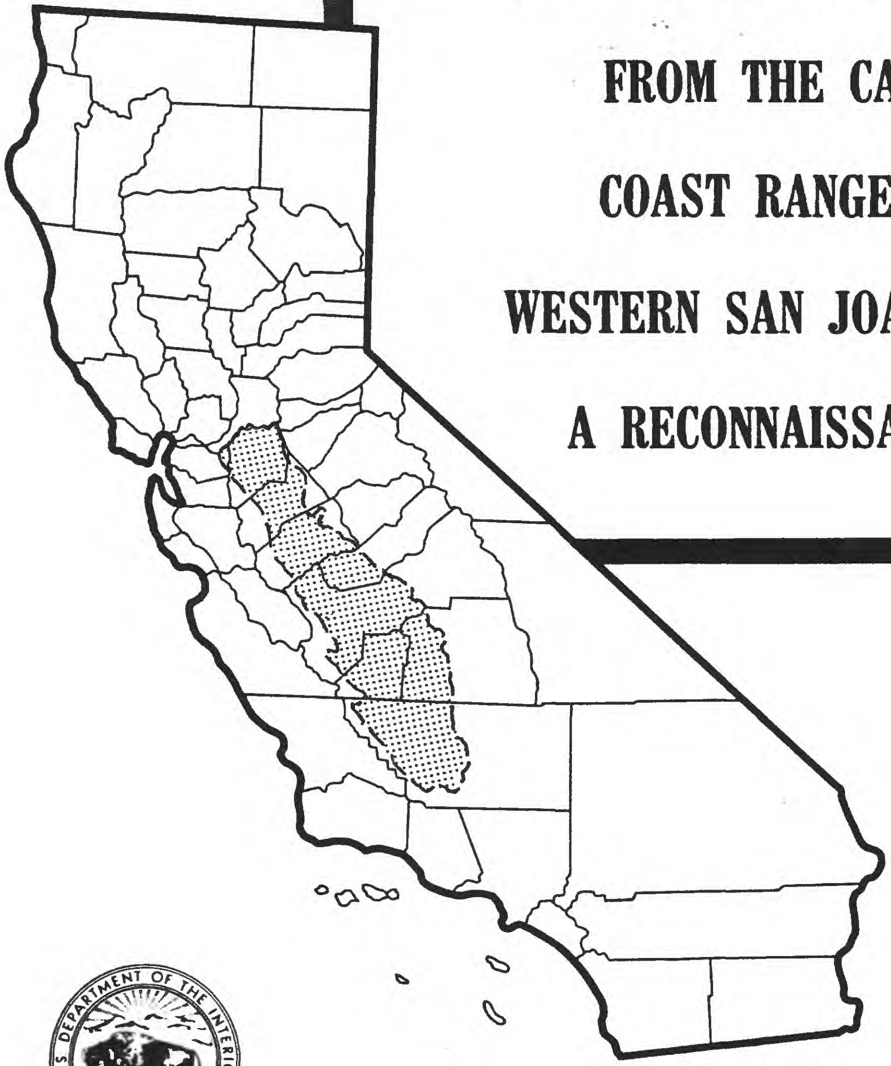
GEOLOGIC SOURCES, MOBILIZATION, AND TRANSPORT OF SELENIUM FROM THE CALIFORNIA COAST RANGES TO THE WESTERN SAN JOAQUIN VALLEY: A RECONNAISSANCE STUDY



U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 90-4070

Prepared in cooperation with the
SAN JOAQUIN VALLEY DRAINAGE PROGRAM

This report was prepared by the U.S. Geological Survey in cooperation with the San Joaquin Valley Drainage Program.

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.

Inquiries concerning the San Joaquin Valley Drainage Program may be directed to:

San Joaquin Valley Drainage Program
Federal-State Interagency Study Team
2800 Cottage Way, Room W-2143
Sacramento, California 95825-1898

GEOLOGIC SOURCES, MOBILIZATION, AND TRANSPORT OF SELENIUM FROM THE CALIFORNIA COAST RANGES TO THE WESTERN SAN JOAQUIN VALLEY: A RECONNAISSANCE STUDY

By Theresa S. Presser, Walter C. Swain, Ronald R. Tidball, *and* R.C. Severson

---

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 90-4070

Prepared in cooperation with the

SAN JOAQUIN VALLEY DRAINAGE PROGRAM

6439-62

Menlo Park, California
1990

U.S. DEPARTMENT OF THE INTERIOR
MANUEL LUJAN, JR., *Secretary*

U.S. GEOLOGICAL SURVEY
Dallas L. Peck, *Director*

For sale by the Books and
Open-File Reports Section,
U.S. Geological Survey
Federal Center, Box 25425
Denver, CO 80225

For additional information write to:
T.S. Presser
U.S. Geological Survey, WRD
345 Middlefield Road, MS 435
Menlo Park, CA 94025

CONTENTS

FIGURES

TABLES

Conversion Factors

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

Multiply	By	To obtain
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre-foot (acre-ft)	1,233	cubic meter (m^3)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
foot (ft)	0.3048	meter (m)
inch (in.)	25.4	millimeter (mm)
mile (mi)	1.609	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)

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

$$°F=1.8(°C)+32$$

By weight:
microgram per gram (µg/g) is equivalent to parts per million (ppm)
1 microgram (µg) = 10^{-6} gram (g)

For concentrations of dissolved solids less than approximately 7,000 mg/L:
milligrams per liter (mg/L) is equivalent to parts per million (ppm)
micrograms per liter (µg/L) is equivalent to parts per billion (ppb)
1,000 micrograms per liter (µg/L) = 1 milligram per liter (mg/L)

Abbreviations used:

µg/L	microgram per liter
mg/L	milligram per liter
meq/L	milliequivalent per liter
ppm	parts per million
µm	micrometer

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.

GEOLOGIC SOURCES, MOBILIZATION, AND TRANSPORT OF SELENIUM FROM THE CALIFORNIA COAST RANGES TO THE WESTERN SAN JOAQUIN VALLEY: A RECONNAISSANCE STUDY

By Theresa S. Presser, Walter C. Swain, Ronald R. Tidball, *and* R.C. Severson

Abstract

Studies of ecological damage at Kesterson National Wildlife Refuge in the western San Joaquin Valley, California, have implicated enrichment of the trace element selenium and increased salinity in subsurface agricultural drainage waters as major factors. Through reconnaissance sampling of waters, evaporative salts, soils, and bedrock from a geologically diverse 1,000-square-mile area, that encompasses 11 Coast Range basins draining into the western valley, the mobility of selenium has been traced and a conceptual model developed.

In the study area, elevated concentrations of selenium are seen in the extensive surficial exposures of the shales of the Upper Cretaceous-Paleocene Moreno and Eocene-Oligocene Kreyenhagen Formations which provide the primary sources of selenium to the west-central valley. These formations are not as extensively exposed to the north or to the south of the area implicated to be the source of selenium at Kesterson National Wildlife Refuge. Alternative source materials investigated, including Cretaceous and Tertiary sandstones, Pliocene-Pleistocene continental rocks, acid mine drainage from New Idria Mercury Mining District, and waters from the eugeosynclinal Franciscan assemblage and serpentinites, are comparatively barren of selenium.

Selenium is mobilized by oxidative weathering of these pyritic shales as evidenced by characteristic pH 4 seeps and abundant evaporative sodium and magnesium sulfate salts. The selenate form of selenium is concentrated in these soluble salts, which act as temporary geologic sinks. Theoretically, the open lattice structures of these hydrous minerals could incorporate the selenate (SeO_4^{2-}) anion in the sulfate (SO_4^{2-}) space. When coupled with an arid climate, fractional crystallization and evaporative concentration can occur creating a sodium-sulfate fluid that exceeds the U.S. Environmental Protection Agency limit of 1,000 µg/L for a toxic selenium waste.

For waters, the model also accounts for the generation of a wide variety of selenium transport patterns (elevated selenium in runoff and throughflow) and cycles (depleted selenium in the alluvial ground-water system), resulting from the various ways in which sulfur and selenium can be oxidized and reduced. For solid phase transport, the characteristic landscape instability associated with these steeply dipping marine shales, which is manifested by elevated levels of suspended solids in streams and by extensive mass wasting in the form of landslides, slumps, and mudflows, moves both salts and a residual insoluble form of selenium.

INTRODUCTION

The geologic setting and climate of the west-central San Joaquin Valley of California have created soil salinization problems. Agricultural productivity in this arid environment is linked not only to irrigation but also to disposal of irrigation waters used to leach salinized soils. Engineering solutions to save waterlogged agricultural lands have themselves created problems that affect the quality of irrigation return waters. It is in this part of the valley where the element selenium is being mobilized in subsurface agricultural drainage systems.

Biological effects of the contamination of this area by the naturally occurring selenium were observed in 1983 at Kesterson National Wildlife Refuge (KNWR) (fig. 1). The refuge was a wetland habitat of 4,620 acres with 1,280 acres of evaporation ponds on the San Joaquin Valley floor. The ponds were created as part of the San Luis Drain subsurface drainage facility (fig. 1). The observed effects attributed to selenium included bioaccumulation in the food chain and a 64 percent rate of deformity and deaths in embryos and hatchlings of wild aquatic birds (Presser and Ohlendorf, 1987); less than 2 percent is considered normal (Hoffman and others, 1987). Similar biological effects also were seen more recently in the 1987 through 1989 breeding seasons at

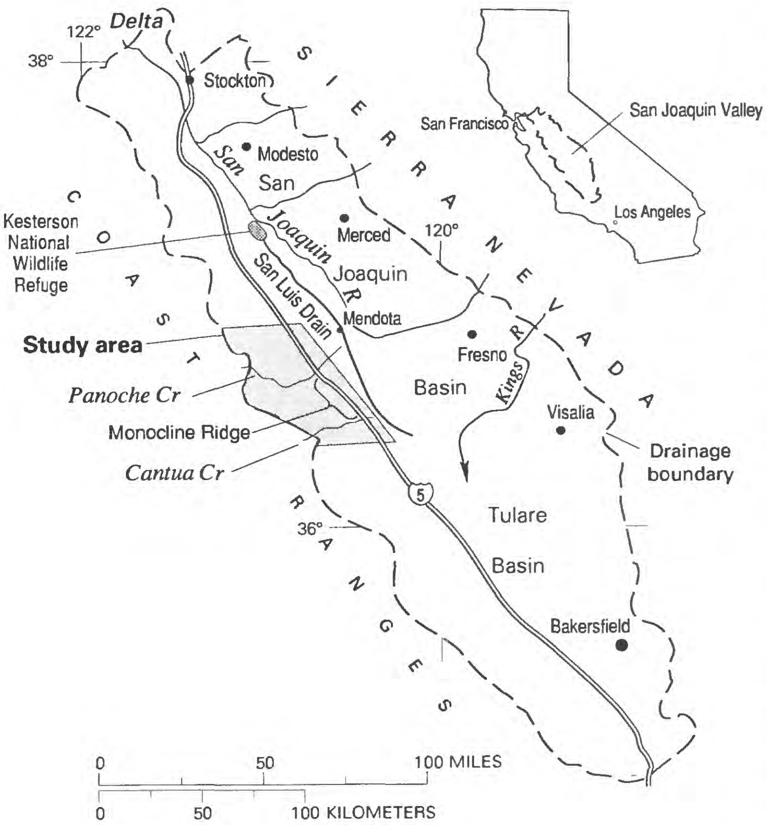


Figure 1. Location of the San Joaquin Valley and the study area in California.

agricultural drainage ponds in the hydrologically closed Tulare Basin, 96 miles south of KNWR (fig. 1) (Schroeder and others, 1988; Skorupa and Ohlendorf, 1989; Ohlendorf and Skorupa, 1990). Presently, shallow saline ground water is drained into approximately 6,680 acres of evaporation ponds; planned expansion would result in a five-fold enlargement of the complex within 10 years. Deformed waterbird embryos from five different species were found at four of five of the Tulare Basin ponds studied; the maximum rate of embryonic deformities approached 38 percent.

