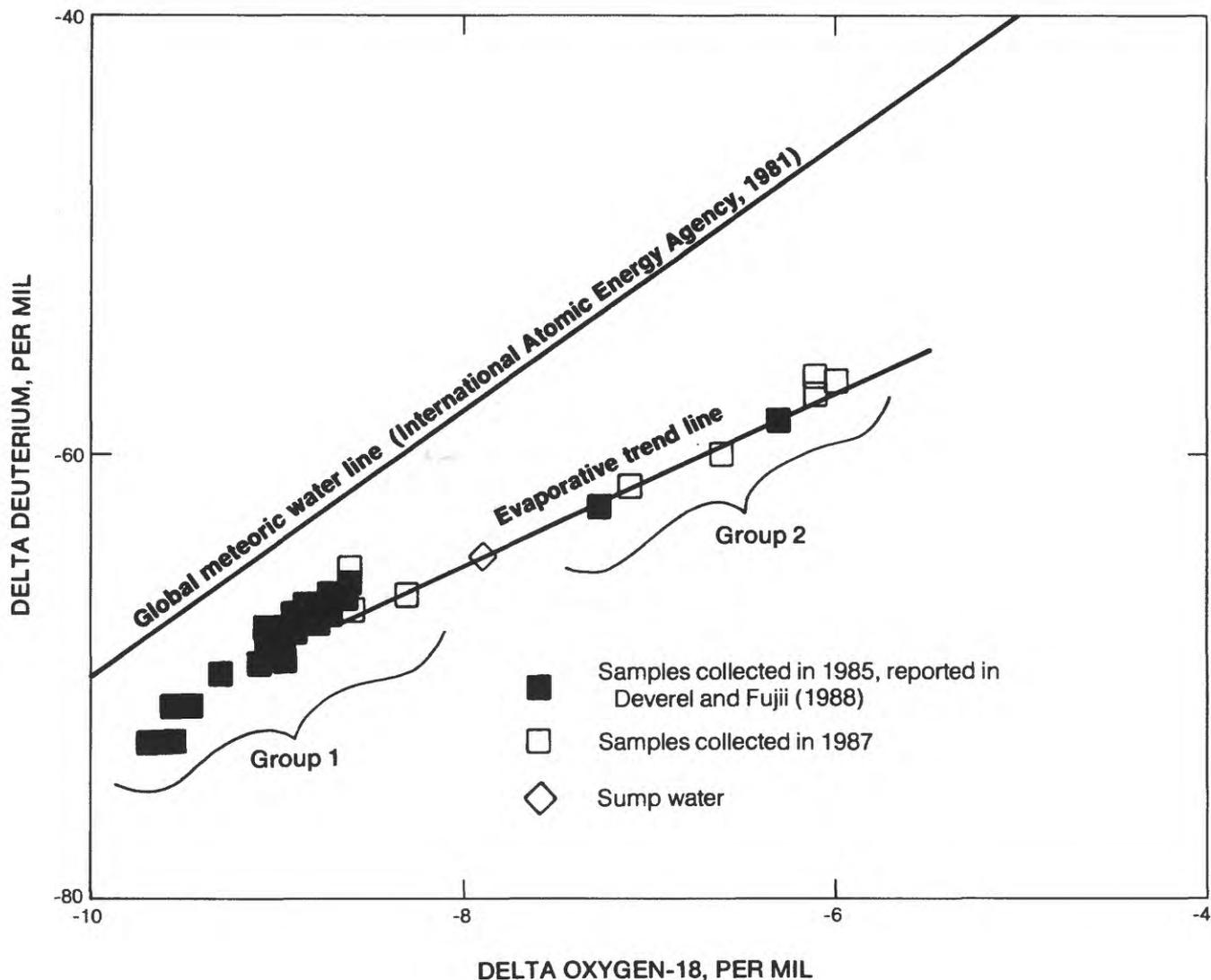


FIGURE 58.— Isotopic composition of samples of ground water from the 15-year field.

A few water samples from the field are intermediate in isotopic composition between the old, partially evaporated water (group 2) and the more recently recharged water closer to the land surface (group 1). The drain-sump sample (fig. 58) is a mixture of the two isotopic compositions (groups 1 and 2), and contains between 30 and 40 percent of the older partially evaporated water. The isotopic composition of the drain-sump water varies less than 10 percent over time, indicating that this proportional relation is relatively consistent.

Figure 59 shows results of a simulation of the approximate flow paths and traveltimes for infiltrating irrigation water entering the saturated zone at various points along section A-A'. The flow paths and traveltimes were obtained from simulation results using the U.S. Geological Survey three-dimensional ground-water flow model. The model uses a finite-difference approximation to the ground-water flow equation and solves for hydraulic head (McDonald and Harbaugh, 1984). The resulting head distribution was used to estimate flow paths, and traveltimes along flow paths were determined with the ground-water flow distribution calculated from head values of adjacent finite-difference cells.

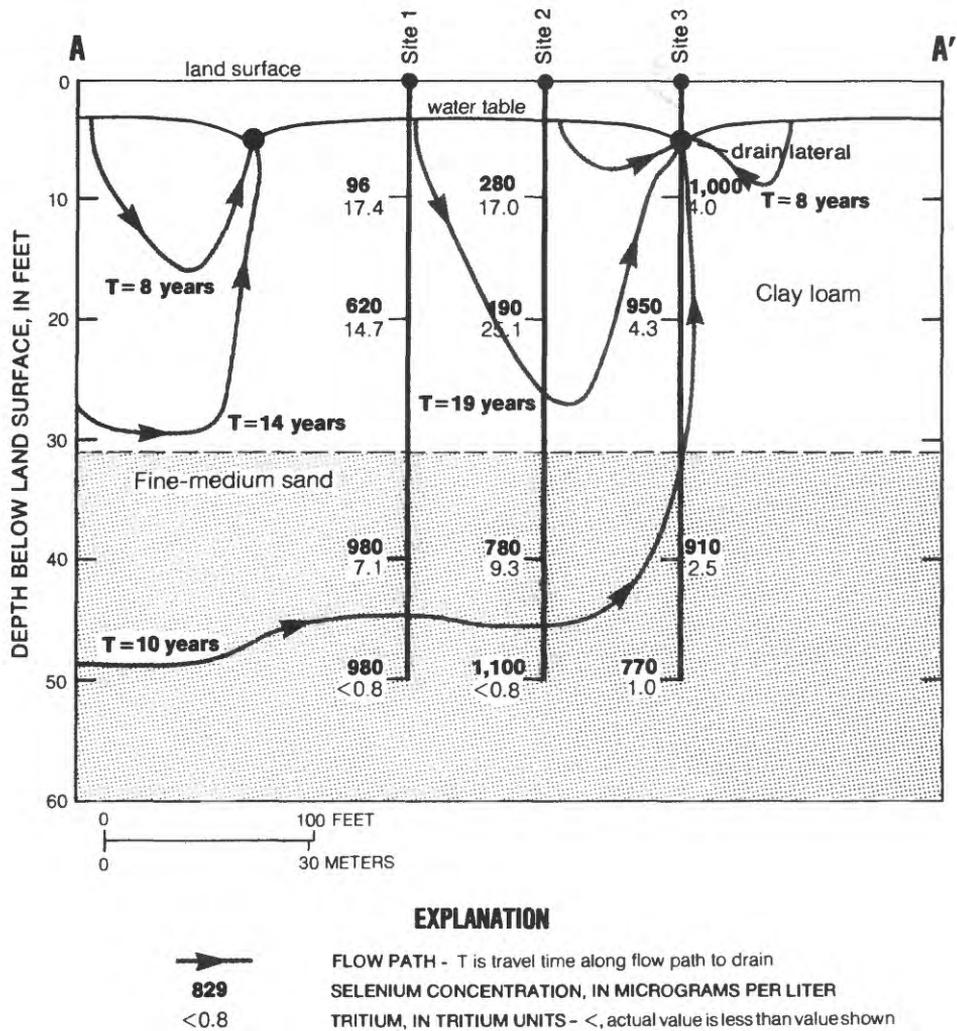


FIGURE 59. — Selenium and tritium concentrations, and simulated ground-water flow paths along geohydrologic section A-A' in the 15-year field. Sites indicate locations of observation wells along the section; site 1 is projected on to the section from 100 feet to the south.

The present-day distribution of selenium in relation to stable isotopes and tritium in ground water of the 15-year field, combined with evidence that the water table has always been within several feet of the land surface, indicate the likely hydrologic and geochemical influences on selenium concentrations. Water with very low and less than detectable tritium concentrations that occurs at about 50 feet below the land surface (fig. 59) probably originated as irrigation water withdrawn from wells prior to 1952. This water, which has since moved downwards because of downward gradients in the regional flow system and the continuing additions of irrigation recharge, was concentrated by evapotranspiration when it was near the land surface. At about 40 feet below land surface is water with a similar evaporative history, but higher tritium concentrations, indicating the presence of irrigation water recharged after 1952. At 40 and 50 feet below land surface, selenium concentrations are between 500 and 1,000 $\mu\text{g/L}$, the highest concentrations measured in ground water of this field. Ground water similar to that which occurs at 40 and 50 feet extends upward toward the drain lateral because of its movement into the drain (fig. 59).

Water in the upper 20 feet of the saturated zone has high tritium concentrations and lower selenium concentrations, and has been subjected to little evaporative enrichment. This shallowest water is mainly irrigation water applied since 1952, and primarily after drains were installed in about 1970. The drains keep the water table several feet below the land surface so that evapotranspiration of ground water is minimized. The nature of the flow system is such that more dilute recent water gradually will become a greater proportion of drain flow, but deeper ground water occurring in the sand zone provides a long-term source of water with high selenium concentrations.

Murietta Field

The Murietta field has been irrigated about the same length of time as the 15-year field--about 45 years--but ground water was used for irrigation until 1970 at the Murietta field, compared to 1952 at the 15-year field. The Murietta field has been drained for about 9 years and the concentration of selenium in drain water is 800 to 1,000 $\mu\text{g/L}$. In 1952, the water table at the Murietta field was about 40 feet below land surface, but by 1970 had risen to less than 10 feet from the land surface. This hydrologic history has resulted in a much different evaporative history than that which occurred at the 15-year field. Figure 60 shows a schematic of the drainage system in the Murietta field. Drain laterals in the Murietta field are farther apart than in the 15-year field, with lateral spacing of 380 feet compared to 150 to 200 feet. Observation wells ranging in depth from 10 to 50 feet (as at the 15-year field) were installed at 24 cluster sites along transects perpendicular to drain laterals in the Murietta field, including 7 locations along section A-A' in figure 60.

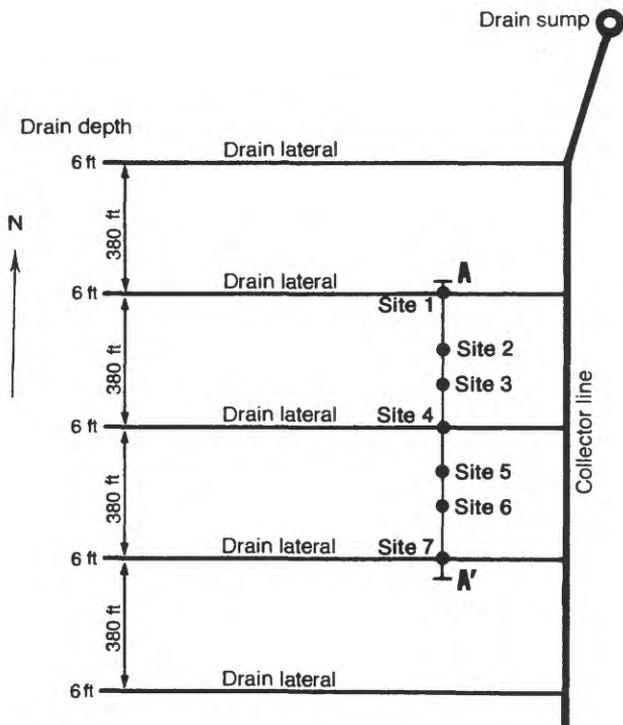


FIGURE 60. — Drainage system for the Murietta field showing sites of observation wells and location of A-A' geohydrologic section.

The results of analyses of samples collected from various depths for oxygen and hydrogen stable isotopes indicate the processes that have occurred in this field since the onset of irrigation. Samples collected from wells perforated at 20 and 30 feet below land surface are the most evaporated (fig. 61). Data for sites along section A-A' show that the highest selenium concentrations (1,200 to 7,300 $\mu\text{g/L}$) occur at these depths and tritium concentrations are low or undetectable (fig. 62). Samples from wells at the 10-foot depth are less evaporated (fig. 61) and, as shown in figure 62, have lower selenium concentrations (320 to 2,700 $\mu\text{g/L}$) than at the 20- to 30-foot depths. This shallower water, which has higher tritium concentrations, has displaced the more enriched underlying water since the mid-1970's when the area had a water table within about 3 feet of land surface. The water table has fluctuated between 5 and 10 feet of land surface since drains were installed in 1980.

Samples collected from wells at a depth of 40 feet are similar in composition of stable isotopes to the samples collected in wells at a depth of 10 feet, but tritium is undetectable. The water at 40 feet probably is water that was applied at land surface more than 25 years ago when the water table was far below the land surface. The lower selenium concentrations in this ground water (800 to 1,452 $\mu\text{g/L}$), compared to the water at 20 and 30 feet below land surface, probably are the result of leaching of soluble selenium from the unsaturated zone when the Murietta field was initially irrigated with ground water, but before a shallow water table resulted in further evaporative concentration. The local well water used to irrigate the Murietta Field until 1970 has less than 10 $\mu\text{g/L}$ of selenium.

In contrast to the 15-year field, drains in the Murietta field collect very little of the ground water that contains the highest selenium concentrations. The highest selenium concentrations occur in the range of 20 to 30 feet below land surface, and hydraulic data collected thus far indicate that the drain laterals affect the hydraulic gradients only within about 20 feet of each lateral. Directions of ground-water flow perpendicular to drain laterals were estimated from data collected during the irrigation season in wells installed along section A-A' (fig. 62). Coarse-grained deposits at depths of 15 to 30 feet below land surface seem to capture flow from above and below and may transport ground water to the east or to regional collector drains. Future work will quantify rates and directions of ground-water flow in this field by numerical simulation.

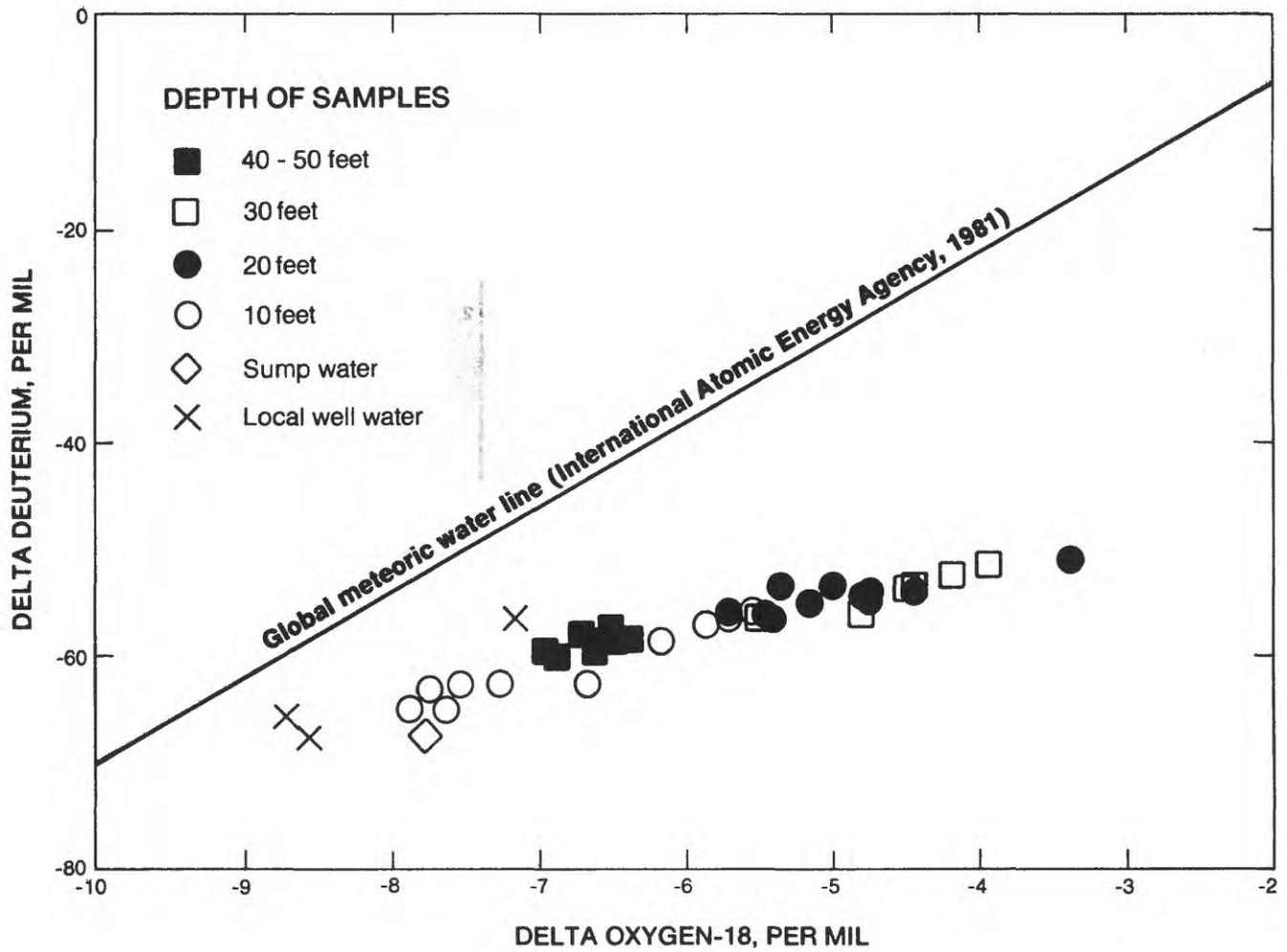
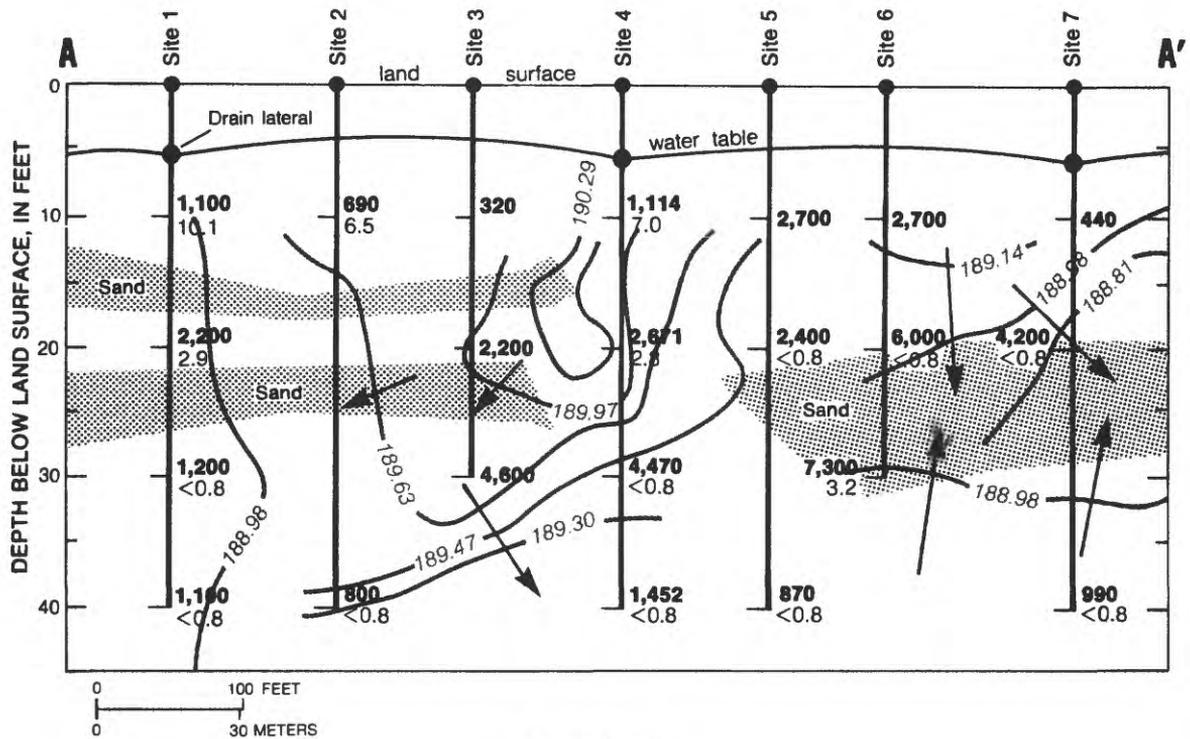


FIGURE 61.— Isotopic composition of samples of ground water from the Murietta field.



EXPLANATION

- 320** SELENIUM CONCENTRATION, IN MICROGRAMS PER LITER
- <0.8** TRITIUM CONCENTRATION, IN TRITIUM UNITS - <, actual value is less than value shown
- 189.30—** LINE OF EQUAL HYDRAULIC POTENTIAL, IN FEET
- ←** DIRECTION OF GROUND WATER MOVEMENT

FIGURE 62. — Selenium and tritium concentrations, and directions of ground-water flow along geohydrologic section A-A' in the Murietta field. Sites indicate locations of observation wells along the section.

MOBILITY OF SOIL SELENIUM

by *Roger Fujii*

Soils may be a long-term source of selenium even after the most mobile forms have been leached. Although there is evidence for some locations that recent irrigation has contributed water containing lower concentrations of selenium to the ground water than in the past, these concentrations remain at undesirably high levels. In order to determine the magnitude and longevity of future contributions of selenium from soil, the amount and character of soluble forms that are still present in the soil need to be assessed.

Distribution of Soluble and Total Selenium in Unsaturated Soils

Processes affecting the distribution of selenium in shallow ground water and soils of agricultural fields located on the lower alluvial fan of Panoche Creek were studied by Deverel and Fujii (1988), Fujii and Deverel (in press), and Fujii and others (1988). Three of the fields studied are the 1-year, 15-year, and the Murietta fields, which were discussed in the previous section on drain-water selenium concentrations. The 1-year and 15-year fields are within about 5 miles of each other, had been drained for about 1 and 15 years, had been irrigated for about 45 years, and had drain-water selenium concentrations of about 4,000 and 400 $\mu\text{g/L}$, respectively, in 1985. The Murietta field, on the southern margin of the Panoche Creek fan, had been drained about 7 years, irrigated for about 45 years, and had a drain-water selenium concentration of about 1,000 $\mu\text{g/L}$.

Soil samples were collected in 12-inch increments from the land surface to below the water table during the augering of boreholes along transects perpendicular to the drain laterals in each field. Figure 63 shows median concentrations of total and soluble selenium for the unsaturated soils from the three fields. Soluble selenium was determined from saturation extracts. Saturation extracts were prepared by saturating soil samples to about 50 percent moisture with distilled water, waiting 16 to 20 hours, extracting the moisture, and then filtering through a 0.45- μm filter. Water contents of the saturated soil samples, prior to extraction, are near the top of the range of moisture contents measured in saturated field soils (30 to 50 percent). Selenium concentrations in the saturation extracts probably are an estimate of the minimum concentration expected under field conditions when infiltrating water passes through that soil. The mass of selenium in the extract solution, divided by the total mass of selenium in the soil sample, is an estimate of the proportion of soil selenium in readily soluble forms.

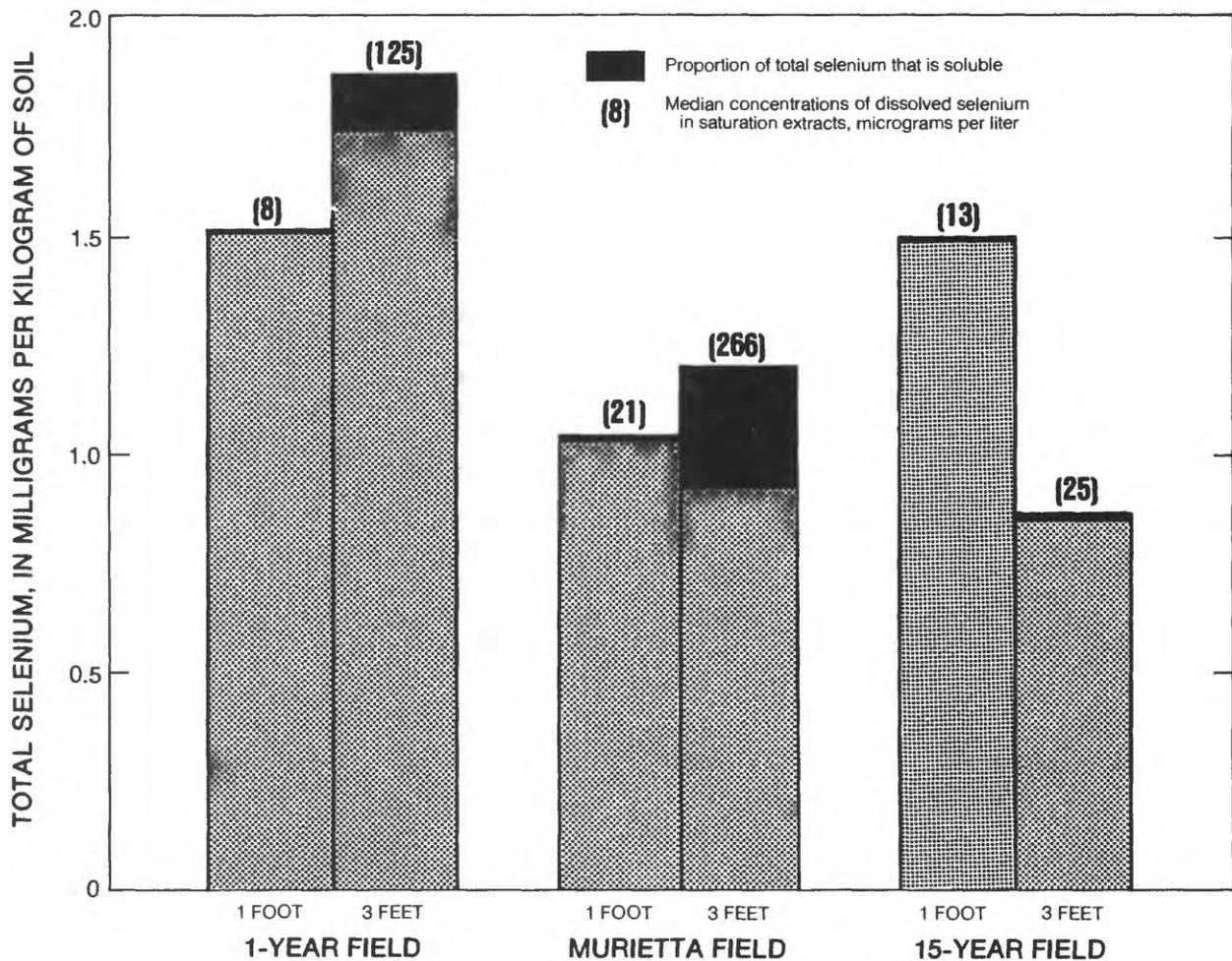


FIGURE 63.— Concentrations of total and soluble selenium in unsaturated soils of three fields.