Presser and Ohlendorf (1987) stated that the unique environment created in the San Joaquin Valley has provided all the conditions necessary for selenium contamination to have occurred. Weathering of marine shales and sandstones of the Coast Ranges generates soluble sulfate minerals and produces highly saline alkaline soils. A semiarid to arid climatic regime results in evapotranspiration and the accumulation of salts on soil surfaces. The subsequent availability of abundant imported water for irrigation has enabled marginal lands to be brought into agricultural production. Beneath the surface, alluvial clay layers act as impediments to the downward movement of irrigation water, causing a rising water table and waterlogged soils. As a consequence, subsurface drains were emplaced to provide disposal of soil leachate waters that were eventually stored in a biologically active marsh which provided bioaccumulation opportunities. Throughout these processes it is the unique chemical properties of selenium that lead to its biogeochemical cycling and subsequent toxicity at KNWR. KNWR was at the north end of a general wetland area in the floodplains of the San Joaquin River used heavily by the Pacific Flyway migratory waterfowl population. Because of a loss of 95 percent of the historic wetland habitat in California, birds have been concentrated into remaining limited refuge areas, causing increased vulnerability to environmental toxicants and disease (Gilmer and others, 1982).

Geochemically, a cycle similar to that of sulfur has been proposed for selenium (Shrift, 1964). Characteristics common to the cyclable elements are that they exist as gases (hydrogen sulfide and hydrogen selenide) in at least one stage of transformation and that they undergo a change in oxidation state(s) (-2 → 0 → +4 → +6) (Konetzka, 1977). Steps chemically favored in the cycling of selenium include weathering of elemental selenium (Se^0) and metallic selenides (for example, ferroselite, $FeSe_2$) in the parent rocks or sediments to selenite (SeO_3^{2-}) under acidic and oxidizing conditions and selenate (SeO_4^{2-}) under alkaline conditions (Lakin, 1961a; National Academy of Sciences, 1976; U.S. Environmental Protection Agency, 1979). Selenite forms stable ferric oxide-selenite ($Fe_2(OH)_4SeO_3$) complexes resulting in the immobilization of selenium (Geering and others, 1968; Howard, 1977) while selenate forms compounds that are soluble and therefore mobile (Lakin, 1961a).

In 1984, subsurface drainage water in the area near KNWR contained up to 4,200 µg/L selenium in the selenate form (Presser and Barnes, 1985). This concentration exceeds the toxic waste limit of 1,000 µg/L selenium set forth by the U.S. Environmental Protection Agency (1980). Although KNWR has been closed to further drainage flows, selenium remains at high concentrations in the shallow ground water of the western valley (Deverel and others, 1984; California Department of Water Resources, 1988; California Regional Water Quality Control Board, 1988) and continues to be transported to the San Joaquin River and local evaporation ponds by agricultural drainage systems (Gilliom and others, 1989). The U.S. Environmental Protection Agency (1987) water quality criteria for selenium for the protection of freshwater aquatic life are 5 µg/L (4-day average) and 20 µg/L (1-hour average). It has been suggested that levels for protection of aquatic ecosystems be revised downward to 2 to 5 µg/L total selenium (Lemly and Smith, 1987).

Tracing of elements contained in subsurface drainage water at KNWR led to the consideration of the amount of selenium in soils in the San Joaquin Valley. Surveys by Tidball and others (1986, 1989) conducted in 1982 and 1985 showed the highest selenium concentrations (maximum ungridded value 4.5 ppm; geometric mean 0.68 ppm) in the western San Joaquin Valley below Monocline Ridge in the interfan area between Panoche Creek in the north and Cantua Creek in the south (figs. 1 and 2). The fact that selenium concentrations do not follow the creek drainages, as in the cases of arsenic and mercury, suggests that selenium in a soluble form has been leached out of the alluvial fans (Gilliom and others, 1989). On the valley floor, relict forms of selenium more resistant to solubilization may contribute a background of leachable selenium over time. Further tracing of elements contained in soils led to the consideration of primary geologic source materials, mainly marine sediments (shales and sandstones) in the Coast Ranges, which provide the alluvium and dissolved constituents that discharge into the San Joaquin Valley from the west.

Studies of selenium in geologic materials by the U.S. Department of Agriculture conducted from 1935 to 1941, the most comprehensive studies to date, showed selenium concentrations of up to 103 ppm in the Cretaceous marine Pierre Shale, which has extensive exposures in North Dakota, South Dakota, Nebraska, Wyoming, Colorado and New Mexico (Byers, 1935 and 1936; Byers and others, 1938; Williams and others, 1940 and 1941). Few analyses of selenium are available for water and geologic materials from California. A reconnaissance in 1941 (Lakin and Byers, 1941), which included 56 samples of shale and soil from 16 counties, showed an average of 1.4 ppm selenium. The highest value determined (28 ppm selenium) was that from the Coast Range Upper Cretaceous-Paleocene Moreno Formation in an area in the northwestern San Joaquin Valley. This area contains the same formations as those draining into the west-central San Joaquin Valley, but rainfall is somewhat higher, providing an increased opportunity for removal of soluble elements.

In a preliminary study in 1985 by the U.S. Department of the Interior of water quality, soils, sediment, and biota in other areas of the western United States containing seleniferous source rocks and using irrigation return flows from U.S. Bureau of Reclamation (USBR) water projects, 18 of 23 sites were identified as problem areas (U.S. Department of the Interior, 1985). The existing information suggests the potential for such waters to cause harmful effects on human health, fish, and wildlife, or reduce its suitability for beneficial use. In field reconnaissance studies in 1986-87, nine areas in seven Western States were studied by the U.S. Department of the Interior (Sylvester and Wilber, 1989). More detailed studies in four of these areas were started in 1988: the Salton Sea National Wildlife Refuge in California, Stillwater Wildlife Management Area in Nevada, the Kendrick Reclamation Project in Wyoming, and the Middle Green River Basin in Utah. Shallow groundwater quality in the Tulare Basin, California, is presently being studied by the U.S. Geological Survey (USGS). Some observations about the nature of these irrigation induced contamination problems that can be made (Sylvester and others, 1988), were that selenium clearly is the constituent of concern most frequently detected at elevated levels and the level of selenium measured in bird liver samples ranged up to 170 ppm, a concentration exceeding that which caused deformities at KNWR (63 ppm). This study is a part of a comprehensive investigation of the hydrology and geochemistry of the San Joaquin Valley by the U.S. Geological Survey in cooperation with the San Joaquin Valley Drainage Program.

PURPOSE AND SCOPE

Our study is the first one of a selenium source area, the California Coast Ranges (fig. 1), targeted as a problem area through association with KNWR. This reconnaissance level study, started in 1984, is designed to examine the geologic sources of selenium in the Coast Ranges and to present a conceptual model of the dynamic processes of selenium mobilization and transport in stream and debris flows from the Coast Ranges to the west-central San Joaquin Valley floor. Identification of geologic source formations is based on samples of soils, geologic materials, efflorescent salts and stream sediments and associated seep and spring waters. Stream transport of selenium is based on analysis of streamflows which are in response to precipitation events, perennial springs which discharge directly into stream channels, and ephemeral pools. Mobilization

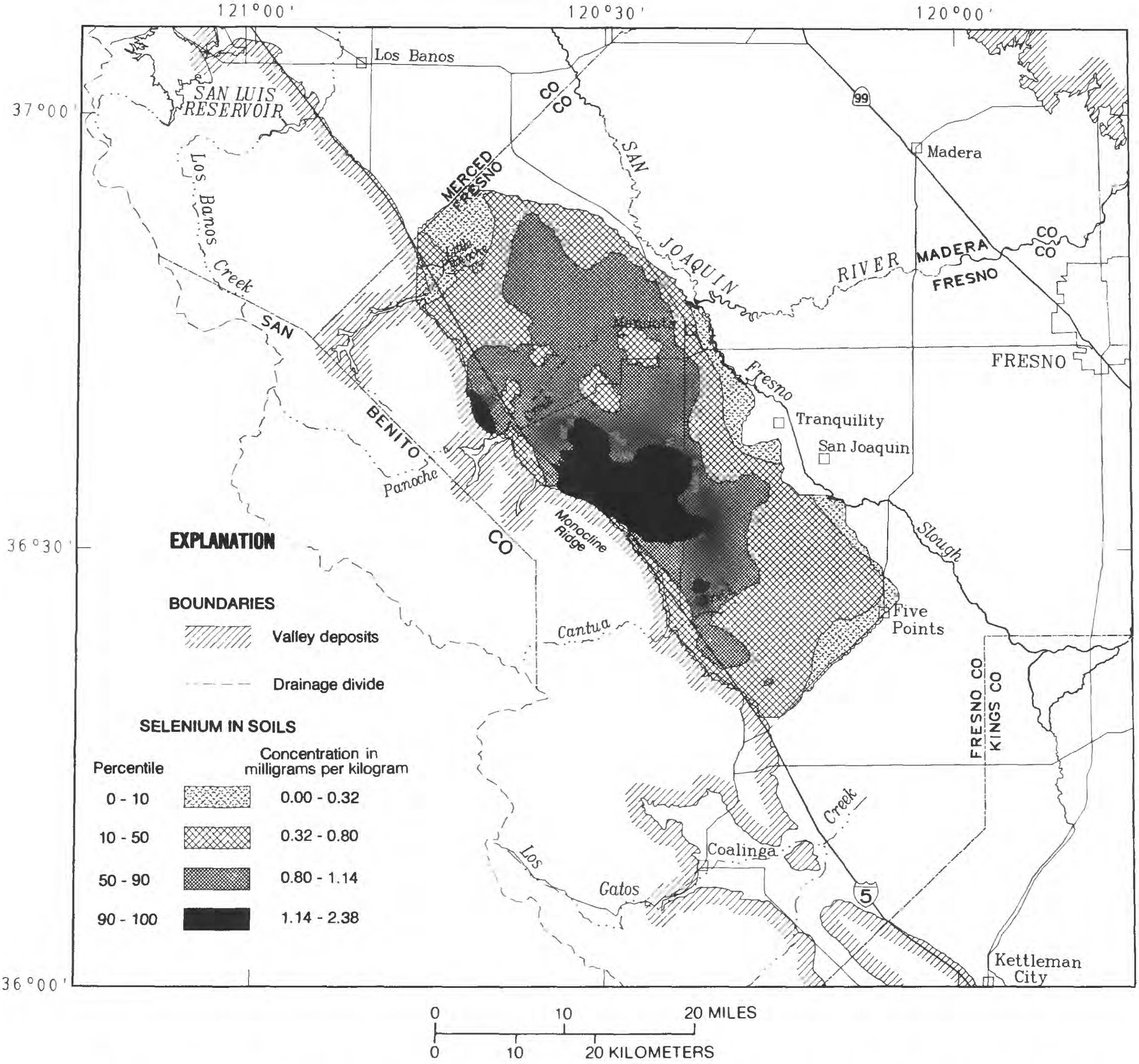


Figure 2. Areal distribution of estimated total selenium concentrations for the 66- to 72-inch-depth interval in soils of the central part of the western San Joaquin Valley. (Adapted from Tidball and others, 1986.) The values given in explanation are gridded (kriged) and contoured.

processes are inferred from chemical characteristics and transformations of the element selenium in samples derived from identified source formations.

The study area (fig. 3) in the Coast Ranges encompasses 11 drainage basins in approximately 1,000 mi^2. The area is bounded on the east by the San Joaquin Valley floor, on the west by the Coast Range divide, on the north by Little Panoche Creek and on the south by Salt Creek (immediately south of Cantua Creek).

ACKNOWLEDGMENTS

The authors wish to acknowledge the help of others in making this report possible: J. Cooper and staff in the San Joaquin District of the California Department of Water Resources, Fresno, California, for runoff samples and analyses; K. Arrouse in the California Soil Conservation Service, Hanford, California, for additional soil samples and analyses; and the Bureau of Land Management, the Silver

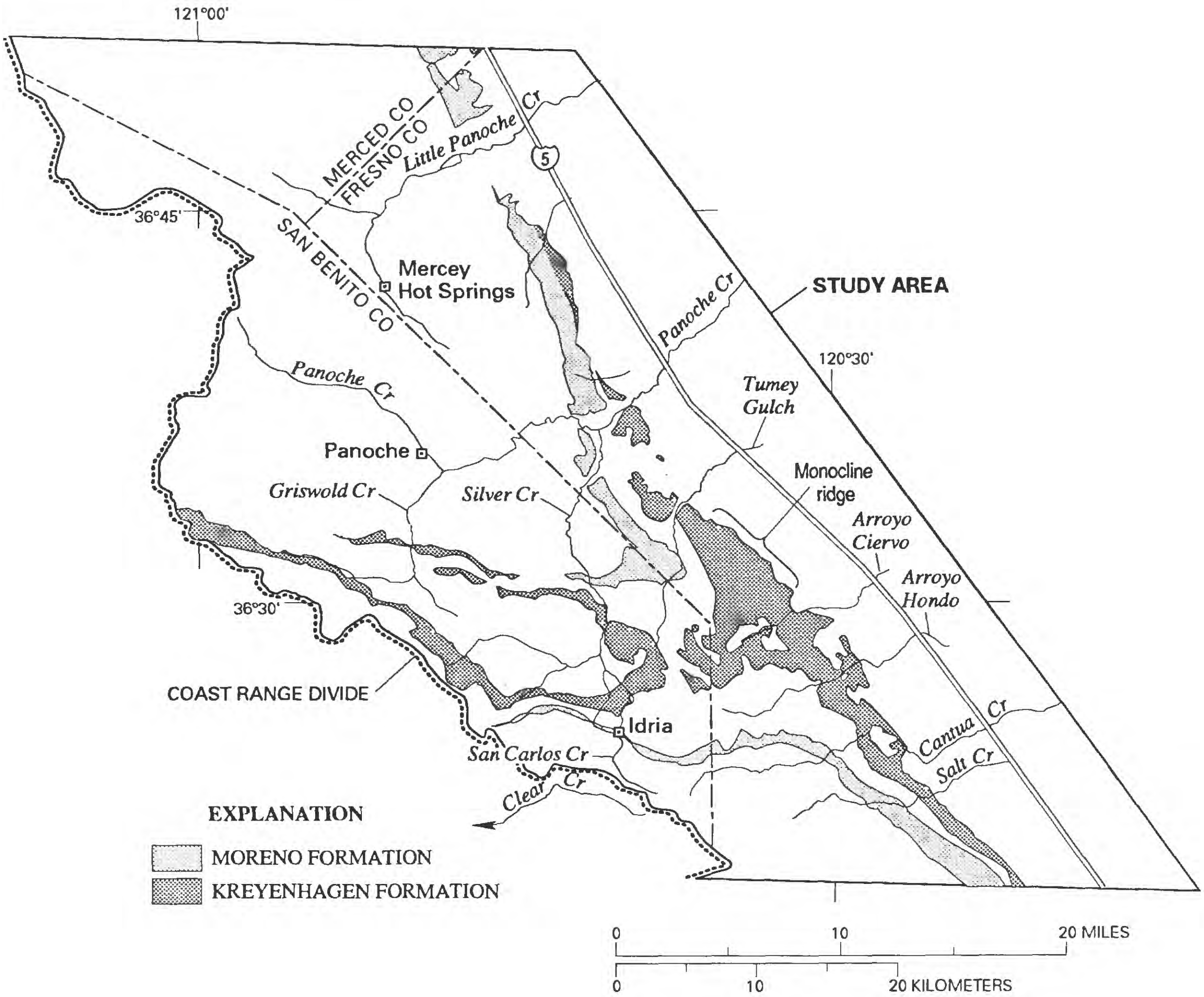


Figure 3. Surficial exposures of the Moreno and Kreyenhagen Formations and location of principal creeks in the study area. (Adapted from Dibblee, 1971, 1975; Bartow, 1988a, 1988b.)

Creek ranch personnel and other landowners for access to their lands and/or wells. Members of the U.S. Geological Survey who deserve thanks are: S.A. Wilson and staff of the Branch of Geochemistry, Denver, Colorado, for selenium analyses of geologic and stream sediment samples; T.L. Fries, Branch of Geochemistry, Menlo Park, California, for selenium analyses of transect samples; R.H. Mariner for assistance with x-ray diffraction analyses; and L.D. White and Mark Huebner for isotope analyses.

DESCRIPTION OF STUDY AREA

DRAINAGE SYSTEMS

In the semiarid to arid west-central San Joaquin Valley, subsurface drains are commonly used to remove saline shallow ground water from agricultural fields. Since 1960, drains have been installed in approximately 85,000 acres (California State Water Resources Control Board, 1985). It is estimated that 169,000 acres now need subsurface drainage and that this area will increase to 381,000 acres by the year

2020 (U.S. Bureau of Reclamation, 1984; California State Water Resources Control Board, 1985). Most of the subsurface drainage north of Mendota (fig. 1) is eventually discharged into the San Joaquin River, the only natural outlet from the valley. The San Luis Drain (U.S. Bureau of Reclamation, 1984) was built between 1968 and 1975 to extend the subsurface drainage system southward into the hydrologically closed basins beyond the San Joaquin River. Like the San Joaquin River it would, if completed, discharge to the north into the San Francisco Bay delta estuary (delta). Once into the delta system, these mixed waters would be a source of drinking water for southern California (through the California Aqueduct) and for the south San Francisco Bay area (through the South Bay Aqueduct) (Brown, 1985). The delta system then further connects to the immense, already stressed ecosystem of the San Francisco Bay (Greenberg and Kopec, 1986; Nichols and others, 1986). However, after 85 miles of the drain were completed, construction stopped in 1975 at KNWR because of appropriation restrictions. KNWR was originally designed with 1,280 acres of evaporation ponds to regulate flows to the delta.

GEOGRAPHIC SETTING

The Coast Ranges of California to the west of the San Joaquin Valley (fig. 1) are composed of several nearly parallel ranges of north-northwest trending mountains and intervening valleys. They are greater than 400 miles long and approximately 50 miles wide. The Coast Ranges evolved as a result of complex folding and faulting of geosynclinal sedimentary rocks of Mesozoic and Tertiary age (Davis and others, 1959; Norris and Webb, 1976; Presser and Ohlendorf, 1987). Deformation began in middle-Miocene time and continued at intervals until the middle-Pleistocene, when the mountains were raised to their present maximum height of 4,000 to 5,000 feet (Taliaferro, 1951).

GEOHYDROLOGY AND CLIMATE

Alluvial deposits in the central and south part of the western San Joaquin Valley derive primarily from the Coast Ranges of California. Sediment derived from the Sierra Nevada (fig. 1) is primarily confined to the eastern side of the valley, but some interfingering takes place on the valley floor. Sedimentary structures indicate that most of the deposits were transported by stream flows. The geomorphic character of the alluvium laid down by streams draining the east-central Coast Ranges reflects late Cenozoic uplift of the foothills and subsidence of the valley (Lettis, 1982). Lettis, however, suggests that superimposed on a background of tectonism is control by climate for deposition of the post-Tulare alluvial units. Field observations suggest that the alternating periods of deposition and landscape stability are caused principally by shifts from humid to more arid conditions.

The west side of the San Joaquin Valley lies in the rain shadow of the Coast Ranges (Davis and others, 1959). This causes the average annual precipitation in the higher elevations of 15 to 20 inches, while the valley floor receives approximately 7 inches (Rantz, 1969). The westside alluvial fans are complex and coalescing forms that are characteristic of areas with low, erratic rainfall. Heavy precipitation is infrequent but causes surface runoff, subsurface throughflow, extensive mass wasting, gully erosion and channel erosion (Lettis, 1982; Bull, 1964a).

Two types of streams, neither of which reach the San Joaquin River (fig. 1), are found in the study area: (1) short ephemeral streams which discharge into interfan areas that are characterized by debris flows; and (2) larger intermittent streams which discharge onto the larger fan heads, such as Panoche and Cantua Creeks. Infiltration and recharge occur during the winter rains; evaporation rates are high, ranging up to 90 inches per year. The greatest soil salinities occur at the distal fans and at areas between fans; the lowest occur at fanheads where streams discharge onto the fan. Soil compaction data indicate that natural recharge does not occur in interfan areas but only at fanheads (Belitz and Heimes, 1990).

The winter daily mean temperature in January is approximately 2 °C. The typical daily maximum temperature for summer is 38 °C (Lettis, 1982).

WEATHERING AND SALTS

Selenate (SeO_4^{2-}) concentrations in the inflow waters to KNWR were significantly correlated with sodium and sulfate (SO_4^{2-}) (Presser and Barnes, 1985). Recognition of this fact led to the identification on the valley floor of salts of hydrated evaporative sulfate minerals such as mirabilite ($Na_2SO_4{\bullet}10H_2O$) and bloedite [$MgNa_2(SO_4)_2{\bullet}4H_2O$], which contained elevated levels of selenium (up to 17 ppm). These same soluble sulfate salts are observed to form in the deep weathering profiles of the pyritic shales of the Coast Ranges.

These sulfate minerals show that the chemistry of weathering of reduced organic shale (oxidation of sulfide) is largely a reversal of the chemistry of its early diagenesis (reduction of sulfate) (Murata, 1977; Berner, 1984). During burial and compaction of marine sediments, sulfate from sea water is reduced and pyrite (FeS_2) is formed. When the sediment is then exposed to weathering during uplift and emergence, the reduced sulfur is again oxidized to the sulfate form (SO_4^{2-}). Ion exchange also plays a part in the cycling of elements as exemplified by the Upper Cretaceous marine Mancos Shale which is a major contributor to the dissolved mineral load in the Colorado River (Whittig and others, 1982). As Evangelou and others (1984) describe it, sodium and magnesium are preferentially adsorbed by phyllosilicates within the shale and calcium is precipitated as calcite and gypsum. This cycle is essentially reversed in the present-day environment, where dispersed gypsum and alkaline earth carbonates provide soluble calcium to displace adsorbed sodium and magnesium.