Soluble selenium comprised less than 5 percent of the total selenium in soil at the 1-foot depth in all three fields (fig. 63). Similar results for soils from the Panoche Creek alluvial fan have been reported by Amundson and others (1987). They found that selenium extractable with 0.01 M potassium phosphate, which yields another type of estimate of readily mobile forms of selenium, comprised 1 and 2 percent of the total selenium concentrations in two Panoche soils. In the 15-year field, the proportion of soluble selenium was also relatively low at the 3-foot depth, but the 3-foot depth in the other fields had much greater quantities of soluble selenium. The greater quantities of soluble selenium in the lower unsaturated zone of the 1-year and Murietta fields indicate a greater potential for leaching of selenium to ground water with continued irrigation.

Factors Affecting the Mobility of Selenium in Unsaturated Soils

The distribution of soluble selenium in unsaturated soils of the three fields reflects the historical leaching of selenium by irrigation water. For each field, concentrations of dissolved selenium in saturation extracts of soil samples from the 1-foot depth were significantly ($\alpha=0.05$) lower than the concentrations at the 3-foot depth, indicating downward leaching of soluble soil selenium (fig. 63). Salinity, as measured by the specific conductance of saturation extracts, also was significantly higher at the 3-foot soil depth compared to the 1-foot depth, indicating similar leaching of all soluble salts. Much lower concentrations of selenium in saturation extracts for water samples from the 3-foot depth at the field drained for 15 years suggests that leaching has progressed further in this field than in the other two fields that have been drained for less time.

Relations between selenium and salinity in saturation extract solutions for the 15-year and 1-year fields indicate changes in the mechanisms of selenium release from soil as leaching progresses. In the less leached soils at the 3-foot depth, selenium in extract solutions is significantly ($\alpha=0.05$) correlated with specific conductance ($r^2=0.25$ and 0.40), indicating the dissolution of readily soluble salts that contain selenium. The lower correlation is for the 15-year field, which has less soluble selenium. In extracts from highly leached soils from the 1-foot depth at both fields, selenium is not significantly ($\alpha=0.05$) correlated with specific conductance, indicating that the dissolution of soluble salts may not be the primary mechanism for selenium release from these soils.

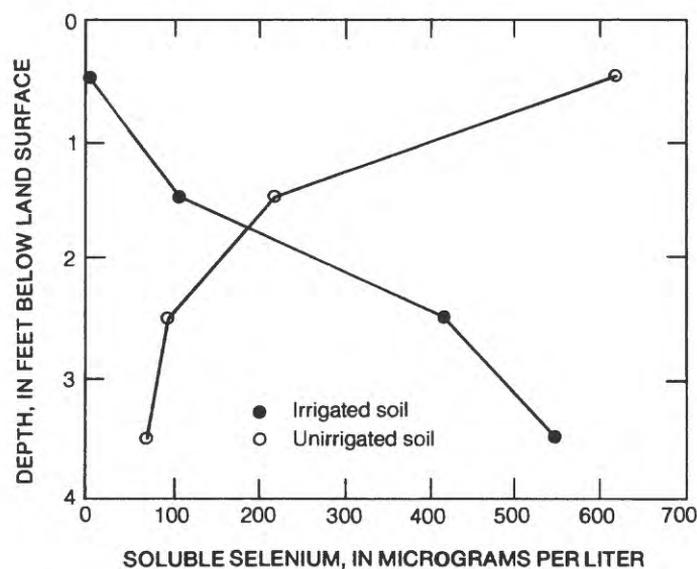


FIGURE 64.— Relation between selenium concentrations in saturation extracts and depth in an irrigated and an unirrigated soil.

Data for two unsaturated soil profiles, one from the Murietta field and one from an unirrigated site about 2 miles away, directly depict the contrast in the distribution of soluble selenium before irrigation and after 45 years of irrigation (fig. 64). Both sites are on Ciervo silty clay soil. The distribution of soluble selenium in the unirrigated soil profile shows the natural accumulation of soluble selenium in the upper part of the profile and the decrease in soluble selenium with depth. The reverse trend was found for the irrigated soil, reflecting the downward leaching of soluble selenium as a result of irrigation.

Soluble Selenium Species in Unsaturated Soils

For the same two soils, one irrigated for more than 40 years and one never irrigated, the selenate form of selenium was found to comprise more than 99 percent of the soluble selenium at all depths in both soils, except the highly leached surface soil at the Murietta field. Analytical methods are described in Fio and Fujii (1988). Similar results were found for four soil solutions obtained from the 2-, 3-, 4-, and 5-foot depths using porous ceramic-cup extractors at one site in the field drained for 15 years. These soil-solution samples were found to contain 29 to 49 $\mu\text{g/L}$ of dissolved selenium and, more than 96 percent was present as selenate. Selenate is expected to be the predominant soluble selenium species resulting from evaporative concentration of soluble salts under alkaline and oxidized conditions. These results also are consistent with the 98 percent selenate found in the shallow ground water in this area (Deverel and Millard, 1988).

In contrast, the leached surface soil from the Murietta field yielded only 7 $\mu\text{g/L}$ of selenium in the saturation extract, of which 57 percent was selenate, 29 percent selenite, and 14 percent organic selenium. The analytical method for organic selenium is described in Fio and Fujii (1988). Similar distributions of selenium species also have been found for highly leached soil samples from the 15-year field. The saturation extract for the surface soil from a soil profile in the 15-year field had a soluble selenium concentration of 16 $\mu\text{g/L}$, of which 78 percent was selenate and 22 percent was selenite. Soluble selenium concentrations in unsaturated soils below the surface soil at this site ranged from 21 to 40 $\mu\text{g/L}$, and more than 95 percent was present as selenate.

The substantial amount of selenite found in extracts of leached surface soils indicates that processes such as sorption reactions involving selenite, dissolution of soil minerals, and release of organic selenium may control the movement of selenium from unsaturated soils after the most soluble forms of selenium have been leached. Even though the total concentrations of soluble selenium released in saturation extracts and soil solutions of these highly leached soils are relatively low, 7 to 49 $\mu\text{g/L}$, they still represent a significant long-term management problem. For example, they are greater than the 4-day average criterion of 5 $\mu\text{g/L}$ for protection of freshwater aquatic life (U.S. Environmental Protection Agency, 1988).

Sorption of Selenite and Selenate

For unsaturated soils, sorption reactions probably control the transport of selenite but not selenate. Sorption of selenite is much greater than selenate on goethite (Leckie and others, 1980; Hayes and others, 1987; Balistriero and Chao, 1987) and on ferric oxide gel (Ryden and others, 1987). Selenite and phosphate were sorbed to similar extents on goethite (Balistriero and Chao, 1987) and on ferric oxide gel (Ryden and others, 1987), probably resulting from the ligand-exchange mechanism hypothesized for both constituents. Selenate and sulfate were shown to sorb to similar extents on ferric oxide gel (Ryden and others, 1987). These data are consistent with results of

Hayes and others (1987), which indicated that selenite forms a strongly bonded, inner-sphere complex at the goethite-water interface, similar to that formed by phosphate. In contrast, selenate forms a weakly bonded, outer-sphere complex, similar to that formed by sulfate.

Results reported for soils from the western San Joaquin Valley show that selenate does not adsorb to any appreciable extent (Sposito and others, 1987), especially from gypsum solutions containing high concentrations of sulfate (Burau and others, 1986, 1987; Fio, 1987). Shallow ground water in much of the western valley is saturated or supersaturated with gypsum (Deverel and Gallantine, 1988). In contrast, selenite has been shown to adsorb strongly on western valley soils and competes with phosphate for binding sites (Neal and others, 1987b). The adsorption of selenite on soil decreases with increasing pH. The relation between adsorption and pH varies among different soils below pH 6, but is similar for most soils above pH 6 (Sposito and others, 1987). These results support the hypothesis that selenite sorbs through a ligand exchange mechanism in these soils. The importance of phosphate competition with selenite for specific adsorption sites in these alkaline soils, which have a pH of about 8, is probably minimal because of the low solubility of phosphate under these conditions. Adsorption of selenite by these soils has been shown to be strong, even at pH 8 (Neal and others, 1987a; Burau and others, 1987; Fio, 1987). The high affinity of these soils for selenite greatly limits the mobility of this selenium species.

Adsorption and desorption of selenite in soils from the Panoche fan area have been shown to follow distinctly different isotherms (Burau and others, 1987; Fio, 1987), and this difference must be considered in any transport model of selenite in soils. Fio (1987) described the adsorption of selenite by a Freundlich model. Selenite desorption was modeled as a family of curves originating at the adsorption curve. Fio (1987) incorporated these models into a one-dimensional solute transport model (Grove and Stollenwerk, 1984). Simulation of selenite transport under saturated conditions showed strong retardation of selenite transport in soils such as these.

Estimation of Adsorbed Selenium

Estimation of adsorbed selenium is affected by the method used to determine this phase, and requires careful explanation. Fujii and others (1988) developed an extraction procedure to estimate adsorbed selenium. The method is based on the assumption that high concentrations of phosphate would exchange with adsorbed forms of selenium. The results discussed in the preceding section support this assumption since selenite probably is the predominant adsorbed selenium species and it sorbs by the same mechanism as phosphate. The method also required an initial extraction with potassium chloride in order to remove soluble and exchangeable calcium from the soil, and prevent precipitation of calcium phosphates of low solubility during the phosphate extraction. Development of this method is discussed in detail by Fujii and others (1988).

Estimates of adsorbed selenium for unsaturated soils from the 1-year and 15-year fields indicated that selenite comprised 46 to 88 percent of the extracted selenium; the remainder was selenate. Because selenate is not sorbed to a large extent, these results indicate possible dissolution of soil minerals

and release of selenate and possibly selenite. The mass of selenium extracted by phosphate represents less than 4 percent of the total selenium. Sorption reactions would most affect selenium retention and immobilization if conditions became slightly reducing and the selenite species became dominant. The presence of selenite in solutions from phosphate extractions under oxidized and alkaline conditions, when selenate predominance is expected, suggests disequilibrium and kinetic constraints on the transformation of selenite to selenate. Kinetic constraints on the oxidation of selenite may be a mechanism that limits the rate of release and mobilization of selenium in unsaturated soils.

Other Forms of Selenium in Soils

Most of the selenium in unsaturated soils is in solid phases that are less soluble than the soluble and adsorbed phases or is contained in soil organic matter. The relatively insoluble solid-phase selenium and the soil organic matter represent potential long-term sources of selenium to ground water.

Selective extraction techniques commonly used to identify solid-phase associations of trace metal cations in sediments and soils (Chao, 1984; and Tessier and others, 1979) are not readily applicable to redox-sensitive trace elements, such as selenium. Gruebel and others (1988) reported that selenium and arsenic associated with amorphous iron oxides are re-adsorbed onto other minerals after reductive dissolution, a method commonly used to evaluate trace-metal association with iron oxides (Chao and Zhou, 1983). They also reported that oxidants used to dissolve organic matter, such as hydrogen peroxide or sodium hypochlorite, oxidized selenite adsorbed on mineral surfaces to selenate, which was released to solution. Thus, if these selective extraction techniques are applied to soils and sediments, they may underestimate the mass of selenium and arsenic associated with amorphous iron oxides and overestimate the mass of selenium and arsenic associated with organic matter.

Bureau and others (1987) reported that selenium contained in soil organic matter was a substantial part of the total soil selenium. They extracted the soil organic matter with sodium hydroxide and sodium pyrophosphate. They further fractionated the extracted organic matter into humic acids and three fulvic acid fractions using liquid chromatography. The largest amount of selenium was found to be in the humic-acid fraction. The substantial amount of organic selenium represents a potential source of mobile selenium. Decomposition of soil organic matter by soil microbes can release soluble forms of selenium to the soil solution or may result in volatilization of selenium.

Soil microbes have been shown to affect the distribution of selenium species in the presence of added carbon sources. Selenium immobilization and volatilization by soil microbes has been reported by Frankenburger and others (1986, 1987) for soils from the Panoche and Cantua Creek alluvial fans. The laboratory results showed that volatilization of dimethylselenide was greatest under aerobic conditions, when a carbon source was added, and when the soil was amended with selenite. Frankenburger and others (1987) also applied artificial drain water spiked with selenite to a laboratory soil column and found reduction of selenite to elemental selenium by soil bacteria under aerobic conditions. Selenate, the predominant soluble species in unsaturated soils, was not removed under similar conditions.

SOURCES AND CONCENTRATIONS OF SELENIUM IN THE SAN JOAQUIN RIVER

by *Daphne G. Clifton and Robert J. Gilliom*

Drain water from about 77,000 acres of tile drained farmland eventually flows to the San Joaquin River, mainly through two tributaries, Salt and Mud Sloughs. Concentrations of selenium in water from individual drainage systems that discharge to waterways that eventually reach these sloughs or smaller tributaries ranged from less than 10 to 4,000 $\mu\text{g/L}$, with mixtures of these waters in larger collector drains ranging from 20 to 100 $\mu\text{g/L}$ (Deverel and others, 1984; Presser and Barnes, 1985). Future decisions concerning management of subsurface drain water in the area, and protection of the water quality of the San Joaquin River, depend on attaining a quantitative understanding of the concentrations, sources, and transport of selenium in the river.

Hydrology

Below its headwaters in the Sierra Nevada, the San Joaquin River flows 192 miles from Friant Dam, located in the foothills, to Vernalis, which is just upstream from tidal backwater influence of the Sacramento-San Joaquin Delta. River gradients are low, ranging from 3.2 ft/mi near Friant to 0.5 ft/mi near Vernalis. Within the first 65 miles between Friant Dam and Mendota, the river has intermittent streamflow and often no river water reaches Mendota Pool, near Mendota. In the next 67 miles between Mendota and Stevinson, the river also has intermittent streamflow, except for a several mile reach just downstream of Mendota, in which flow is perennial. Streamflow in the remaining 60 miles between Stevinson and Vernalis is perennial and increases downstream as tributaries and irrigation-return flows enter the river. Inflows to the river come from surface runoff and subsurface drain water from irrigated areas, ground water, and runoff from the Sierra Nevada.