Some attention has been paid to general effects of salt on soils of arid and semiarid regions (Driessen and Schoorl, 1973) and quantitatively predicting salt production in wildland watersheds (Wagenet and Jurinak, 1978), but the study of the interrelation between the mineralogy of efflorescent salts on shales and soil materials has been limited (Whittig and others, 1982). Eight hydrated sulfate salts of sodium and magnesium, including mirabilite and bloedite, were found associated with the Mancos Shale by Whittig and others (1982).

Fractional crystallization during wet and dry cycles of the semiarid climate in the Coast Ranges could produce brines which deposit different minerals. During evaporation, calcium would be eliminated by precipitation as calcite or gypsum, resulting eventually in a sodium-magnesium-sulfate brine that could deposit bloedite (Murata, 1977). Trace elements contained in pyrite (for example, selenium) could be greatly concentrated by this "pumping effect" in minerals that result from weathering reactions (Barnes, 1986).

GEOLOGY

STRATIGRAPHY OF THE COAST RANGES

Simplified descriptions of the formations in the study area are given below in ascending order.

Jurassic

Ultramafic rocks--Includes ophiolite sequences and serpentinites at the base of the Upper Jurassic to lower Tertiary Great Valley sequence (Page, 1966). In the study area, the serpentine core rimmed by the Franciscan assemblage was uplifted in stages mostly in late Cenozoic time, and was locally extruded at the surface in middle Miocene time (Eckel and Myers, 1946; Linn, 1968). Thickness: 2,000 ft

Upper Jurassic to Upper Cretaceous

Franciscan assemblage (eugeosynclinal)--Dominant graywacke, but shale, altered mafic volcanic rocks (greenstone), chert and minor limestone are part of the assemblage; includes metamorphic rocks of the zeolite, blueschist (glaucophane schist) and eclogite facies. Ultramafic rocks, largely serpentinites, are associated with the assemblage, but are now excluded from it (Bailey and others, 1964). Thickness: 5,000 ft

The following geologic descriptions of sedimentary formations are taken from Anderson and Pack (1915) and Sullivan and others (1979).

Upper Cretaceous

Panoche Formation (marine)--Interbedded massive yellow-brown concretionary sandstone and thin gray to black shales and conglomerates; part of Great Valley sequence. Thickness: 5,000 to 20,000 ft

Upper Cretaceous to Paleocene

Moreno Formation (marine)--Foraminiferal and diatomaceous chocolate-brown to maroon platy, friable shales; lower section contains numerous beds of sandstones with concretions and dikes; upper section contains diatomaceous and organic shale more pure than those which occur later; forms extensive colluvial slopes; type locality is Moreno Gulch; part of Great Valley sequence. Thickness: 1,000 to 3,000 ft

Paleocene and Eocene

Lodo Formation (marine)--Gray shale or mudstone; includes Cantua Sandstone Member: yellow-brown sandstone with subordinate beds of gray shale. Thickness: 5,000 ft

Laguna Seca Formation (marine)--Previously considered as lateral equivalent of Lodo Formation; massive sandstone lacking organic shale and conglomerate (Payne, 1951); of minor extent.

Eocene

Domengine Sandstone (marine)--Tan to white sandstone and minor brown to pale-green shale and siltstone; of minor extent.

Eocene and Oligocene

Kreyenhagen Formation (marine)--Homogeneous white diatomite interbedded with chocolate-brown diatomaceous and foraminiferal shale and clay shale; feldspathic sandstone near base and quartzitic sandstone beds in higher horizons. Thickness: 1,500 ft

Oligocene

Tumey Formation (marine)--Assigned to Kreyenhagen at times; a sequence of brown to tan diatomaceous shale, and gray and buff to brown friable sandstone; base is coarse, pebbly sandstone (Atwill, 1935). Thickness: 1,600 ft

Miocene

Temblor Formation (marine)--Interbedded sandstones and siltstones; of minor extent.

Big Blue Formation--Serpentinous mudstone, sandstone and breccia; of minor extent.

Monterey Formation (marine)--Siliceous shale with diatomaceous, cherty and porcelaneous members; some shale of high organic content exists as lamina; of minor extent.

Santa Margarita Formation (marine)--Sequence of fine-grained, brown, pebbly or fossiliferous sandstone; of minor extent.

Miocene and Pliocene

Etchegoin Formations (marine and lacustrine)--Includes Jacalitos of former usage (Dibblee, 1973); cross-bedded bluish and brownish consolidated sandstones with reddish and greenish clay or clay shale and coarse sand; of minor extent.

Oro Loma Formation (non-marine)--A sequence of loose, reddish, sand, silt and gravel (Briggs, 1953); may be lateral equivalent of Jacalitos and Etchegoin (J.A. Bartow, U.S. Geological Survey, personal commun., 1990); of minor extent.

Pliocene and Pleistocene

Tulare Formation (continental)--Brown sands, argillaceous sand and mudstones containing gravel lenses; northern exposures reflect the influence of the Franciscan assemblage; contains the Corcoran Clay Member which is a homogeneous diatomaceous greenish to bluish silty clay. Thickness: 3,000 ft

STRUCTURAL GEOLOGY AND FLUIDS OF THE COAST RANGES

A simplified structural model of central and northern California is given by Irwin and Barnes (1975). It shows the Salinian block along the west side of the San Andreas fault and the Franciscan assemblage and Great Valley sequence along the east side. The Coast Range thrust fault is the regional contact between the Franciscan assemblage (lower plate) and serpentinite at the base of the Great Valley sequence (upper plate). A thick sequence of Tertiary sediments and some volcanic rocks locally overlie the region. Tectonic piercement of the Great Valley nappe by the underlying Franciscan rocks occurs at Mt. Diablo, the Diablo Range, New Idria, and Parkfield. In the northern Coast Ranges, most of the nappe has been removed by erosion, so the structurally lower Franciscan rocks are exposed over a wide area.

Characteristic fluids issue from these principal tectonic blocks. Magnesium bicarbonate waters (with low pCO_2) are common to ultramafic rocks and serpentinites of the Alpine type in the Coast Ranges (Barnes and O'Neil, 1969). The occurrence of a unique calcium-hydroxide water of pH greater than 11 is restricted to fresh ultramafics and is related to the near surface formation of serpentine; the process leaves lime (CaO) behind in a water saturated with brucite (Barnes and others, 1967). Chloride springs emanate from Great Valley sequence rocks (Panoche and Moreno Formations) and identify the Great Valley geochemical province. Fluids rich in carbon dioxide (with high PCO_2) are found in the Coastal geochemical province (Barnes and others, 1973a). The carbon dioxide in these springs, which issue from the Franciscan and along faults between the Franciscan and Great Valley sequence rocks, is postulated to be a separate phase being derived from metamorphic reactions at depth (Barnes and others, 1973b). Metamorphic fluids also participate in the alteration of serpentinite to silica-carbonate rocks which are the host of many mercury deposits in the Coast Ranges.

The New Idria piercement structure (Page, 1966) is a prominent feature in the area of the Coast Ranges implicated to be the source of selenium contamination at KNWR. Acid mine drainage from the New Idria Mining District discharges into Panoche Creek via Silver Creek. The district consists of about 20 quicksilver deposits that rim a fault-bounded core of serpentine and Franciscan rocks which have been extruded through beds of Upper Cretaceous Panoche Formation. The most productive mercury deposits are found in hydrothermally altered and fractured Panoche Formation along the perimeter of the core (Linn, 1968; Barnes and others, 1967; Eckel and Myers, 1946). The mine ranks second in all-time production of mercury in North America.

Although examples of all the previously described waters were identified in the study area, most waters were of the sodium- and sodium-magnesium-sulfate type, some with a pH of 4. Although the rules defined by Barnes and others (1975) were followed to classify the springs in the study area as chloride, bicarbonate or mixed chloride-bicarbonate, they did not address sulfate concentrations. In the original list of eight springs from Berkstresser (1968) in the study area, chloride was dominant in one, bicarbonate in two, and sulfate in three; one was a mixed chloride-bicarbonate and one a mixed bicarbonate-sulfate-chloride water. Therefore historically, the importance of sulfate waters have been ignored in the discussion to identify geochemical provinces.

Davis (1961) sampled streams of the Coast Ranges at low flow, when the contributions from ground water to stream flow would be maximized. He showed that both bicarbonate and sulfate waters are of perennial supply in the area. Streams were classified by comparing chemical analyses of water with the percentage of different geologic units exposed in the respective drainage areas which were determined by planimeter from the 1:750,000-scale geologic map of California. Bicarbonate waters were thought to be predominantly from the Franciscan assemblage and Cretaceous marine sediments and sulfate waters from Tertiary marine sediments and continental deposits. Davis included both the Panoche and Moreno Formations in his Cretaceous division, but noted that the Moreno is an exception to the general lithology of the rocks of Cretaceous age; it is predominantly a siliceous organic shale and in part diatomaceous. From the original Anderson and Pack (1915) description of the formation, it was concluded that the organic siliceous deposits were formed during a time when physical conditions were different from those prevailing in the rest of Cretaceous time.

Murata (1977) found minor occurrences of bloedite as an efflorescent mineral in the Miocene shale and other shales of the Diablo and Temblor Ranges of the Coast Ranges. He found that the occurrence of bloedite was noteworthy because it had not been previously reported except in regard to saline lakes. He also reported two spring waters and one brine water (in Tumey Gulch) which are sodium-sulfate waters with large amounts of magnesium. The brine pool water contained 134,000 mg/L sulfate and deposits bloedite.

STUDY DESIGN AND SAMPLING SITE LOCATIONS

The purpose of this reconnaissance level study is to identify the principal geologic sources of selenium within the Coast Ranges study area, the probable mobilization processes, and the pathways by which selenium is transported from the Coast Ranges to the west-central San Joaquin Valley floor. The phases attendant to the dispersal of such a chemically and biologically complex element as selenium are then organized into a comprehensive model.

Little information was available at the beginning of the study on selenium concentrations in primary geologic source materials. In California, an elevated value of selenium (28 ppm) was reported for the Moreno Formation, a marine Upper Cretaceous-Paleocene shale implicated from the fact that other Upper Cretaceous marine shales e.g. Pierre and Niobrara Shales, were elevated in selenium (Lakin and Byers, 1941). The geology of the study area is complex. Bedrock units include the Jurassic eugeosynclinal Franciscan assemblage, serpentinites, marine sedimentary formations ranging in age from Late Cretaceous to Miocene, and continental deposits. Also located in the study area is the New Idria Mercury Mining District whose cinnabar or accompanying pyrite could contain selenium. Boctor and others (1987) reported that the CO vein of metacinnabar ore at New Idria contained up to 6.15 weight percent selenium with most analyses of the vein containing between 1 and 2 percent; selenium analysis was not performed on the accompanying pyrite. They postulated that the sulfur in the mercury ore was derived at least in part by leaching of syngenetic, framboidal pyrite from the surrounding shales.

Interfan soils between Panoche and Cantua Creeks were found by Tidball and others (1986) to have the highest known selenium concentrations on the San Joaquin Valley floor. This suggests that one or more of the middle to late Tertiary marine formations present in the Monocline Ridge area above this interfan area have elevated selenium concentrations; Monocline Ridge is dominated by the Eocene-Oligocene Kreyenhagen Formation.