The information presented herein focuses on data from 11 study sites on the perennial-flow part of the San Joaquin River and tributaries between Stevinson and Vernalis (fig. 65). Water that reaches the perennial-flow part of the San Joaquin River from the predominantly intermittent parts of the river upstream from Stevinson is monitored at the San Joaquin River near Stevinson (site 1). During low-flow conditions, most water reaching site 1 is irrigation-return flow, but during high-flow periods most of the water is Sierra Nevada runoff.

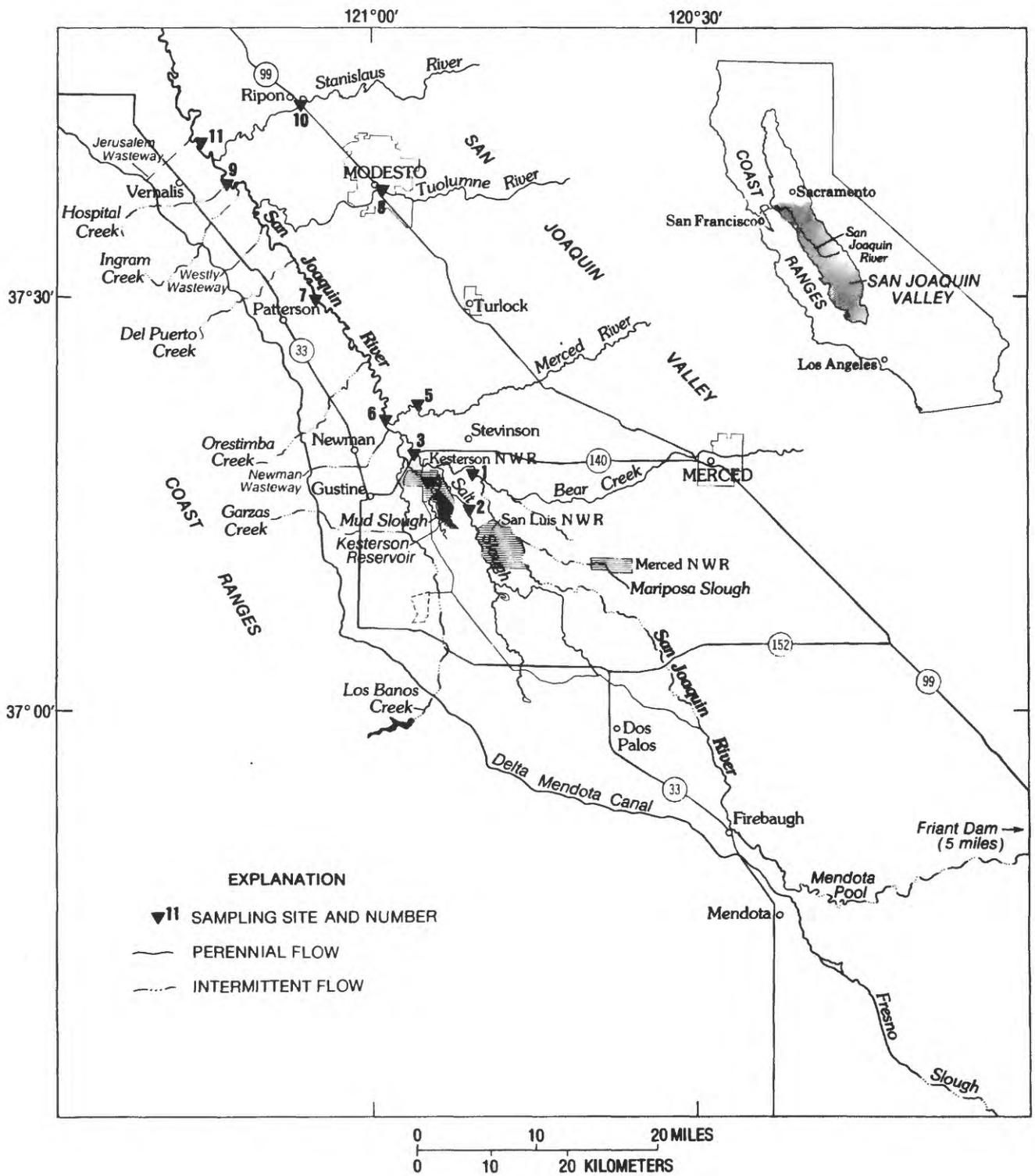


FIGURE 65.— Location of study sites on the San Joaquin River and its tributaries.

The first tributaries to enter the river downstream from Stevinson are Salt Slough (site 2) and Mud Slough (site 4), with a combined drainage area of 470 mi². One source of water in these sloughs is subsurface agricultural drain water, some of which is high in dissolved solids and selenium. The sloughs also receive irrigation-return flow and ground-water inflow. The sloughs are connected upstream to a network of water distribution and drain water collection canals so that some inflows can be alternately conveyed to one slough or the other.

The three major eastside tributaries that originate in the Sierra Nevada have a combined drainage area of about 3,860 mi² and account for most of the tributary inflow to the San Joaquin River (U.S. Geological Survey, 1987). These tributaries are the Merced River (site 5), the Tuolumne River (site 8) and the Stanislaus River (site 10). Twenty percent of the natural flow in these tributaries during high runoff years, and as much as 90 percent of the flow during low runoff years, is stored in reservoirs or diverted for irrigation. The lower reaches of these tributaries receive substantial quantities of irrigation-return flow.

Sites downstream from Stevinson on the lower San Joaquin River are distributed among the five main tributaries. Fremont Ford Bridge (site 3) is downstream of Salt Slough. Newman (site 6) is downstream from Mud Slough and the Merced River. Patterson (site 7) is downstream of Newman. Maze Road (site 9) is downstream of the Tuolumne River. Vernalis (site 11) is the site located farthest downstream and is downstream of the Stanislaus River and upstream from the tidal backwater influence of the delta.

Streamflow is a major factor determining the amount of a constituent transported through a river system. Daily mean streamflow at Vernalis during October 1985 to March 1987 shows three relatively distinct flow regimes (fig. 66). Low-flow periods occurred from October 1985 to mid-February 1986, and from mid-May 1986 through March 1987, during which daily mean streamflow was less than 10,000 ft³/s at Vernalis. These two periods are combined in subsequent analyses and discussed as the low-flow period. The high-flow period from mid-February to mid-May 1986 includes the rising waters of a major flood event and the recession to 10,000 ft³/s at Vernalis.

Monthly mean streamflows at Vernalis during the low-flow period prior to mid-February 1986 were in the 11th to 33d percentiles in relation to the long-term monthly means for 1975-87 (fig. 66). During the high-flow period, monthly mean streamflows were in the 76th to 89th percentiles relative to monthly mean streamflows for 1975-87. Although the initial peaks of the flood were in mid-February and March of 1986, the recession of the flood waters took several months. This prolonged recession resulted in greater than normal flows during mid-May through December 1986, partly because of continuing release of water from reservoirs in the Sierra Nevada. From January to April 1987, monthly mean streamflows were less than the 50th percentile of monthly mean streamflows during 1975-87.

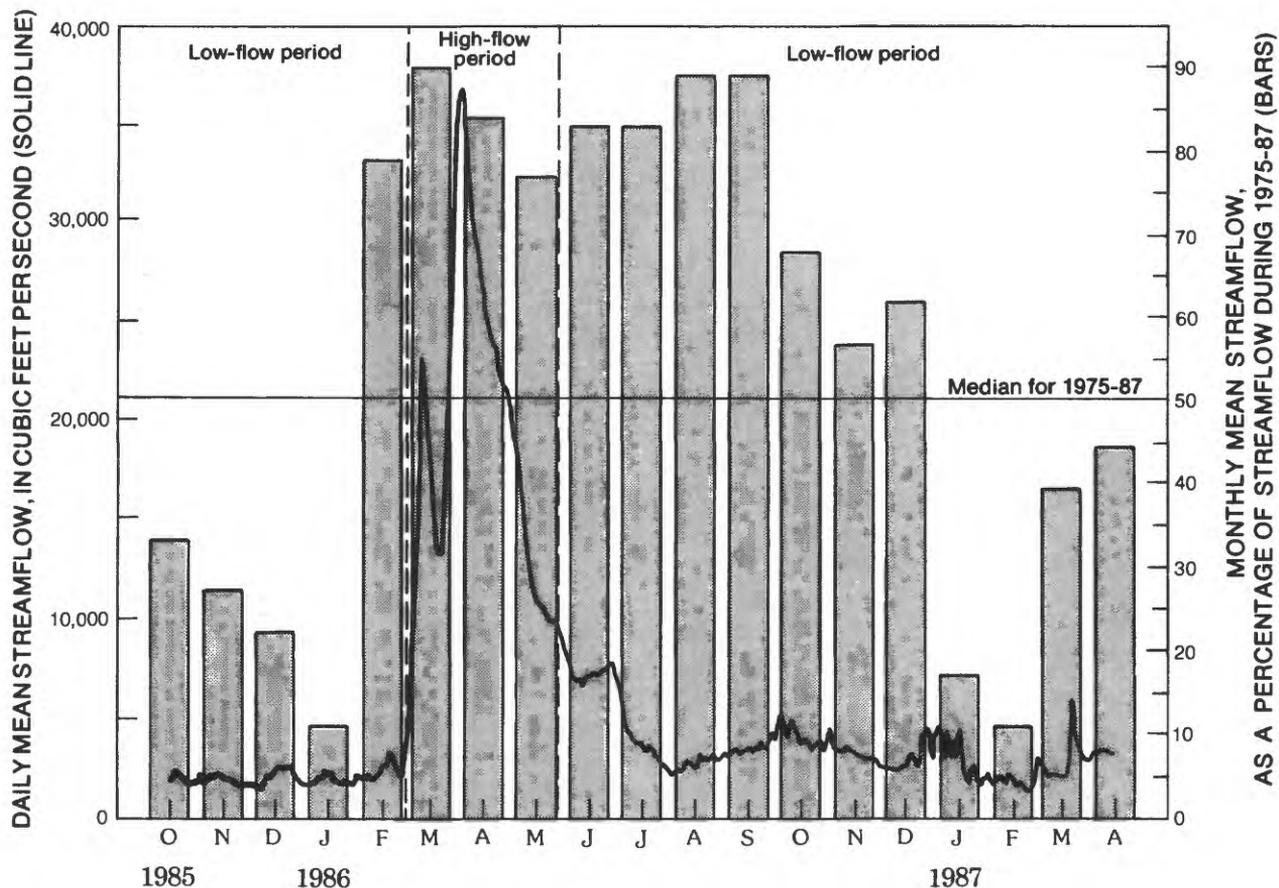


FIGURE 66.— Daily mean streamflow at site 11, near Vernalis, compared to monthly mean streamflow as percentage of flows for the same month during 1975-87.

Daily mean streamflows at Vernalis were summed for the entire 18-month study period to determine the quantity of water contributed by the San Joaquin River to the Sacramento-San Joaquin River delta. Of a total of 6.3×10^6 acre-ft of streamflow during the study period, 49 percent occurred during the 15-month combined low-flow period and 51 percent during the 3-month high-flow period.

Low Flow

During the combined low-flow period, the sum of total streamflows of the upper San Joaquin River and the five main tributaries to the lower river accounted for 80 percent of the total streamflow at Vernalis, where the median streamflow was 2,860 ft³/s (table 3). The eastside tributaries alone (sites 5, 8, and 10) contributed 65 percent of the streamflow at Vernalis. The San Joaquin River near Stevenson (site 1) contributed 6 percent of the Vernalis streamflow, and Salt and Mud Sloughs (sites 2 and 4) only 9 percent. The median streamflow in Salt Slough was more than three times that in Mud Slough. Total streamflows indicate that about 20 percent of the streamflow measured at Vernalis was from unmeasured sources between sites.

TABLE 3. Summary of streamflow in the San Joaquin River and its tributaries

[ft³/s, cubic feet per second]

Streamflow at study sites								
Site No.	Low-flow period (468 days)				High-flow period (79 days)			
	Total stream-flow (percent-age of site 11)	Streamflow (ft ³ /s)			Total stream-flow (percent-age of site 11)	Streamflow (ft ³ /s)		
		25th percentile	Median	75th percentile		25th percentile	Median	75th percentile
1	6	60	102	205	41	4,943	9,181	12,359
2	7	141	212	304	2	339	388	424
3	14	237	325	565	42	4,943	8,828	11,652
4	2	29	60	117	1	145	240	350
5	11	226	244	321	12	2,225	2,507	3,390
6	28	530	742	1,024	56	6,356	11,652	15,536
7	37	742	1,024	1,377	58	7,062	12,005	15,890
8	30	459	671	1,201	26	4,590	5,650	6,356
9	75	1,624	2,013	2,684	90	12,359	18,714	23,658
10	24	530	706	1,165	15	1,518	3,648	4,237
11	100	2,154	2,860	3,743	100	14,124	19,774	25,423
Total streamflow at site 11: 3.1×10 ⁶ acre-feet				Total streamflow at site 11: 3.2×10 ⁶ acre-feet				

Within-reach changes in streamflow						
River reach (down-stream site No.)	Low-flow period (21 measurements)			High-flow period (6 measurements)		
	Gain or loss (percentage of site 11)			Gain or loss (percentage of site 11)		
	25th percentile	Median	75th percentile	25th percentile	Median	75th percentile
3	0.3	0.8	1.5	-3.1	0.1	1.6
6	.3	1.3	2.3	.5	.7	1.5
7	6.8	8.9	12	2.5	4.8	8.8
9	5.3	9.8	13	3.0	8.0	10
11	-2.2	2.6	4.3	-7.6	-5.6	-2.5

Within-reach (between-site) changes in streamflow during the low-flow period were determined between each San Joaquin River site and its upstream tributaries for each of 21 days during which samples were collected for analyses of water chemistry. If all streamflows into a reach are accounted for at monitoring sites, then the sum of measured streamflows at upstream tributary sites should equal streamflow at the downstream end of that reach, after adjusting for traveltime within the reach. A gain within the reach indicates

addition of water from unmeasured sources; a loss indicates seepage losses or withdrawals. In table 3, within-reach changes are expressed as a percentage of streamflow at Vernalis in order to emphasize their relative importance.