Based on this minimal information, the study design was developed to allow broad based sampling of soils and weathered geologic materials. Specific geologic formation locations were derived from the maps of Dibblee (1971, 1975) and Bartow (1988a, 1988b). Emphasis was placed on the Moreno and Kreyenhagen Formations whose surficial exposures are displayed on the study area base map in figure 3. Figure 4 shows the sampling sites of geologic materials for which total selenium was determined. The initial USGS study included 96 samples from 68 locations. Additional sampling and data in the study area was provided by the U.S. Soil Conservation Service (SCS) (K. Arrouse, written commun., 1988).

For the 21 SCS samples, soil type and pH of saturated pastes was determined in addition to total selenium. Forty-seven percent of the SCS sampling locations were classified as badlands, that is, lands 85 percent barren of vegetation; five locations were not designated.

Current concern locally to landowners and water managers is the impoundment of floodflows and suspended solids containing selenium. Agricultural interests have proposed the construction of flood control structures to prevent discharge of these flows to the Panoche Creek alluvial fan on the valley floor. Effects of grazing practices on runoff and erosion in

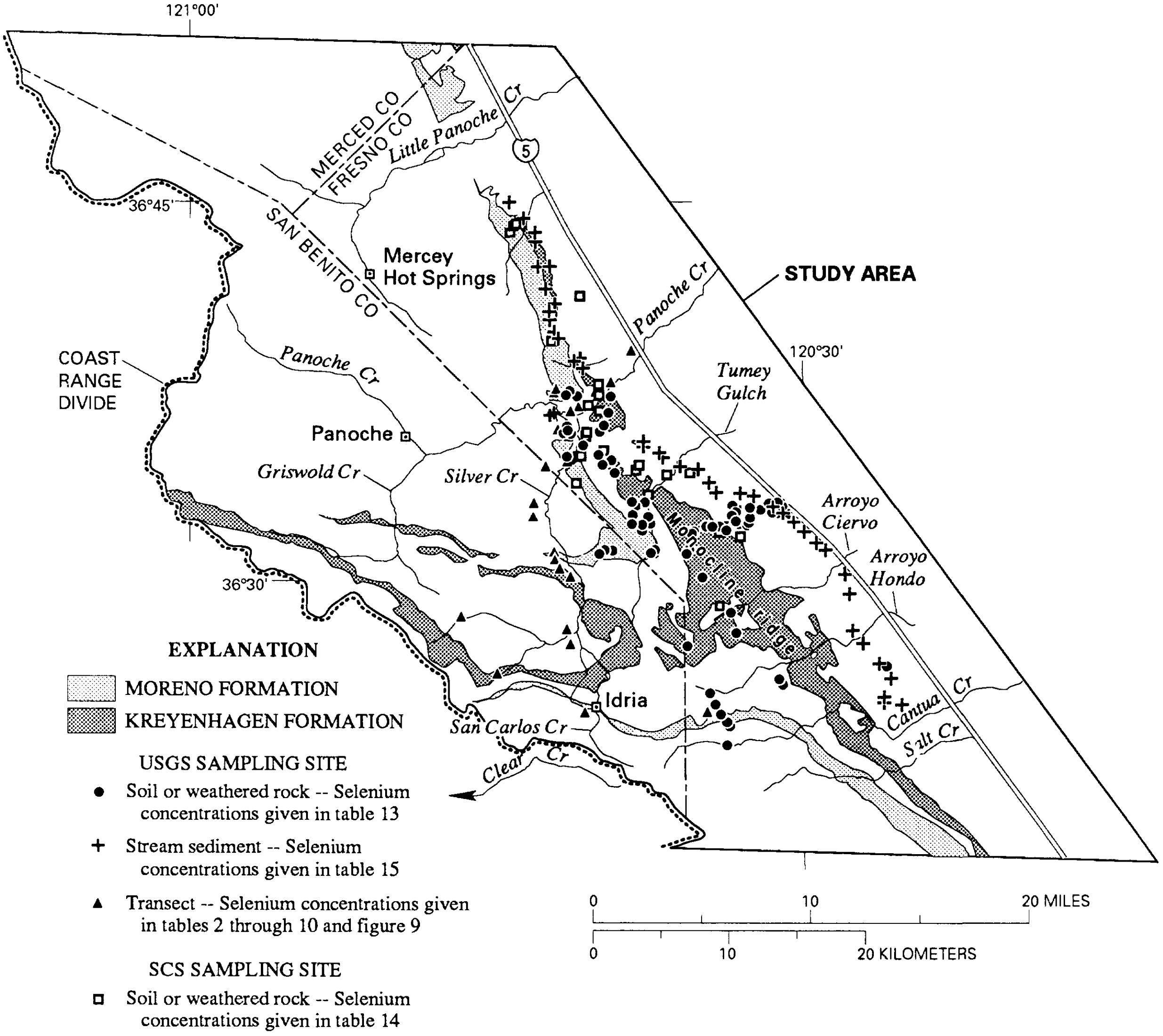


Figure 4. Areal distribution of the U.S. Geological Survey (USGS)and U.S. Soil Conservation Service (SCS) geologic sampling sites in the study area.

the area are suspected to be significant and adverse. Pronounced terracing and soil disturbance with associated mass wasting occurs under heavy grazing on steep, comparatively well vegetated north and east facing hillslopes.

To address this concern, stream sediments in ephemeral channels discharging directly to the valley floor were sampled. These 48 sampling sites are shown at 43 locations in figure 4. The samples were collected in 1986 with supplemental sampling in 1987 and 1988, all on a one-time basis. In addition, a longitudinal transect of the San Carlos/Silver Creek/lower Panoche Creek stream bed was taken. At the 21 transect sites shown in figure 4, the two banks and the center of the channel bed were sampled.

Selenium concentrations in the various geologic formations were evaluated by both direct and indirect methods. Evaporative salts and spring/seep waters were frequently used as proxies for direct analysis of soils and rocks in evaluating a given formation as a potential source of selenium. Relying on recent geologic mapping of the study area, water sampling points were selected on the basis of specific geologic formations affecting different drainages. Figure 5 shows the different drainages in detail in the study area and the 62 hydrologic sampling sites. These drainage basins, from north to south are: Little Panoche Creek, Moreno Gulch, Escapardo Canyon, Panoche Creek, Griswold Creek, Silver Creek, Tumey Gulch, Arroyo Ciervo, Arroyo Hondo, Cantua Creek and Salt Creek.

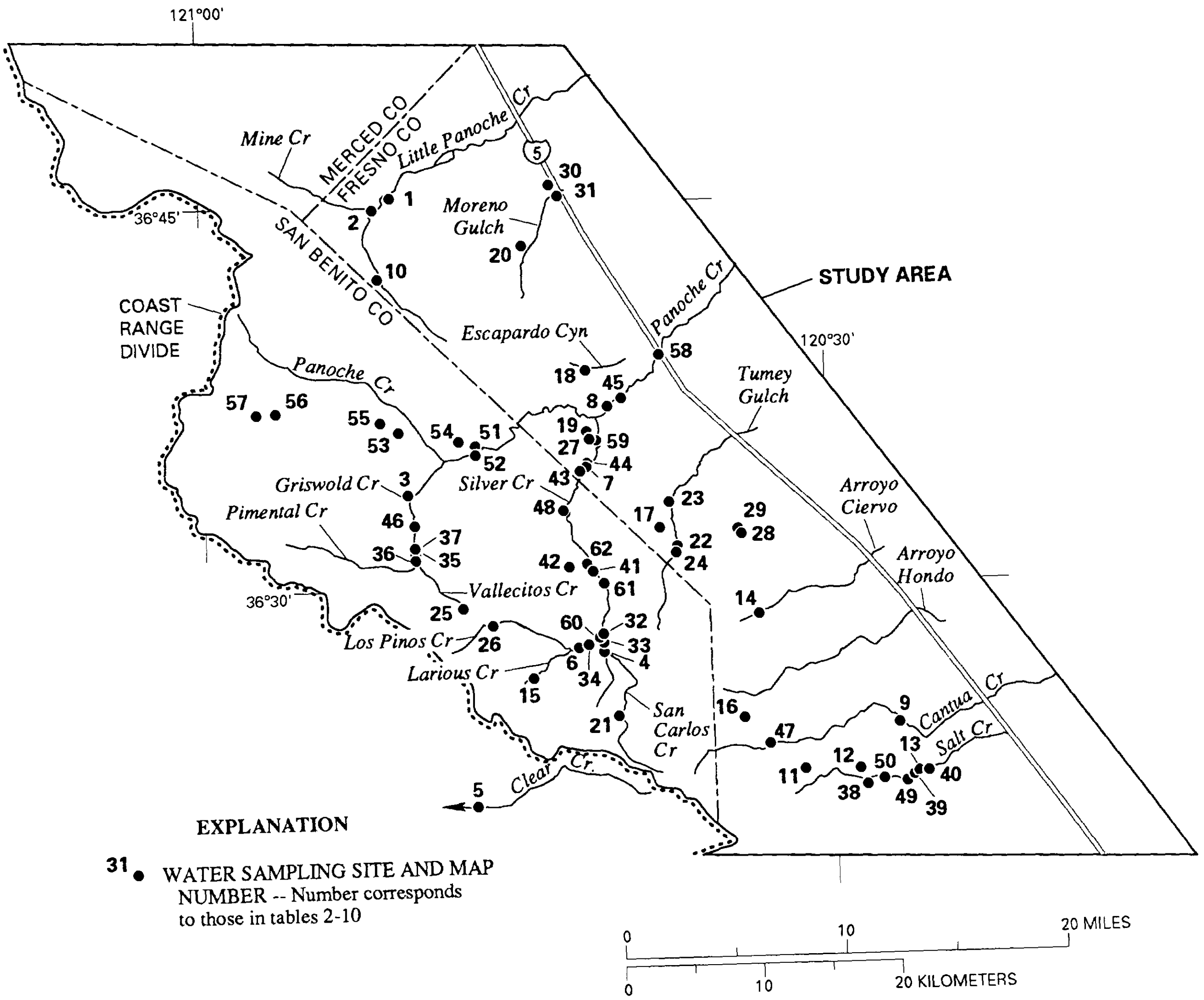


Figure 5. Location of creeks and water sampling sites in the study area.

In order to evaluate selenium transport temporally, water and evaporative salts from some sites were resampled periodically from 1984 to 1989. Water sampling was handicapped due to a continuing drought in the region and the paucity of water available even during the wetter years.

Samples collected in the latter part of the study may be representative of a water-stressed system. An example of this is shown in the five samplings of a perennial spring in the upper reaches of Panoche Creek drainage whose selenium concentration increased from 24 to 141 µg/L in the period from September 1985 to February 1989 as the drought progressed.

After sufficient information from the earlier years of the study had been accumulated, runoff sampling was considered. Because runoff events were relatively infrequent and short-lived, sampling was not successful until the winter of 1987-88 when the California Department of Water Resources installed computerized monitoring of precipitation events. The two runoff events sampled were in October 1987 and January 1988; there were no subsequent runoff events in 1988, or during the winter of 1988-89.

STUDY METHODS

Our methods of elemental analysis of waters were adapted for geochemical environments; complete sampling and analytical method references are given by Presser and Barnes (1985). In general, grab samples of water were filtered through 0.45-µm membrane filter and acidified for trace and major cation analysis. Major cations were analyzed by atomic absorption spectrophotometry (AAS) while major anions were measured by either colorimetry or ion chromatography. The trace elements selenium, arsenic and mercury were analyzed by vapor generation AAS; other trace elements were analyzed by sequential inductively coupled argon plasma atomic emission spectrometry.

Initial efforts to isolate the suspected toxicant selenium at KNWR were hampered by complex analytical methodology for aqueous samples (Presser and Barnes, 1984). Chemical complexities involved both the high salinities present in the water samples and the existence of the different species or oxidation states that are known to exist for selenium. These oxidation states are: SeO_4^{2-}, selenate (Se +6); SeO_3^{2-}, selenite (Se +4); elemental selenium (Se 0); and H_2Se and organic forms, (Se -2).

The method of choice for the analysis of selenium in water and soluble minerals proved to be hydride generation with heated quartz tube atomization and detection by atomic absorption spectrophotometry (Pierce and Brown, 1977; Gunn, 1981; Nakahara, 1983). Inherent in the hydride technique is the removal of gaseous selenide from its interfering background, as the gas is physically purged from the liquid sample. Great care must be taken however, in sample pretreatment, in a method to determine total dissolved selenium. Steps must be included both to digest organic selenium and to convert all forms to selenite, as only the +4 oxidation state is detected in the hydride method. After digestion of the sample, it proved imperative that conversion conditions used in the laboratory be optimized because too mild a reduction could lead to incomplete reduction of selenate and too rigorous a reduction to plating out of elemental selenium (Cutter, 1978; Presser and Barnes, 1984). It was estimated that failure to include the reduction step for the analysis of subsurface agricultural waters in the hydride generation technique could have accounted for up to 98 percent of the total selenium not being measured initially (Presser and Barnes, 1984). Recovery of selenium added averaged 98 percent; results of selenium analysis compared favorably with those from two independent laboratories (U.S. Fish and Wildlife Service and U.S. Geological Survey Central Laboratory, Denver) and within specified limits of a standard reference water sample (Presser and Barnes, 1984).

Because different sensitivities are exhibited for selenite and selenate in the hydride generation technique, this supposed disadvantage has potential for use in the selective determination of the different oxidation states of selenium (Presser and Barnes, 1984).

A sequential analytical procedure for determining the soluble forms of selenium was developed for shales and sediments. A solid sample was put into suspension with water, allowed to stand and then filtered. The filtrate was collected and analyzed for selenite and total selenium. The solids remaining on the filter paper were resuspended in water and analyzed for total selenium.

Soils and geologic materials were sampled by auger or from exposed soil profile and integrated over various depths up to 6 feet. In the laboratory, all samples were air dried, sieved through a 2 mm stainless steel screen, and a subsample was ground in a ceramic mill to pass a 100 mesh screen. During the dry season, stream sediment samples at depths of 0.5 to 1.5 inches were collected which consisted of the less than 2 mm size particles.

Total selenium was analyzed in solids by hydride generation AAS after digestion in acids (nitric, sulfuric, perchloric, hydrofluoric, and hydrochloric) or persulfate and acids (Briggs and Crock, 1986).

Minerals were identified by x-ray diffraction using a Nicolet Model I2 Diffractometer. X-ray analysis was difficult because of the transient nature of some of the hydrated salts. These are labile salts which change in response to changes in temperature and humidity.

Computer programs used for reduction of data were SOLMNEQ (Kharaka and Barnes, 1973; Kharaka and others, 1988) and SNORM (Bodine and Jones, 1986). SOLMNEQ gives solution-mineral equilibrium data for 162 aqueous species and 158 minerals at the measured temperature. SNORM gives the types of salts (from a possible list of 63) which would crystallize if the water were evaporated to dryness at 25 °C. Stiff (1951) plots were used to show comparisons of water type and ionic composition.

MODELING OF THE SOURCES, MOBILIZATION, AND TRANSPORT OF SELENIUM

The conceptual model consists of three main components: sources of selenium; selenium mobilization mechanisms; and selenium transport mechanisms. Under each component are listed general statements of observations and consequences deduced from the collected data.

Data used in the delineation of the model are given in tables 1 through 15. Efflorescent salts identified in the study area are given in table 1. Waters sampled were divided into nine categories: creeks (table 2); springs (table 3); acid seeps in the Moreno Formation and acid mine drainage from New Idria Mercury Mine (table 4); evaporatively concentrated ephemeral streams (table 5); seeps in the Moreno Formation, Kreyenhagen Formation, and Panoche Formation (table 6); integrated watershed samples (table 7); headcuts, channel seeps and contact seeps (table 8); wells (table 9); and runoff (table 10). Given in these tables are location, concentration of selenium in salts, salt type, concentration of selenium in stream sediment transects, concentration of selenium in waters, water type, and water chemistry. Trace element analyses for selected representative water samples are given in table 11. Headspace gas analyses for selected acid seep samples are given in table 12. Solids sampled were divided into four categories: surficial materials collected by the USGS (table 13); surficial materials collected by the Soil Conservation Service (table 14); stream sediments (table 15); and a longitudinal transect of San Carlos Creek/Silver Creek/lower Panoche Creek (tables 2-10). Given in these tables are location and selenium concentration in the solid.

SOURCES OF SELENIUM

- **A sulfate/selenate chemical regime dominates drainage from the eastern flanks of the central Coast Ranges.** Cretaceous and Tertiary marine sediments dominate the eastern flanks of the central Coast Ranges. These marine shales and sandstones weather into a sulfate regime evidenced by extensive surficial salt efflorescences and evaporites at water and shale surfaces. A list of the eighteen predominately sodium and magnesium sulfate minerals found in the study area are given in table 1. Chemistry of stream and seep waters of the drainage basins in the study area is controlled by sodium and magnesium sulfates and contain selenium as selenate (tables 2-10; fig. 5). Characteristic of these waters is high dissolved solids (up to 421,409 mg/L). The highest concentration of sodium is 44,000 mg/L, magnesium, 56,000 mg/L, and sulfate, 318,000 mg/L. The significance of the selenium concentrations in these waters and salts will be discussed specifically as they relate to the aspects of the model given below.

- **Water issuing from other chemical regimes is barren of selenium.** Previously reported types of waters in California in the Coast Ranges are: bicarbonate waters from the Franciscan assemblage; chloride waters from the Great Valley sequence (Panoche and Moreno Formations) and a zone of hydrothermal alteration (Mercey Hot Springs); ultrabasic, high magnesium waters from serpentinites; and acid mine drainage from the New Idria Mercury Mining District. In our reconnaissance these water types are represented by the following.

Waters influenced by both the Franciscan assemblage and Tulare Formation, Little Panoche Creek and Mine Creek, contain sodium and bicarbonate as major components and less than 2 µg/L selenium (table 2). Secondary chloride shows up in Little Panoche Creek because of contact with the Panoche Formation. Monthly sampling of Little Panoche Creek by the USBR from March 1984 to May 1986 showed no concentration of selenium greater than 2 µg/L (U.S. Bureau of Reclamation, 1987).

Alkaline seeps surveyed as part of the Great Valley sequence in the Panoche Formation (table 6) are mainly sodium-chloride waters that contain less than 2 µg/L selenium. One extremely concentrated magnesium-sulfate water was found but it contains less than 2 µg/L selenium. Additionally, efflorescent salts from the Panoche are predominantly halite (table 6).

Waters discharging from serpentine, Larious Creek and Clear Creek at the San Benito River, are of the magnesium-bicarbonate type (table 2). The creek downstream of the New Idria Mercury Mine, San Carlos Creek, at its confluence with Silver Creek, yields a magnesium-sulfate water (table 2) showing influence by both serpentine (Mg) and acid mine drainage (H_2SO_4). All these waters contain 3 µg/L selenium or less.

Zones of hydrothermal alteration and mercury deposits exist at the south end of Little Panoche Valley in the study area. Some are near Mercey Hot Spring, a sodium-chloride spring with less than 2 µg/L selenium (table 3). This spring water was included among the waters in which trace elements were analyzed and contains 0.1 µg/L mercury (table 11).

Water from the New Idria Mercury Mine discharges into San Carlos Creek and consequently into Silver and Panoche Creeks. The water is an acid (pH 3) iron-magnesium-sulfate water containing less than 2 µg/L selenium (table 4). The constituents of this water are interpreted to be derived from the oxidation of the sulfides associated with the mercury ore. Dissolved solids concentrations are as high as 9,553 mg/L. High concentrations of metals are transported in this pH 3 water (iron 640 mg/L, aluminum 88 mg/L, manganese 10 mg/L, zinc 3.0 mg/L, nickel 1.4 mg/L, cobalt 0.6 mg/L, cadmium 0.1 mg/L and chromium 0.07 mg/L) (table 11). Additionally at New Idria a transect (table 4, fig. 4) was taken across San Carlos Creek below the discharge point from the mine. The bank material contains 0.6 ppm selenium. The channel material, including an iron-hydroxide mat, is mostly jarosite and the efflorescent salts are hexahydrite, bloedite, and epsomite; both mat and salts contain less than 0.1 ppm selenium.

- **Springs and intermittent flow of lower reaches of streams do not represent a significant source of selenium.** Our early reconnaissance of Panoche and Cantua Creeks, two of the larger creeks draining into the western valley, showed selenium concentrations of 5 and 6 µg/L selenium, respectively (table 2). Sampling by the USBR at monthly intervals (not in response to precipitation events) from March, 1984 to May, 1986 showed an average selenium concentration for Panoche Creek of 3.7 µg/L with a high of 10 µg/L; a smaller sampling of Cantua Creek showed an average of 6 µg/L (U.S. Bureau of Reclamation, 1987). Silver Creek and Griswold Creek, tributaries to Panoche Creek showed concentrations of selenium of 2 and 13 µg/L (average) respectively (table 2). Other creeks in the study area were not represented by intermittent reaches.

In the vicinity of Salt Creek, a main tributary to the valley, are located Harris and Greenwater Springs and a developed spring near the creek itself. All these spring waters contain less than 2 µg/L selenium (table 3). Harris spring yields a sodium-bicarbonate water; Greenwater and the developed spring yield sodium-sulfate waters. Ciervo Spring in Arroyo Ciervo yields a sodium-magnesium-calcium-sulfate water containing less than 2 µg/L selenium (table 3).

Larious Spring on Larious Creek yields a sodium-sulfate water containing less than 2 µg/L selenium (table 3). It was sampled when there was no flow in the creek. Larious Creek is a tributary to Silver Creek, which discharges into Panoche Creek.