The median value and the 25th and 75th percentiles were determined from estimates of the within-reach change in streamflow for each water-chemistry sampling date. Within-reach gains in streamflow were significant ($\alpha=0.05$) for all reaches except the one ending at site 11. Based on median values, the greatest within-reach gains occurred between sites 6 and 7, and between sites 7 and 8 and site 9. The within-reach gains represented a combined total of about 19 percent of the streamflow at Vernalis, which agrees with the estimate from total streamflow that about 20 percent of Vernalis streamflow was not measured at study sites.

Within-reach gains in streamflow during low-flow conditions were more closely examined in a streamflow accounting study during October 28-29, 1986. Every discharge to and withdrawal from the San Joaquin River was monitored in the reach between sites 6 and 7. During the 2-day study, the within-reach gain in streamflow was 277 ft³/s. Of this gain, 73 percent was from measured surface-water inflows. The remaining 27 percent of the total gain is estimated to be ground-water inflow to the reach between sites 6 and 7.

High Flow

During the high-flow period, the sum of estimated total streamflow of the five main tributaries to the lower San Joaquin River (sites 1, 2, 4, 5, 8, and 10) accounted for 97 percent of total streamflow at Vernalis, where the median streamflow was 19,774 ft³/s (table 3). The eastside tributaries represented 53 percent of the Vernalis streamflow, slightly less than they did during low flow, but the total streamflow of the San Joaquin River at site 1 was 41 percent of the streamflow at Vernalis, compared to only 6 percent during low flow. The source of water upstream of site 1 during the high-flow period was mainly San Joaquin River water released from Friant Dam. Salt and Mud Sloughs represented only 3 percent of the streamflow at Vernalis, about one-third their proportional contribution of streamflow during the low-flow period.

Within-reach gains in streamflow were greatest upstream from sites 7 and 9 (medians of 4.8 and 8.0 percent of streamflow, at those sites, respectively). Although a within-reach loss of water is indicated between site 11 and sites 9 and 10, this may be attributable to measurement problems during high-flow conditions. Generally, between-site differences during high-flow conditions are more difficult to interpret and also represent a smaller component of total flow than during low-flow conditions.

Sources of Selenium

Low Flow

Selenium loading estimated for each site during low flow (table 4), expressed as a percentage of the site 11 load, is shown in figure 67 compared to streamflow and similarly estimated dissolved-solids loads. During the low-flow period, the sum of selenium loads of the upper San Joaquin River and the five main tributaries to the lower river (sites 1, 2, 4, 5, 8, and 10) accounted for 85 percent of the total load at Vernalis (site 11). Together, the eastside tributaries and the upper San Joaquin River combined to account for only 7 percent of the Vernalis load, with median loads ranging from 0.02 to 0.04 ton/yr. Salt and Mud Sloughs contributed 78 percent of the total Vernalis load, with median loads of 1.9 and 0.38 ton/yr, respectively (table 4).

The estimates indicate that most selenium that reaches Vernalis comes from Salt and Mud Sloughs and that within-reach gains of selenium are absent or relatively small. In contrast, Salt and Mud Sloughs accounted for only 40 percent of the low-flow load of dissolved solids at Vernalis, and within-reach gains of dissolved solids were a major source. Total-load estimates indicate a possible loss of selenium between sites 7 and 9, but this loss was not apparent in the sampling-event analysis, and may be the result of an erroneously low estimate of the total load for site 9.

Within-reach changes in selenium loads were more closely examined using mass balances computed for the 21 days during which water samples were collected during the low-flow period (table 4). Estimates of within-reach changes were highly variable and none of the median gains were significantly greater than zero ($\alpha=0.05$). The results of the mass-balance analysis indicate that substantial within-reach losses probably did not occur.

High Flow

During the high-flow period, median selenium loads were higher at all sites (table 4), but the uncertainty in total load estimates is great for the high-flow period. Even though the high-flow period was only about 17 percent as long as the low-flow period, it accounted for about 35 percent of the total selenium load at Vernalis during the study period. Compared to the low-flow period, the contribution to the total Vernalis load from the upper San Joaquin River at site 1 was much greater (20 percent). The relative contribution of Salt and Mud Sloughs (74 percent) was similar to low flow. Median loads in the San Joaquin River increased downstream during the high-flow period from 2.6 ton/yr at site 1 to 11 ton/yr at site 11. Beyond these general patterns, detailed interpretation of loads during the high-flow period, particularly of within-reach changes, is not warranted.

TABLE 4. Summary of selenium loads in the San Joaquin River and its tributaries

[ton/yr, tons per year]

Dissolved selenium loads at study sites								
Site No.	Low-flow period (468 days)				High-flow period (79 days)			
	Total load (percentage of site 11 load)	Load (ton/yr)			Total load (percentage of site 11 load)	Load (ton/yr)		
		25th percentile	Median	75th percentile		25th percentile	Median	75th percentile
1	3	0.02	0.05	0.12	20	1.5	2.6	3.4
2	53	.89	1.9	2.6	41	3.1	3.7	6.0
3	47	.89	1.6	2.0	15	.80	1.7	2.4
4	25	.04	.38	1.6	33	2.1	4.0	5.6
5	1	.03	.03	.04	3	.16	.29	.48
6	89	1.9	2.6	3.5	88	8.1	11	13
7	92	1.3	2.6	4.0	66	4.8	6.8	11
8	2	.04	.06	.08	5	.44	.60	.68
9	71	1.6	2.4	3.0	85	6.8	9.3	12
10	1	.03	.04	.06	3	.17	.33	.56
11	100	2.3	3.1	4.0	100	8.1	11	14
Total load at site 11:					Total load at site 11:			
4.6 tons					2.5 tons			

Within-reach changes in selenium loads						
River reach (downstream site No.)	Low-flow period (21 measurements)			High-flow period (6 measurements)		
	Gain or loss (percentage of site 11)			Gain or loss (percentage of site 11)		
	25th percentile	Median	75th percentile	25th percentile	Median	75th percentile
3	-3.2	1.6	19	-53	-33	6.6
6	-4.4	3.5	15	-5.8	17	53
7	-5.3	4.8	18	-26	-9.4	12
9	-25	9.4	18	-20	2.3	60
11	-16	2.0	18	5.7	12	42

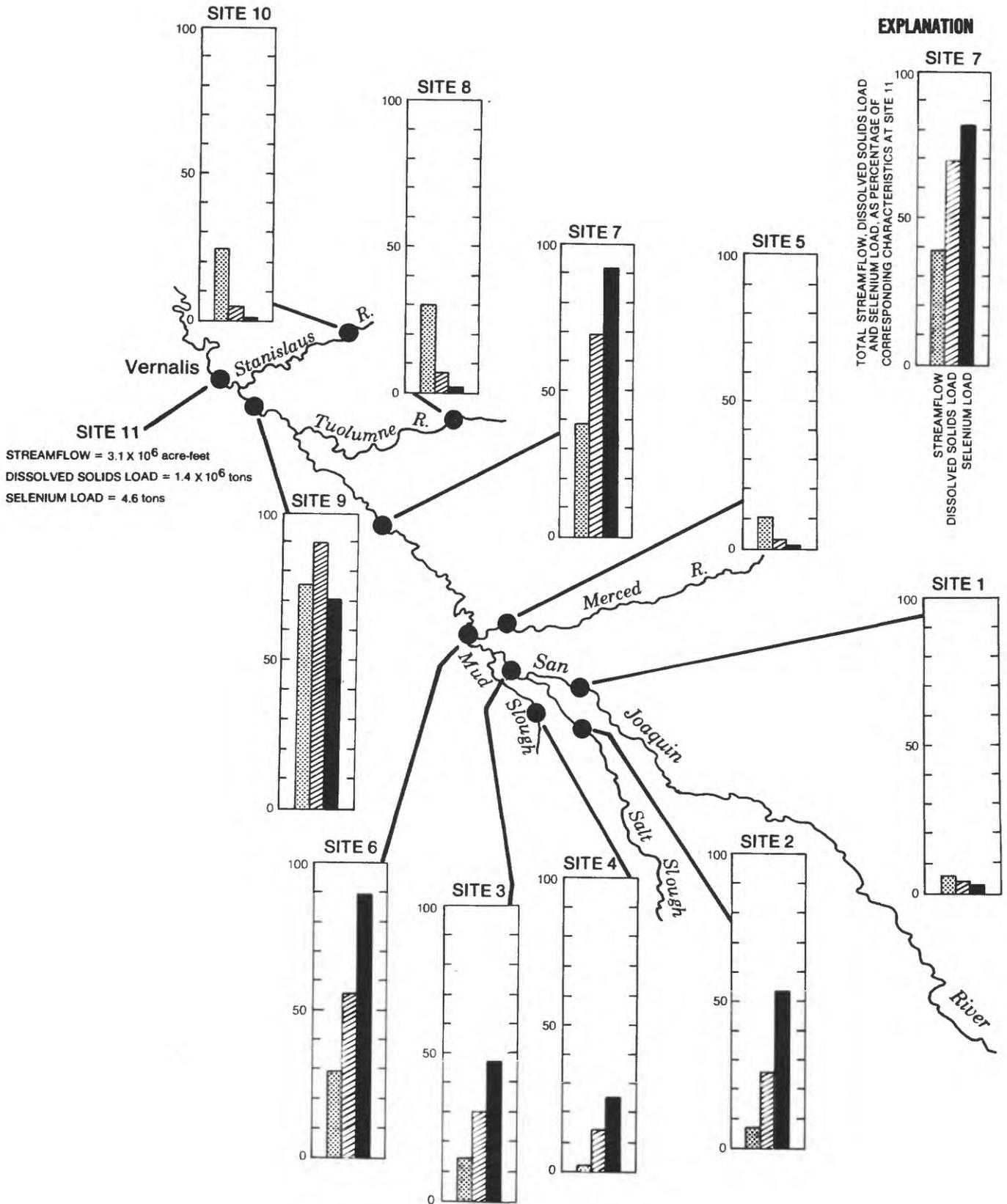


FIGURE 67.— Streamflow and loads of dissolved solids and dissolved selenium in the San Joaquin River during the low-flow period as percentages of those at site 11, near Vernalis. (See figure 65 for locational features.)

Selenium Concentrations

Selenium concentrations in the San Joaquin River and its tributaries are summarized in table 5. During the low-flow period, median selenium concentrations were highest in Salt Slough (5.5 µg/L) and Mud Slough (8.8 µg/L). Both sloughs receive inflows of subsurface agricultural drain water, some of which is high in selenium. In Mud Slough, the maximum selenium concentration measured was 28 µg/L on July 15, 1986, and the maximum selenium concentration measured in Salt Slough was 22 µg/L on January 21, 1987. Median selenium concentrations were lowest in the three eastside tributaries (less than or equal to 0.1 µg/L), and in the San Joaquin River at site 1, upstream of Salt and Mud Sloughs (0.3 µg/L). Median selenium concentrations in the San Joaquin River decreased from 5.2 µg/L at site 3 to 1.0 µg/L at site 11, near Vernalis, as the low selenium water from the eastside tributaries entered the river.

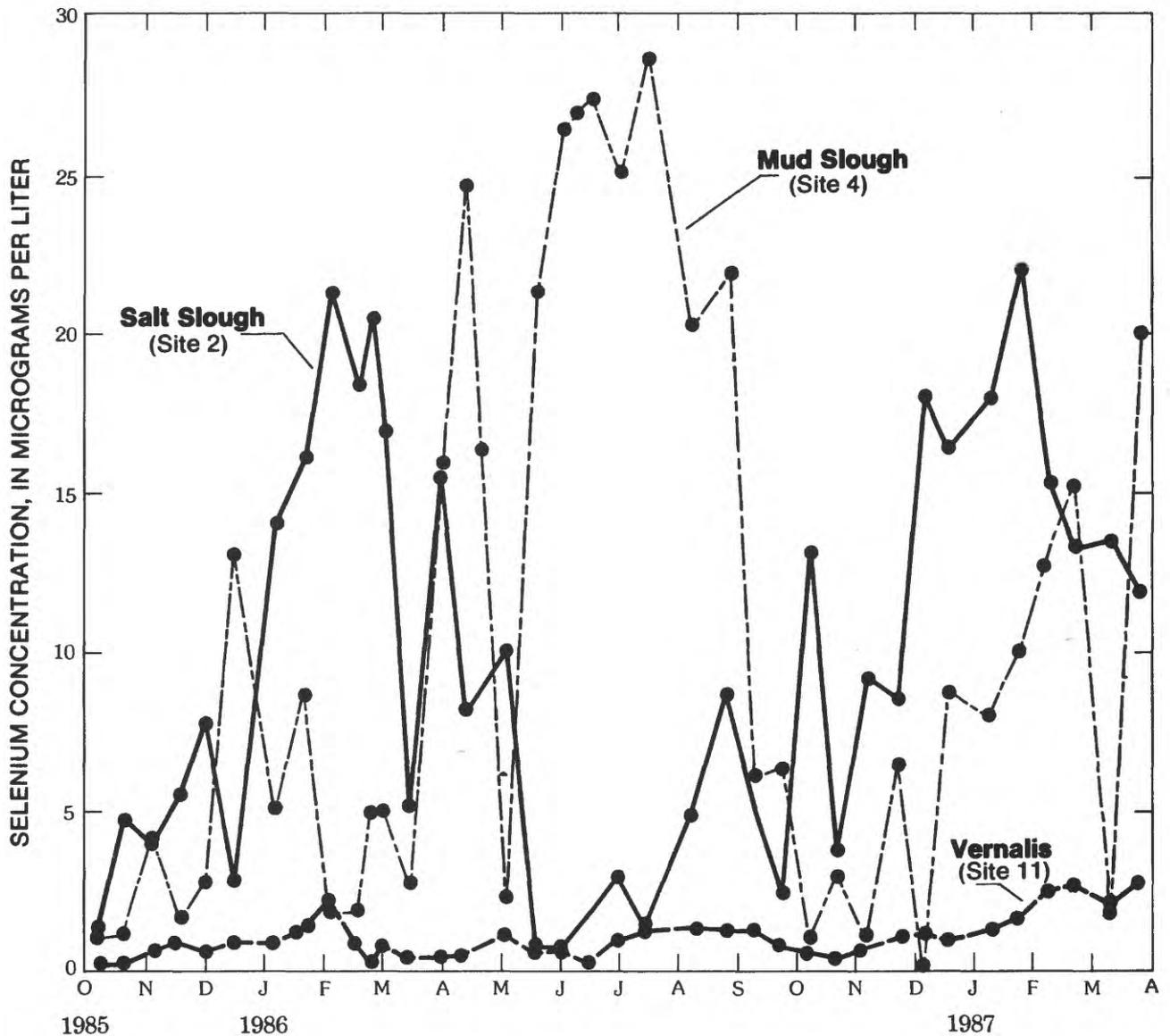
During the high-flow period, selenium concentrations in the San Joaquin River were lower than during the low-flow period because of greater dilution by Sierra Nevada runoff. In contrast, selenium concentrations increased with the increase in streamflow in Salt Slough. Median selenium concentrations were highest in Salt Slough (13 µg/L) and Mud Slough (3.9 µg/L). The maximum selenium concentration measured in Salt Slough during the high-flow period was 20 µg/L on February 26, 1986, and the maximum selenium concentration measured in Mud Slough was 24 µg/L on April 16, 1986. Median selenium concentrations were lowest in eastside tributaries and in the San Joaquin River at site 1 (0.1 to 0.2 µg/L). Median selenium concentrations decreased downstream in the San Joaquin River between sites 6 and 11 from 1.1 to 0.7 µg/L, because of dilution by major eastside tributaries and other smaller inflows.

TABLE 5. Summary of selenium concentrations in the San Joaquin River and its tributaries

[<, actual value is less than value shown]

Site No.	Selenium concentrations, in micrograms per liter					
	Low-flow period (21 samples)			High-flow period (6 samples)		
	25th percentile	Median	75th percentile	25th percentile	Median	75th percentile
1	0.1	0.3	0.6	<0.1	0.2	0.3
2	2.1	5.5	14	7.4	13	18
3	1.4	5.2	8.1	.1	.2	1.2
4	3.0	8.8	21	2.2	3.9	18
5	<.1	.1	.2	<.1	.2	.2
6	1.6	2.7	5.4	.4	1.1	1.3
7	1.3	2.3	4.2	.3	.8	1.3
8	<.1	<.1	.1	<.1	.1	.2
9	.6	1.1	2.0	.4	.7	.8
10	<.1	<.1	.2	<.1	.1	.2
11	.6	1.0	1.4	.5	.7	.9

Selenium concentrations in the San Joaquin River at Vernalis during October 1985 to March 1987 ranged from 0.3 to 2.8 $\mu\text{g/L}$ (fig. 68). Selenium concentrations were low in October and November of both 1985 and 1986 and then steadily increased until February of 1986 and 1987, respectively, corresponding to an increased quantity of subsurface drain water discharged to the river (Wichlens and Nelson, 1987). Selenium concentrations in Salt and Mud Sloughs were more variable (fig. 68). Selenium concentrations in Salt Slough were higher in winter and concentrations in Mud Slough were higher in summer.



Significance to Water Quality

The most probable form of selenium toxicity to fish and wildlife is through bioaccumulation in the aquatic food chain. The California State Water Resources Control Board (1987) has proposed an interim objective of a maximum mean monthly selenium concentration of 5 $\mu\text{g/L}$ in the San Joaquin River at site 6. The State's recommendation is for long-term objectives of 2 $\mu\text{g/L}$ of selenium to protect waters of the San Joaquin River that are impounded for wetland habitat, and 10 $\mu\text{g/L}$ selenium for Salt and Mud Sloughs. The present Federal water-quality criterion for selenium in drinking water is 10 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1986). The Federal selenium criterion for protection of freshwater aquatic organisms is a 4-day average of 5 $\mu\text{g/L}$ no more than once every 3 years on the average, and the 1-hour average selenium concentration should not exceed 20 $\mu\text{g/L}$ more than once every 3 years on the average (U.S. Environmental Protection Agency, 1988).

Cumulative frequency distributions of measured instantaneous selenium concentrations for sites 2, 3, 4, 6, 7, 9, and 11 can be used to estimate the proportion of the study period that a criterion was exceeded (fig. 69). Thirty-seven observations were used at sites 2, 4, and 11, and 27 observations at the remaining sites. Cumulative frequency distributions for the eastside tributaries and the San Joaquin River at Stevinson (site 1) are not shown because selenium concentrations did not exceed 2 $\mu\text{g/L}$.

Sites 5 and 6 are only 0.2 mile apart (fig. 65), and there are no other inflows between them. A mass-balance computation based on data for these sites can be used to estimate selenium concentrations and loads just upstream from site 6, above the inflow of the Merced River. Selenium concentrations were determined by the difference in selenium loads, divided by the difference in streamflows, between sites 5 and 6. Results for this location upstream of site 6 represent the effects of Salt and Mud Sloughs on selenium concentrations in the river prior to dilution by the Merced River.

The cumulative frequency plots show that the drinking-water standard (10 $\mu\text{g/L}$) was exceeded in the San Joaquin River downstream of Salt Slough, at site 3, and upstream of the Merced River, about 10 percent of the time. The standard was exceeded in the Salt and Mud Sloughs about 40 percent of the time. The proposed aquatic-life criterion of 5 $\mu\text{g/L}$ was exceeded in the sloughs more than 60 percent of the time; and in the San Joaquin River at site 3 and just upstream of the Merced River, more than 40 percent of the time. At site 6, downstream of the Merced River, selenium concentrations exceeded 5 $\mu\text{g/L}$ more than 20 percent of the time. The 5 $\mu\text{g/L}$ criterion also was sometimes exceeded in the San Joaquin River at site 7 (8 percent), but not at sites 9 and 11 on the San Joaquin River. If the criterion for selenium were to be 2 $\mu\text{g/L}$, it would have been exceeded at all San Joaquin River sites, except site 1, 10 percent or more of the time during the study period. Seventy-five percent or more of the selenium concentrations were greater than 2 $\mu\text{g/L}$ at Salt and Mud Sloughs, and at sites 3 and 6, 55 percent were greater than 2 $\mu\text{g/L}$.

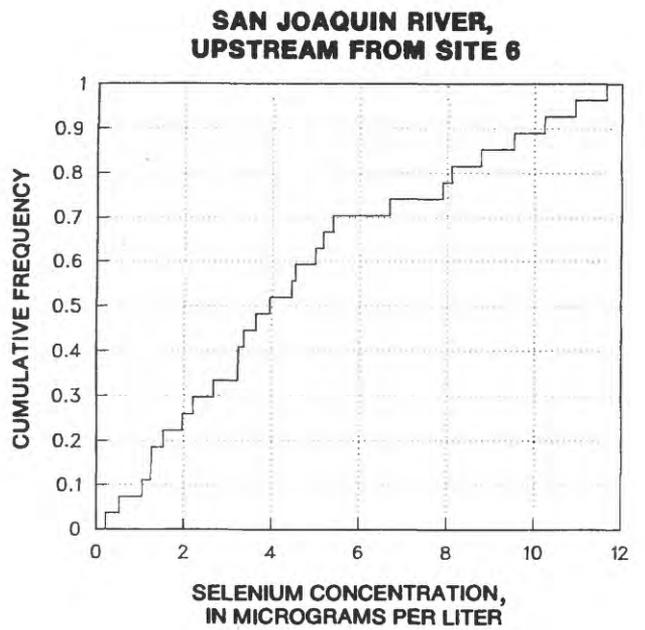
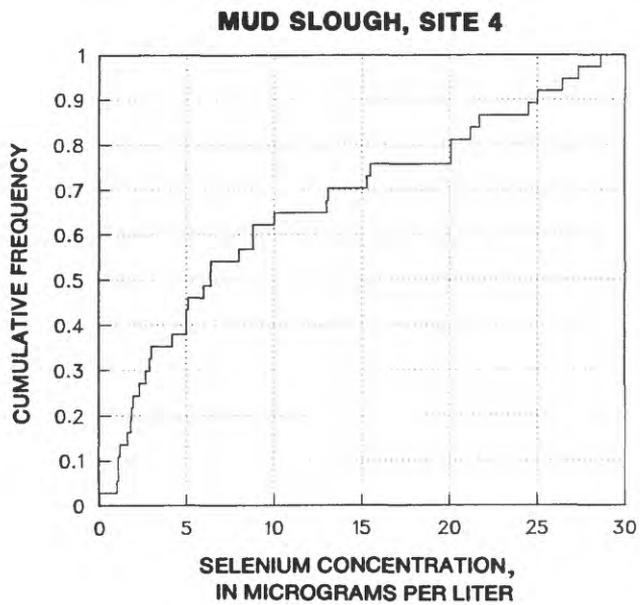
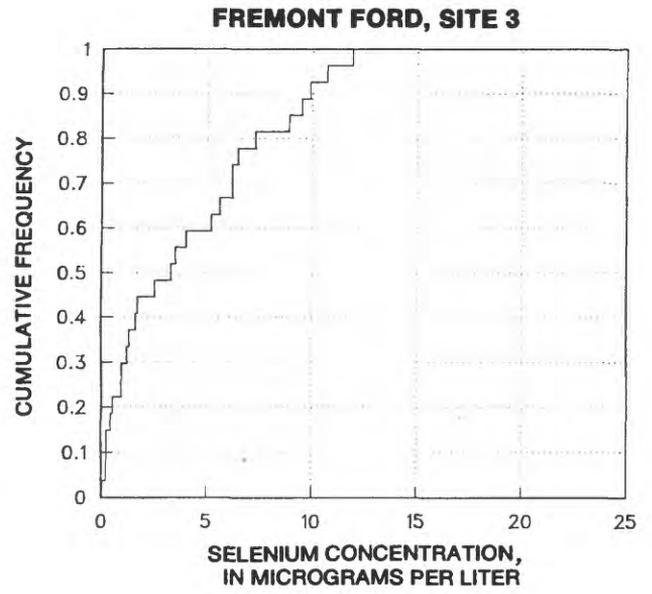
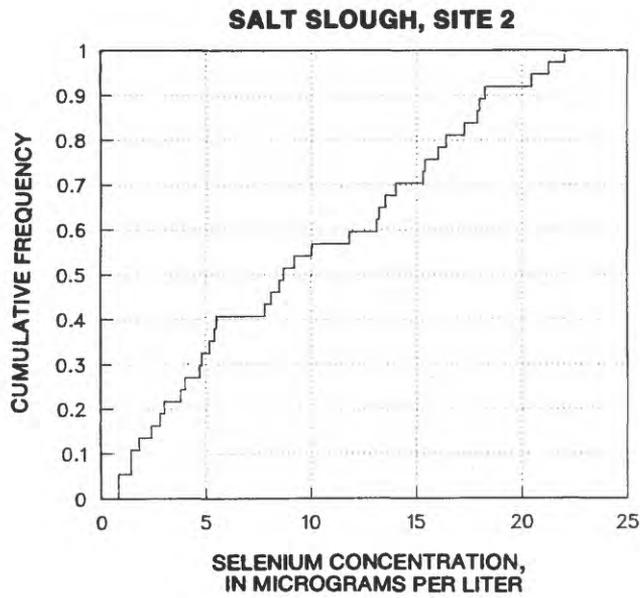


FIGURE 69.— Cumulative frequency distributions for selenium concentrations at selected study sites.