- **Geologic samples from the Moreno and Kreyenhagen Formations show elevated selenium.** From a survey of 117 geologic samples (fig. 4; tables 13 and 14) taken in 1986 in the area, the marine sedimentary Upper Cretaceous-Paleocene Moreno Formation and the Eocene-Oligocene Kreyenhagen Formation (which traditionally includes the Tumey Formation) contain elevated levels of selenium, with medians of 6.5 and 8.9 ppm respectively (fig. 6; table 16). Selenium contents of these shales are compared with the following medians (fig. 6; table 16): the Upper Cretaceous Panoche Formation, 1.0 ppm; the Paleocene-Eocene Lodo Formation, 0.8 ppm; the Eocene Domengine Formation, 0.4 ppm; the Pliocene-Pleistocene Tulare Formation, 1.2 ppm; and the non-marine rocks, 0.7 ppm. The Panoche and Lodo Formations contain extensive sandstones. The Miocene Series is not well represented in the study area and therefore cannot be assessed. The Oligocene is represented by the Tumey Formation (median 7.3 ppm selenium). The Moreno

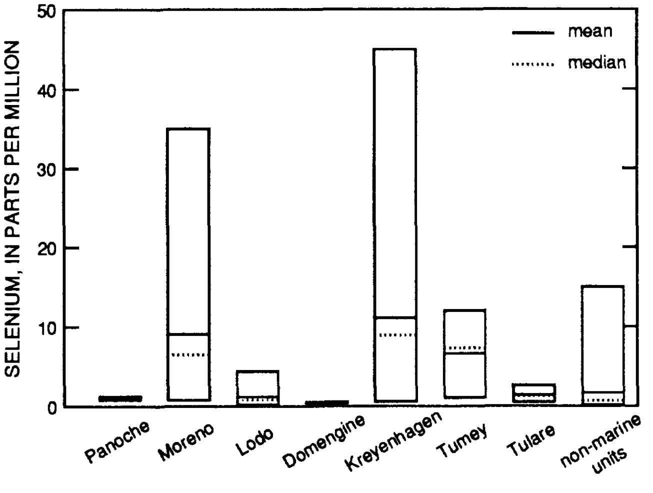


Figure 6. Mean, median, and range of selenium concentrations in geologic materials by formation.

and Kreyenhagen Formations are not as extensively exposed to the north or to the south of the area implicated to be the source of selenium at KNWR.

In the study area, the over-all median for seleniferous formations is 7.3 ppm selenium; for non-seleniferous rocks the median is 0.8 ppm selenium (table 16). The highest selenium concentrations measured are 45 ppm for a sample from the Kreyenhagen Formation and 35 ppm for a sample from the Moreno Formation. Lakin's compilation (1961b), the most complete to date, of Cretaceous sedimentary rocks in the United States, showed the upper part of the Niobrara Shale and the lower part of the Pierre Shale to contain the highest selenium concentrations and to average 20 ppm selenium (range 0.6 to 103 ppm). The median values of weighted-average concentrations of selenium in the Pierre and Niobrara Shales, were 2.2 and 6.5 ppm selenium respectively. Lakin further concluded that in sedimentary rocks, concentrations of greater than 2 ppm selenium was abnormal.

SELENIUM MOBILIZATION MECHANISMS

- **Pyritic shale is weathered.** Berner (1984) considers pyrite to be the main source of sulfur in marine shales forming from the reduction of sulfate-containing pore waters during diagenesis. Pyrite, FeS_2, the reduced iron sulfide, is disseminated throughout the Coast Range marine sediments. In the study area, it constitutes approximately 1 percent of the sandstones and up to 10 percent of the siltstones and shales (Ivan Barnes, U.S. Geological Survey, personal commun., 1985). The general reaction for weathering (oxidation) of pyrite (Berner, 1984; Garrels and Lerman, 1981) modified to show the inclusion of sulfuric acid (H_2SO_4) is:

$$\begin{aligned}&8FeS_2+8CaCO_3+7MgCO_3+7SiO_2+23H_2O+15O_2\rightarrow\\&15CH_2O+8CaSO_4+4Fe_2O_3+7MgSiO_3+8H_2SO_4 \quad (1)\end{aligned}$$

Sulfate ion (SO_4^{2-}), acid ion (H^{+1}), and ferric oxide (Fe_2O_3) or hydrated ferric oxide (limonite) are end products. The oxidation of reduced iron from pyrite is postulated to be biologically mediated/microbially catalyzed (Stumm and Morgan, 1981).

Physical and chemical weathering of diagenetic sediments in the Coast Ranges is extensive and pervasive; no unweathered shale material was available from the study area. Large amounts of oxidized iron are seen in veins and joints in the sediments of the study area. In a humid climate, the iron would be almost all oxidized and precipitated as the oxide; in an arid climate where soluble compounds may persist, ferrous sulfate (ferrohexahydrite) and ferric sulfate (jarosite) would also be produced (Krauskopf, 1967). These latter minerals have been identified as coatings or crusts on sediments of the Coast Ranges (ferrohexahydrite is soluble; jarosite is less soluble) and are the subject of further investigation on the span of oxidation potentials for the weathering of the primary minerals.

- **Selenium occurs in association with sulfur.** Selenium can occur in substitution for sulfur (Wedepohl, 1970; Coleman and Delevaux, 1957) such as in the selenium analog of pyrite, ferroselite ($FeSe_2$), because of its similar chemical and physical properties. It occurs in concentrations of as much as 1000 ppm in remobilized sulfides associated with oxidized sandstone-type uranium deposits (Davidson, 1963; Coleman and Delevaux, 1957) and in the Sudbury pyrites at between 50 and 100 ppm (Hawley and Nichol, 1959). Krauskopf (1955) cites a maximum of 28 ppm for selenium in sedimentary pyrite in his report on enriched concentrations of metals in shales, organic deposits in swamps, and semiarid slopes and basins.

Significant selenium enrichment in geologic materials was thought to have occurred through the increased volcanic activity of the Cretaceous Period. Davidson and Powers (1959) summarized the earlier literature on the primary source of selenium. One alternative is that the selenium contained in the enriched Niobrara and Pierre Shales was a primary constituent of extrusive and intrusive igneous rocks which were eroded and deposited into the Cretaceous sea (Trelease and Beath, 1949). A second alternative is that these two formations may have acquired selenium from gaseous emanations and volcanic dust which accompanied eruptive activity and which were subsequently washed into the oceans by rainfall (Byers, 1936; Byers and others, 1938). The data of Davidson and Powers (1959), from a limited sample set from the western United States, show that the volcanic rocks composed of ash are more seleniferous than crystalline ones. In either case, the Cretaceous sea provided an environment in which selenium could be biologically concentrated in bottom sediments (Presser and Ohlendorf, 1987) to yield the enriched shale concentrations seen today. Black shales have been noted as containing elevated concentrations of minor elements (Krauskopf, 1955; Vine and Tourtelot, 1970) but few reliable selenium data are available (Davidson and Lakin, 1961; Lakin, 1973; Desborough and others, 1984).

Pyritic cuttings from a 16,000 foot-deep well located on the San Joaquin Valley floor near Mendota (outside the study area) may be representative of unweathered material. The well encompasses the geologic section from the Tertiary non-marine rocks to the Upper Cretaceous Panoche Formation. Preliminary analysis on a small sample set from seven different intervals shows an average concentration of 7 ppm selenium for pyrite samples and 1.7 ppm for whole rock samples.

- **Acid sulfate seeps and soils are generated.** The sulfuric acid shown produced in equation 1 is in the dissociated form ($H^{+}+SO_4^{2-}$). Evidence for the oxidation of disseminated pyrite or ferroselite in the study area is shown in the occurrence of acid (pH 4) sodium and magnesium sulfate seeps (table 4) issuing from landslides in the Moreno Formation. Five examples of these pH 4 seeps with elevated levels of selenium were found in widely separated areas of the Moreno Formation: Arroyo Hondo (up to 420 µg/L selenium), Tumey Gulch tributary (up to 211 µg/L selenium), Escapardo Canyon (42 µg/L selenium), the confluence area of Silver and Panoche Creeks (up to 38 µg/L selenium), and Moreno Gulch (87 µg/L selenium) (fig. 5). The pH ranges from 3.6 to 4.5. Acidity (species titratable with base) ranges up to 67 mg/L H^{+} and amounts of sulfate up to 50,000 mg/L. Representative pH 4 seep sample analyses are shown as Stiff plots along with the analysis of the acid drainage water from the New Idria Mining District (fig. 7*A*). With these plots, comparison of water type and ionic content can be made.

Besides elevated levels of selenium, these acid waters contain high levels of dissolved metals (table 11); maximum concentrations are: 188 mg/L aluminum, 95 mg/L manganese, 13 mg/L zinc, 8.8 mg/L nickel, and 1.7 mg/L cobalt. Iron occurs at approximately the 0.4 mg/L level. Again the analysis of water from the New Idria Mercury Mine (pH 3) is shown for comparison; this water contains up to 640 mg/L iron but less than 2 µg/L selenium.

To determine if carbonic acid (H_2CO_3) is a contributing factor to the acidity of pH 4 samples, the chemistry of several headspace gases were analyzed (table 12). These measurements allowed the calculation of (pCO_2) and milligrams per liter of H_2CO_3. Concentrations of carbon dioxide (CO_2) were low, with a high value of 0.07 atmosphere measured at Tumey Gulch tributary seep III. This seep water along with the water at San Carlos Creek at New Idria proved to be anoxic when compared with air saturated water at 15 °C. The analysis also revealed that several of the seeps contained nitrous oxide (N_2O), notably the upper seep at Arroyo Hondo, which could be an indication of microbial activity (Pelczar and others, 1986).

From the computer program SOLMNEQ (Kharaka and Barnes, 1973; Kharaka and others, 1988), the pH 4 seep waters were calculated to be near to equilibrium with gypsum ($\Delta G = -0.1$ kilocalories) (table 17). In the Tumey Gulch tributary seep II waters (table 4, 197 µg/L selenium), however, the presence and solubility of mirabilite (or an equally soluble magnesium or mixed sodium and magnesium sulfate) seems to be controlling the selenium content. An undersaturation for mirabilite of -1.5 kilocalories in this water approaches a value seen in the Tumey Gulch I alkaline water (table 5, 3,500 µg/L selenium) that is precipitating mirabilite (-1.4 kilocalories). These values indicate that the minerals formed may be impure or that the thermochemical solubility or aqueous species complexation data used for mirabilite are slightly inaccurate and thus show a negative deviation from $\Delta G = 0$ at equilibrium.

A reconnaissance was made in the Kreyenhagen Formation on Monocline Ridge for seeps similar to the acid seeps in the Moreno Formation. The five seeps (table 6) surveyed range in pH from 5.87 to 7.74, with varying concentrations of selenium (up to 52 µg/L). They are all sodium-sulfate or sodium-magnesium-sulfate waters.