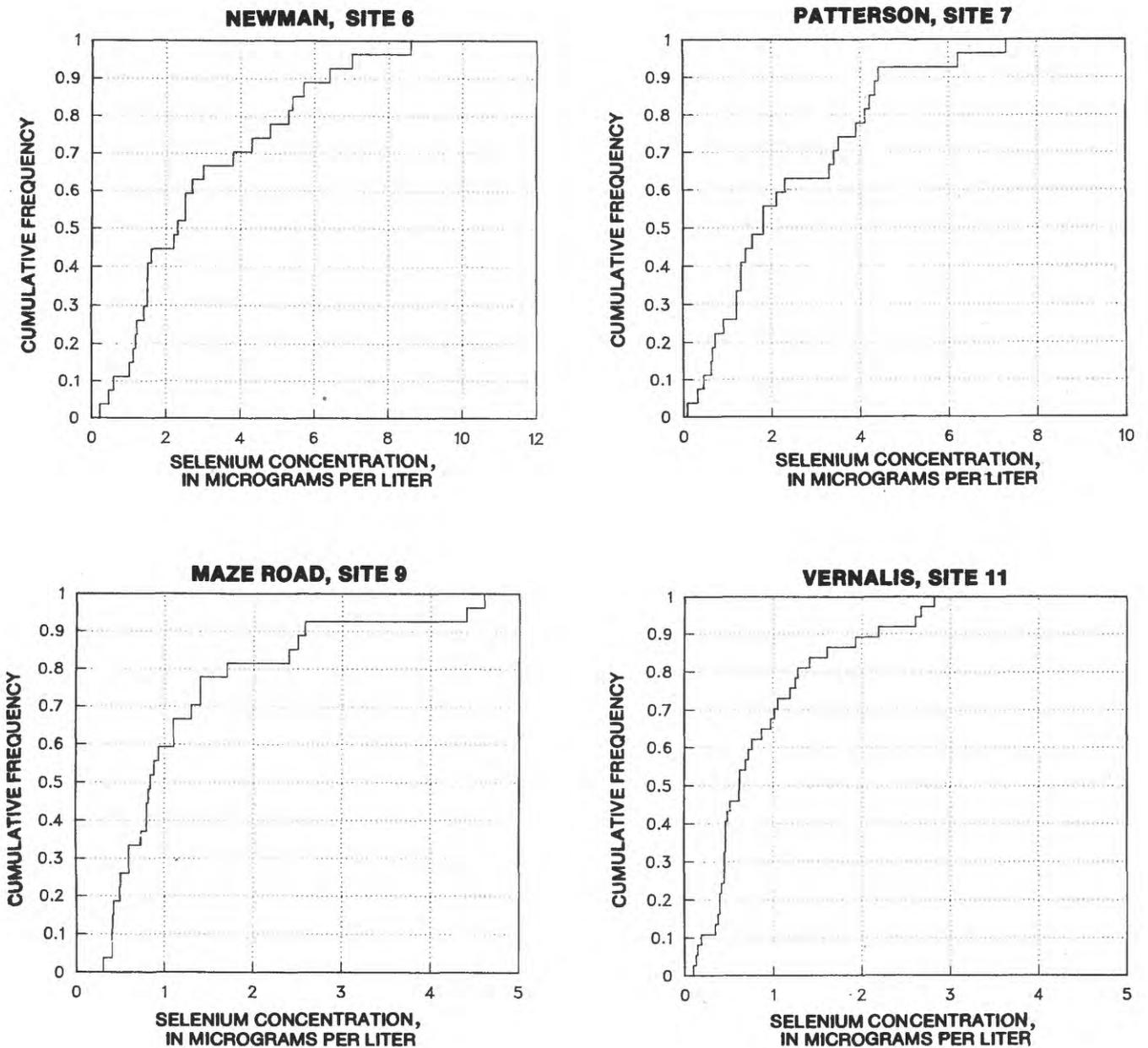


FIGURE 69.— Cumulative frequency distributions for selenium concentrations at selected study sites—Continued.

Selenium Loading to the Sacramento-San Joaquin River Delta

The San Joaquin River contributes most of the riverine load of selenium to the delta, even though the Sacramento River contributes most of the streamflow. Figure 70 shows selenium loading from both rivers for December 1986 through April 1987, a period during which the San Joaquin River contributed 83 percent of the estimated total load of selenium from both rivers. Seldom do waters of the two rivers completely mix before flowing out of the delta to San Francisco

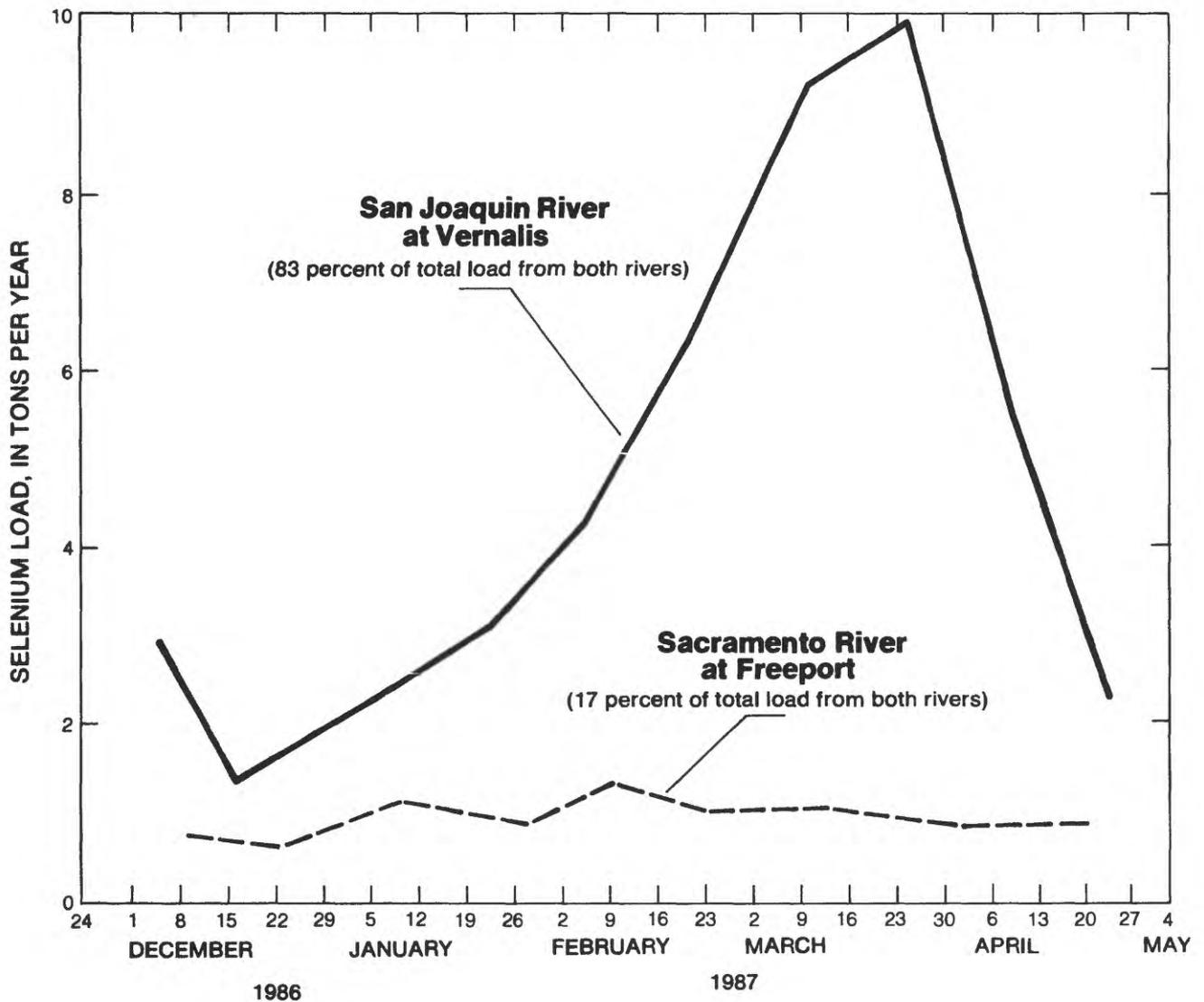


FIGURE 70.— Selenium loads in the Sacramento River at Freeport and the San Joaquin River at Vernalis, December 1986 through April 1987.

Bay. Numerous irrigation withdrawals in the delta, and the large withdrawals of water at Federal and State pumping plants which move water into the Delta-Mendota Canal and the California Aqueduct, greatly complicate the hydrology. At times, most of the San Joaquin River flow is withdrawn in the delta, and flow through the delta to the bay is almost entirely Sacramento River water (Harte and others, 1986).

Selenium concentrations in tissues of the bivalve, *corbicula*, which inhabits the Delta-Bay system and the San Joaquin River, indicate that selenium from the San Joaquin River does not measurably affect the bioaccumulation of selenium in the southern delta or northern San Francisco Bay (Johns and others, 1988). Selenium concentrations in *corbicula* from the western delta and Suisun Bay are higher than from other areas studied and possibly indicate local sources of selenium in those areas.

SUMMARY

Agricultural drainage problems in the San Joaquin Valley have attracted National attention since 1983, when selenium in water from subsurface tile drainage systems was found to have toxic effects on waterfowl at Kesterson Reservoir. Other constituents of drain water, particularly arsenic, chromium, boron, molybdenum, and dissolved solids, also may cause water-quality problems in some areas of the valley, but selenium is the most widespread problem and the most limiting constraint on management alternatives.

Geologic Source of Selenium and Its Distribution In Soils

Water-quality problems associated with selenium are most likely in areas of the San Joaquin Valley where soils are formed of sediments from marine sedimentary rocks of the Coast Range. The occurrence of Coast Range sediments and the highest soil selenium concentrations are clearly linked throughout the valley. Three areas of the western valley--the alluvial fans near Panoche and Cantua Creeks in the central western valley, an area west of the town of Lost Hills, and the Buena Vista Lake Bed area--have the highest soil selenium concentrations. High concentrations of selenium occur in subsurface drain water from some agricultural lands near, but not necessarily within, all three areas.

The central part of the western San Joaquin Valley is the largest area of the valley that has concentrations of total selenium in soil that exceed 0.36 mg/kg, the 90th percentile of concentrations in all valley soils. Within the central western valley, concentrations of selenium are highest in soils between the alluvial fans of Cantua and Panoche Creeks, east of Monocline Ridge. Marine shales exposed in the area of Monocline Ridge probably are the primary sources of sediments that contribute to high total selenium concentrations in these soils.

Although high concentrations of selenium occur in shallow ground water and drain water in parts of the central western valley and in the other areas that have soils with high total selenium concentrations, an exact correlation between the locations of high-selenium soils and high-selenium ground water is not observed. A close spatial correlation does not occur because the distribution of soluble forms in soil can be different than the distribution of total selenium and soluble forms are what affect concentrations in ground water.

Ground-Water Flow System of the Central Part of the Western Valley

One key to evaluating the origin and present-day distribution of agricultural drainage problems and high concentrations of selenium in ground water of the central western valley is to understand changes in the ground-water flow system that have occurred from natural to present-day conditions. In the central western valley, the Corcoran Clay Member of the Tulare Formation divides the ground-water flow system into a lower confined zone and an upper semiconfined zone. The focus of this report is on ground water in the Coast Range alluvial sediments and Sierra Nevada sediments of the semiconfined zone. Under natural conditions, recharge to the semiconfined aquifer was primarily by infiltration of water from intermittent streams. Discharge of ground water under natural conditions was primarily by evapotranspiration and streamflow along the valley trough.

The dominant influences on the ground-water flow system since the early 1900's, when irrigation began, have been increased recharge resulting from percolation of irrigation water past crop roots, and historic pumping of ground water from the confined aquifer beneath the Corcoran. The increased recharge and pumping between 1912 and 1967 simultaneously caused the water table to rise over a large part of the western valley and resulted in a substantial component of downward ground-water flow. Importation of surface water beginning in 1967 led to further increases in application of irrigation water, and hence increased rates of recharge to the system, compared to when ground water was the primary source of irrigation water. Concurrently, pumpage from below the Corcoran decreased since the mid-1960's, which has caused a decrease in the downward head gradient. The decreasing gradient causes a reduction in the downward flow of ground water through the Corcoran and contributes to causing the water table to rise more rapidly. The altitude of the water table has risen 40 ft or more over much of the central western valley since 1952, causing more than 100,000 acres of farmland to have subsurface drainage problems.

A prominent feature of the present-day water table is the ground-water divide that parallels the western boundary of the alluvial fans of the central western valley. The ground-water divide shifts westward between the major alluvial fans of Cantua, Little Panoche, Los Gatos, and Panoche Creeks, and shifts eastward near the upper parts of these fans. To the east of the ground-water divide, the water table lies at shallow depths, is a subdued replica of the topography, and the horizontal component of ground-water flow is eastward and northeastward. Ground-water flow occurs eastward across the valley trough toward active production wells completed above the Corcoran in the Sierra Nevada sediments of the eastern valley, and downward toward the confined zone. West of the ground-water divide, the water table slopes steeply to the west, and flow is toward the west and downward toward the confined zone.

In the past, tile drainage systems have been installed in some areas east of the ground-water divide that have a shallow water table. Drainage systems have been effective in removing enough shallow ground water to maintain the water table at desired depths in the confines of drained areas, but their use is limited because of problems associated with disposing of the poor-quality shallow ground water that they collect.

Selenium in Ground Water of the Central Part of the Western Valley

The feasibility of potential modifications or alternatives to conventional drainage systems for water-table control depends on the areal and depth distribution of selenium in ground water. The highest concentrations of selenium in ground water occur in the upper part of the semiconfined zone in Coast Range alluvial sediments. The upper part of the semiconfined zone contains water that originated from irrigation recharge. In the Coast Range alluvial sediments, irrigation water applied since 1952, which can be identified by the presence of tritium, has reached depths of at least 6 to 161 feet below the water table, with a median of 50 feet. Irrigation water applied before 1952 probably occurs in a 10- to 50-foot interval below these depths. Selenium concentrations in the upper part of the semiconfined zone, which ranged from less than 10 $\mu\text{g/L}$ to more than 1,000 $\mu\text{g/L}$, are correlated with ground-water salinity and the presence of oxic conditions.

Samples of native ground water that underlies the irrigation-derived water in the Coast Range alluvial sediments had selenium concentrations less than 10 $\mu\text{g/L}$. Selenium concentrations did not exceed 2 $\mu\text{g/L}$ in ground water in the confined zone or in Sierra Nevada sediments of the semiconfined zone. The low concentrations in this ground water are attributable to reducing conditions and the low availability of selenium in these sediments. Selenium may be removed from solution if oxic ground water in Coast Range sediments moves into reduced Sierra Nevada sediments.

Two processes have had the greatest effects on the distributions of salinity and selenium concentrations in irrigation-derived ground water in the Coast Range alluvial sediments: leaching of soil salts and soluble selenium by infiltrating irrigation water and evaporative concentration. The areal distribution of selenium concentrations in shallow ground water generally correlates with soil salinity before agricultural development, reflecting the leaching of natural soil salts by irrigation. In areas where the water table has been near the land surface for extended periods, the highest concentrations of selenium have developed in shallow ground water as a result of evapotranspiration of ground water. Selenium concentrations of 20 $\mu\text{g/L}$ to more than 1,000 $\mu\text{g/L}$ occur in shallow ground water in the lower parts of Cantua Creek, Little Panoche Creek, Los Gatos Creek, and Panoche Creek alluvial fans, and between the Panoche Creek and Cantua Creek fans, where natural soil salinity was high and where the water table has been shallow for many years in some places.

In some irrigated areas where the water table is deep enough that evaporative concentration has not been substantive, recently recharged ground water near the water table has lower selenium concentrations than underlying ground water from early irrigation recharge. In these areas, most soluble forms of selenium already have been leached from the soil. This condition is common in the middle fan areas associated with the four largest streams, where selenium concentrations generally are less than 20 $\mu\text{g/L}$ in shallow ground water.

Although the natural processes and human influences that govern the distribution of selenium in ground water in the Coast Range alluvial sediments vary greatly throughout the central western valley, general patterns are evident. Within about 10 to 20 feet below the water table, selenium concentrations commonly range from 10 to 50 $\mu\text{g/L}$, but are 10 to 100 times higher than this where the water table has been near the land surface for an extended period and evaporative concentration has occurred. Water in this shallowest interval is derived principally from the most recent irrigation recharge, probably during the past 10 to 20 years. Within the range of 20 to 150 feet below the water table, an interval of variable thickness occurs in which selenium concentrations are commonly 50 to more than 1,000 $\mu\text{g/L}$. Water in this interval is derived principally from recharge of early irrigation water. Selenium concentrations in both of these depth intervals that are associated with irrigation recharge are in the highest part of the stated concentration ranges where natural soils were most saline. Native ground water, with selenium concentrations less than 10 $\mu\text{g/L}$, is below the ground water derived from irrigation recharge.

Selenium in Ground Water of the Northern Part of the Western Valley

Selenium concentrations are low in ground water of most of the northern part of the western valley, which is mainly in the western parts of Merced, San Joaquin, and Stanislaus Counties, and do not pose the same management problems as do the higher selenium concentrations that occur in the central western valley. An exception is shallow ground water with high selenium concentrations in the southwest corner of the northern part, which is an extension of similar geologic and hydrologic conditions that occur on the larger alluvial fans of the central western valley. One existing production well in the semiconfined zone and one in the confined zone had selenium concentrations exceeding 10 $\mu\text{g/L}$ --the present U.S. Environmental Protection Agency drinking-water standard. As in the central part of the western valley, the highest selenium concentrations in the northern part are associated with oxic Coast Range alluvial sediments and are correlated with salinity. With the exception of shallow ground water, the highest selenium concentrations in the semiconfined and confined zones were near Crow Creek, which contains higher selenium concentrations than most other Coast Range streams. A key finding from study of the northern part of the western valley is evidence that recent irrigation water has moved into deep parts of the semiconfined zone and even into the confined zone. The deepest penetration probably is limited to the vicinity of wells, which have provided a pathway for rapid downward flow.

Selenium in Tile Drain Water

Effective management of existing tile drainage systems and assessments of the use of tile drains as a management option for the future require an understanding of how tile drains interact with the ground-water flow system and the levels and variability of selenium concentrations likely to occur in drain

water. Selenium concentrations vary greatly between drainage systems, from tens to thousands of micrograms per liter, but tend to be relatively consistent over time in drain water from a particular system and are correlated with drain-water salinity. The exception to their consistency over time is the first 1 to 5 years of drainage-system operation, when concentrations tend to be the highest and most variable. There are no clear seasonal patterns common to all systems in the area. The low temporal variability of selenium concentrations in water from existing mature drainage systems underscores the fact that drainage systems withdraw ground water, which tends to be of relatively constant chemical character over time in a particular place.

The high variability in selenium concentrations between existing drainage systems reflects the high spatial variability in shallow ground-water concentrations, the ages of the drainage systems, and variable hydrologic conditions at individual fields. Concentrations in drain water from existing systems in Coast Range alluvial sediments are not predictable from a regionalized assessment of shallow ground-water concentrations derived from observation-well data, however, the age of the drainage systems explained a significant part of the variance in median selenium concentrations. Studies of individual drained fields show how local water-table history, geohydrologic conditions, irrigation history, and drainage-system design can markedly affect the type of water that is removed by the drains. The highest selenium concentrations in ground water occur at varying depths below the water table in different areas. The design of a drainage system and local geohydrologic conditions determine the contributions of water from different depths to drain-water flow. These factors vary greatly between fields and are key reasons why the variability in selenium concentrations between drainage systems is so high.

Mobility of Soil Selenium

Soils are a source of selenium to shallow ground water where irrigation occurs. Readily soluble forms of selenium in present-day soils, predominantly selenate, are only a small fraction of the total selenium content, but the quantities of soluble selenium are substantially different between soils in different fields and at different depths. Forty-five years of irrigation, combined with 15 years of water-table control by a drainage system, resulted in highly leached soils throughout the unsaturated zone in a field drained for 15 years. Irrigation water infiltrating through these soils to the water table probably attains selenium concentrations in the range of 10 to 50 $\mu\text{g}/\text{L}$. In two fields irrigated for just as long, but drained for less than one-half the amount of time, saline soils with substantial quantities of soluble selenium were found at the 3-foot depth, even though the near-surface soils were highly leached. Water percolating through soils of these two fields still contains selenium concentrations greater than 100 $\mu\text{g}/\text{L}$.

Although dissolution of readily soluble soil salts is the primary mechanism of selenium release from saline soils, other mechanisms seem to be more important in highly leached soils. Selenium is correlated with salinity in soil-extract solutions for soils that have substantial quantities of soluble selenium, but such a correlation is not evident for highly leached soils with

little remaining soluble selenium. Saturation extracts of highly leached soils contained a substantial proportion of selenite, whereas selenate dominates in extracts of more saline soils. Processes such as sorption reactions involving selenite, dissolution of soil minerals, and release of organic selenium may control the movement of selenium from unsaturated soils after the most soluble salts have been leached.

Sources and Concentrations of Selenium in the San Joaquin River

Drain water from about 77,000 acres of tile-drained farmland eventually flows to the San Joaquin River. Flow of drain water to the river occurs mainly through two tributaries, Salt and Mud Sloughs. Concentrations of selenium in water from individual drainage systems that discharge to waterways that eventually reach these sloughs or smaller tributaries ranges from less than 10 to 4,000 $\mu\text{g/L}$, with mixtures of these waters in larger collector drains ranging from 20 to 100 $\mu\text{g/L}$.

During October 1985 through March 1987, two relatively distinct flow conditions occurred in the San Joaquin River: a low-flow period consisting of October 1985 to mid-February 1986 and mid-May 1986 through March 1987, and a high-flow period from mid-February to mid-May 1986. Of total streamflow at the farthest downstream study site, the San Joaquin River near Vernalis, 49 percent occurred during the 15-month combined low-flow period and 51 percent during the 3-month high-flow period.

Despite the greater quantity of streamflow during the 3-month high-flow period, 65 percent of the selenium load during the study period occurred during the 15-month low-flow period. During the low-flow period, Salt and Mud Sloughs contributed almost 80 percent of the Vernalis selenium load, despite contributing only 9 percent of the total streamflow, and within-reach gains or losses of selenium were not substantial. The only major change in proportional sources of selenium loading to the river during the high-flow period was the increase from 3 to 20 percent of the total load from the upper San Joaquin River because of much greater streamflow.

During the low-flow period, median selenium concentrations were highest in Salt Slough (5.5 µg/L) and Mud Slough (8.8 µg/L). In Mud Slough, the maximum selenium concentration measured was 28 µg/L on July 15, 1986, and the maximum selenium concentration measured in Salt Slough was 22 µg/L on January 21, 1987. Median selenium concentrations in the San Joaquin River decreased from 5.2 µg/L downstream of Salt Slough to 1.0 µg/L near Vernalis, as water with low selenium concentrations entered the river from the eastside tributaries and other smaller inflows.

During the high-flow period, selenium concentrations in the San Joaquin River were lower than during the low-flow period because of greater dilution by Sierra Nevada runoff. In contrast, selenium concentrations increased with the increase in streamflow in Salt Slough. Median selenium concentrations were highest in Salt Slough (13 µg/L) and Mud Slough (3.9 µg/L). The maximum selenium concentration measured in Salt Slough was 20 µg/L on February 26, 1986, and the maximum selenium concentration measured in Mud Slough was 24 µg/L on April 16, 1986.

The U.S. Environmental Protection Agency drinking-water standard of 10 µg/L was exceeded about 10 percent of the time in the San Joaquin River just upstream of the Merced River, and was not exceeded downstream of the Merced River. The proposed U.S. Environmental Protection Agency aquatic-life criterion of 5 µg/L for selenium was exceeded in Salt and Mud Sloughs more than 60 percent of the time. In the San Joaquin River, just upstream of the Merced River, 5 µg/L was exceeded more than 40 percent of the time, and just downstream of the Merced River, it was exceeded more than 20 percent of the time. The 5 µg/L criterion was exceeded less frequently farther downstream in the San Joaquin River and never was exceeded at Vernalis.

The San Joaquin River contributes most of the riverine load of selenium to the Sacramento-San Joaquin River delta, even though the Sacramento River contributes most of the streamflow. During December 1986 to April 1987, the San Joaquin River contributed 83 percent of the estimated total load of selenium from both rivers. Seldom do waters of the two rivers completely mix before flowing out of the delta to San Francisco Bay. At times, most of the San Joaquin River flow is withdrawn from the delta, and flow through the delta to the bay is almost entirely Sacramento River water. Selenium concentrations in tissues of the bivalve, *corbicula*, which inhabits the delta, Suisun Bay, and the San Joaquin River, indicate that selenium from the San Joaquin River does not measurably affect the bioaccumulation of selenium in the southern delta or Suisun Bay.

IMPLICATIONS FOR WATER MANAGEMENT

Although this report is based on the preliminary results of studies in progress, these results have implications that may affect the ongoing development of water-management alternatives for the central part of the western San Joaquin Valley. These management alternatives are presently being developed by Federal, State, and local water-management agencies. In most instances, the implications are general in nature and will not be quantified until the studies and associated simulation and empirical models are completed. These general implications aid water managers and researchers in setting priorities for completing studies in progress and in guiding the development of study plans for large unstudied areas of the Tulare Lake basin, which may have similar water-quality problems.

- The water table will continue to rise in the central western valley if present irrigation practices continue in the absence of other changes in the ground-water flow system.
- The rising water table, which reflects net recharge to the ground-water flow system in excess of its capacity to discharge water, will enlarge the areas that have a shallow water table and associated drainage problems.
- The rise of the water table can be slowed or stopped by reducing ground-water recharge and increasing ground-water discharge.
- Ground-water recharge can be reduced by increasing irrigation efficiency, reducing seepage losses from canals and water storage facilities, and changing or eliminating agricultural activities in some areas to reduce or eliminate irrigation.
- Ground-water discharge can be increased by tile drainage systems, pumping from wells, or increasing evapotranspiration in selected areas. Although tile drainage systems withdraw shallow ground water, which tends to have the highest selenium concentrations, dewatering wells may allow water-table control by withdrawal of deeper ground water that has low selenium concentrations. Evapotranspiration may be increased in some areas by eliminating artificial drainage and using salt-tolerant plants.
- Water-table management through removal of water from Sierra Nevada sediments by dewatering wells may result in removal of selenium from ground water that moves from Coast Range sediments into Sierra Nevada sediments.
- The large quantity of high-selenium ground water (50 to 1,000 $\mu\text{g/L}$) in the general range of 20 to 150 feet below the water table makes it desirable to use management practices that leave this water where it is, rather than bring it to the land surface or allow it to move into parts of the aquifer that may be used for water supply. Water-table control strategies based on increasing ground-water discharge need to be carefully evaluated with respect to their potential to affect the movement of water with high selenium concentrations.

- The occurrence of ground water with 10 to 50 µg/L selenium in the upper 10 to 20 feet of the saturated zone indicates that, where evaporative concentration is controlled, continued irrigation with water that has low selenium concentration may result in a wider interval of this lower concentration water. Drainage strategies aimed at removing this ground water near the water table may be feasible in some areas.
- The highest concentrations of selenium in shallow ground water have developed and will continue to develop in irrigated areas where evaporative concentration is not controlled by water-table management.
- Selenium concentrations vary greatly between drainage systems, but tend to be consistent over time in drain water from a particular system after the first 1 to 5 years of operation. When selenium concentrations vary, they tend to be correlated with drain-water salinity. Periodic selenium measurements, on the order of 2 to 4 times per year, combined with frequent specific conductance monitoring, are an effective strategy for monitoring drain-water selenium concentrations.
- If drainage flows from a particular drainage system are reduced, selenium concentrations in drain water probably will remain relatively constant, resulting in a decreased selenium load. However, a reduction in dilution by low-concentration water from irrigation could lead to a gradual increase in drain-water selenium concentration if irrigation volume is decreased. In the long term, this may partially offset load reductions achieved by decreasing drain flows.
- Selenium concentrations in drain water from existing systems in Coast Range alluvial sediments are not predictable from a regionalized assessment of shallow ground-water concentrations derived from observation-well data. Prediction of selenium concentrations for future drainage systems presents a particularly difficult problem because of highly variable geohydrologic and ground-water quality conditions at different sites.
- Accurate predictions of selenium concentrations for new drainage systems probably will require relatively detailed site-specific data on the depth distribution of selenium and the local geohydrology.
- Even after the most soluble forms of selenium are leached from the soil by early irrigation, continued irrigation results in recharge to ground water that contains lower, but still undesirably high, selenium concentrations (10 to 50 µg/L). Therefore, long-term management alternatives must address the continued presence of such selenium concentrations in shallow ground water.
- Continuation of present management practices will sometimes result in selenium concentrations in the San Joaquin River and Mud and Salt Sloughs that exceed Federal and State criterion for protection of aquatic life.
- Selenium concentrations in the sloughs and the river can be decreased by reduction of selenium loading and addition of dilution water from low selenium sources. Conjunctive management of the timing of selenium loading and addition of dilution water may help meet water-quality criteria.

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