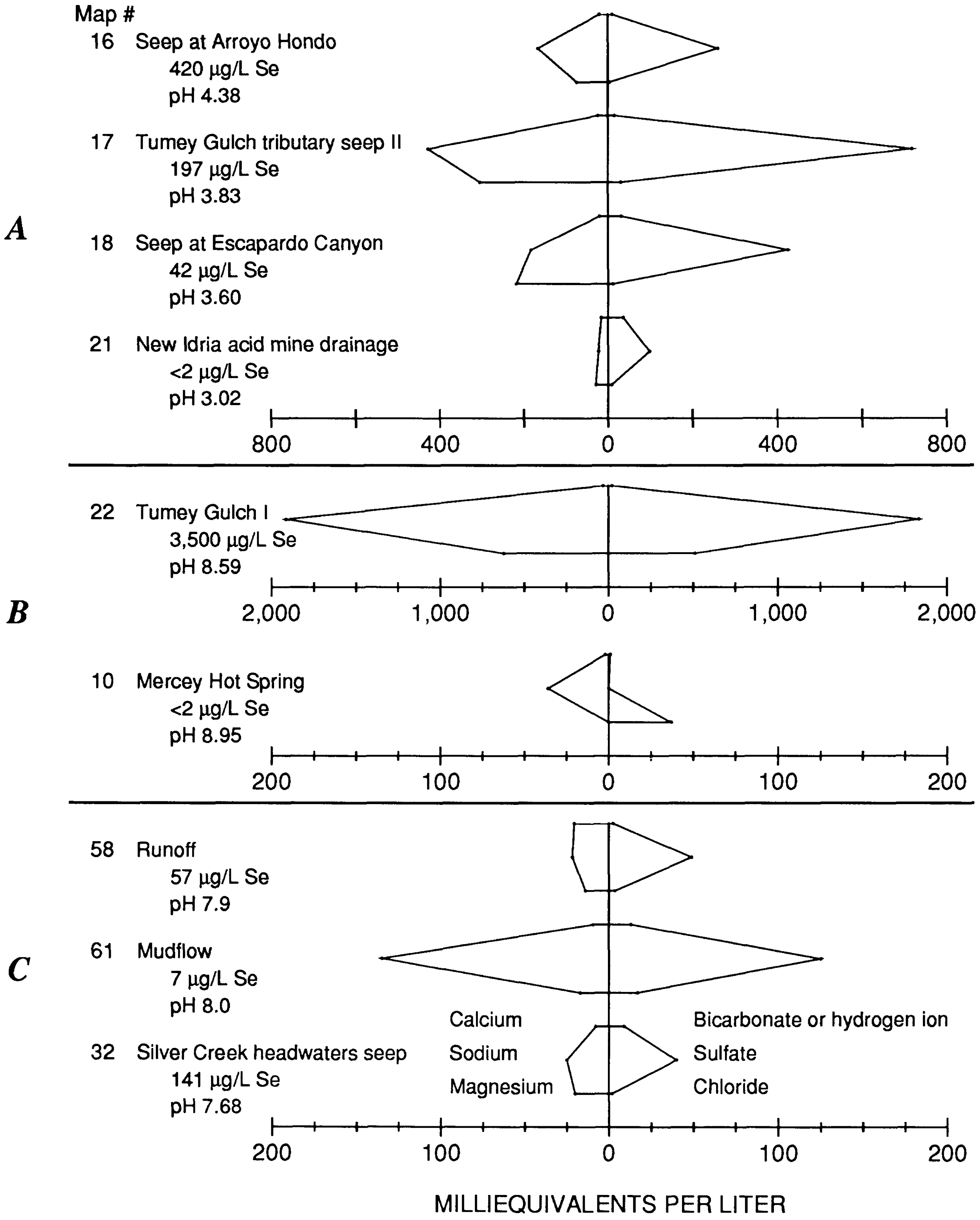


Figure 7. Water type, ionic composition, and selenium concentrations for selected water samples. *A*, Acid (pH 4). *B*, Alkaline. *C*, Transport.

Soil samples from the Moreno and Kreyenhagen Formations show a correlation between acid soil pH (4) and elevated selenium concentrations (up to 25 ppm) (table 14). In the study of 21 soil samples from six formations by the SCS in which soil pH was measured, the seven highest selenium concentrations are from the Moreno and Kreyenhagen Formations (median 12 ppm) and all are acid with five being approximately pH 4.

From the limited information available on other source areas associated with selenium contamination, one pH 4.5 seep has been reported near the Sun River Project (Montana) containing 580 µg/L selenium (Knapton and others, 1988). Major ion water chemistry was not available.

- **Elevated alkaline and oxygenated conditions ensure formation and release of selenate.** Although it takes some acid to produce ferric iron from ferrous iron (Stumm and Morgan, 1981), neutralization drives equation 1 to the right. A concentration range of 2,100 to 3,500 µg/L selenium was found in the water of an alkaline ephemeral stream in the main channel of Tumey Gulch (fig. 5 and table 5). This concentration of selenium is approximately an order of magnitude greater than other concentrations measured in water in the study area and exceeds the U.S. Environmental Protection Agency (1980) criterion for a toxic waste (>1,000 µg/L selenium). Tumey Gulch is one drainage to the south of Panoche Creek and it receives approximately 7 inches of rainfall yearly; flows issuing from it rarely reach the valley floor, making this a mainly closed evaporative system. The site of this ephemeral alkaline stream is about 0.25 mile away from the pH 4 seeps in a tributary of Tumey Gulch containing approximately 200 µg/L selenium (table 4). Geologically similar to the acid site, the alkaline site is dominated by the shales of the Moreno Formation but the stream water is strongly buffered by bicarbonate water derived from the Lodo Formation. The ephemeral stream water has a bicarbonate concentration of up to 1,415 mg/L; the water is approximately 2 *M* (molar) in sodium sulfate salt and precipitates mirabilite upon standing. The analysis of this sample is shown in figure 7*B*. For comparison, the analysis of the alkaline hydrothermal water at Mercey Hot Springs (less than 2 µg/L selenium) is plotted.

A theoretical description and examples of the oxidation/reduction process of selenium are given by Lakin (1961a) and are summarized as follows. The oxidation to selenite (+4) takes place easily. This selenite may combine with iron to form the very insoluble basic ferric selenite ($Fe_2(OH)_4SeO_3$). The presence of 12 ppm of selenium in acid Hawaiian soils under an annual rainfall of about 100 inches is an example of the occurrence and insolubility of this iron-Se compound. In acid conditions (pH 1), the oxidation potential for selenite (+4) to selenate (+6) is high, but as the pH increases, the oxidation can occur through oxygenated water. If the selenite were distributed in moist porous alkaline media, its oxidation by air might proceed at a measurable rate. Previous reports in the literature were that selenate either was unstable or did not form (Wedepohl, 1970). By differential analysis (Presser and Barnes, 1984), the selenium in the alkaline ephemeral stream water in Tumey Gulch was found to be in the selenate state. The buffering capacity of the Lodo Formation along with that of the Panoche Formation and Franciscan assemblage which were also found to be high in carbonate, provides an alkaline, oxidizing environment ensuring the concentration and mobility of selenium as selenate.

There are clear divisions between the pH 4 seep waters and the pH 8.6 ephemeral stream water in regard to metals transported; as compared with the acid waters, measured concentrations of metals in the alkaline water are very low (table 11). The analysis of the alkaline hydrothermal water at Mercey Hot Springs, which contains 0.1 µg/L mercury, is included for comparison. Also included in table 11 are two more alkaline selenium transport waters also low in other trace elements, which will be discussed later.

Although the Tumey Gulch drainage is considered to be unique, other instances of alkaline ephemeral streams at Vallecitos (tributary to Griswold Creek) and Los Pinos (tributary to Silver Creek) Creeks were sampled. Waters at these two sites (table 5) contain lesser amounts of selenium (12 to 24 µg/L respectively) and are sodium-sulfate type waters whose bicarbonate concentrations range from 471 to 751 mg/L. While salt effloresences are found at both sites, these sites are dominated geologically by Quaternary deposits rather than the Moreno Formation as at Tumey Gulch.

- **Selenate substitutes for sulfate in Na and Mg hydrous salts.** The sulfate regime in the east central Coast Ranges is readily recognized by the prevalence of sulfate salts as efflorescences on rock surfaces and evaporites at water interfaces. Eighteen predominately sodium and magnesium sulfate evaporite minerals, with up to 10 waters of hydration, were identified from saline geologic formations in the study area (table 1). Thenardite (dehydrated mirabilite) and bloedite were the dominant minerals found by x-ray diffraction (tables 2 through 10). Even though care was taken to preserve the natural state of the minerals and to x-ray immediately upon return, the hydrous minerals are labile and dehydration took place in the laboratory and on the mount used for x-ray diffraction resulting in intermediates being found. For example, the newly identified mineral konyaite (van Doesburg and others, 1982; Shayan and Lancucki, 1984) was found in mixtures with other salts; it dehydrated to bloedite and loeweite.

Concentrations of selenium in evaporites at each water sampling site are given in tables 2 through 10. By differential analysis (Presser and Barnes, 1984), selenium in the sodium and magnesium sulfates was found to be in the selenate state. The hydrated sodium and magnesium sulfate minerals have an open lattice structure which could theoretically incorporate the selenate (SeO_4^{2-}) anion in the sulfate (SO_4^{2-}) space. This replacement would cause an enrichment of selenium and thus provide a temporary geologic sink for selenium.

Evaporites that contain the highest selenium (up to 25 ppm selenium), are associated with drainage from the Moreno Formation (site 19). Evaporites in Tumey Gulch (site 17) contains up to 15 ppm selenium and at Arroyo Hondo (site 16) up to 12 ppm selenium. Evaporites from acid seeps in the Moreno average 7.0 ppm selenium (table 4). At the toe of one landslide in the Moreno, an extensive layer of thenardite 3 in. thick has developed; the salt contains 4 ppm selenium (site 17). In contrast, the sandstones of the Lodo Formation issue massive amounts of sodium and magnesium sulfate salt (approximately 1250 square feet at 2 in. thick) into the Panoche-Silver Creek drainage, but little selenium is found (less than 2 µg/L in water and less than 0.5 ppm in evaporites, site 41). Additionally salts from the sandstones of the Panoche Formation (sites 30 and 31) are predominantly halite and the loeweite found did not contain selenium (less than 0.1 ppm).

In comparison with sodium and magnesium sulfate salts, gypsum, the principal calcium sulfate mineral represented ($CaSO_4 \cdot 2H_2O$), does not seem to tolerate the substitution of selenate, measuring less than 0.5 ppm selenium in various samples including gypsum quarried locally for use as a soil amendment. This could be an exclusionary and consequently a concentrating mechanism for selenium in sodium and magnesium sulfate salts and in soil solutions.

The calcium and sodium geochemical regimes however, were found linked through the identification of the hydrous sulfate mineral hydroglauberite (table 1). Hydroglauberite, $[Na_{10}Ca_3(SO_4)_8 \cdot 6H_2O]$, was identified in evaporite crusts (tables 4, 5, and 8) from Tumey Gulch that contain up to 14 ppm selenium (site 17). It shows a distinct crystalline habit (acicular crystals radiating from a central nucleus) and is noted to break down to gypsum with increases in moisture. At the original mineral occurrence (Fleischer, 1970), it was found associated with halite and mirabilite along with polyhalite and astrakhanite.

Efflorescent salt crusts form on shales exposed at the surface. They were always found to be enriched in selenium when compared with those shales. By sequential extraction of selected shale samples of the weathered Moreno Formation, it was found that 95 percent of the selenium was in the soluble fraction and that it was in the selenate state.

• **Salts accumulate in an arid climate.** Isotopic analyses of oxygen ($^{18}O/^{16}O$) and hydrogen($^2D/^1H$) for 72 water samples show evaporative concentration of spatially and chemically divergent ground and surface waters (fig. 8). The results are expressed in the δ-notation as per mil referenced to Standard Mean Ocean Water (SMOW); the Meteoric Water Line (MWL) is plotted for reference (Craig, 1961). The water sampling points fall on an evaporative trend line with a correlation coefficient of 0.93, indicating a single source for the waters. This suggests that the solute chemistry of the brines is controlled and/or modified by solution-reprecipitation processes of surficial and subsurface evaporites rather than by the mixing of distinct water sources. The most evaporatively concentrated sample, Tumey Gulch ephemeral stream, also has the highest measured selenium.

Solute sources also are predicted through calculation of normative salt assemblages for these waters by the computer program SNORM (Bodine and Jones, 1986). The assemblages found, thenardite, bloedite, and glauberite (table 17), indicate, according to Bodine and Jones, oxidation of sulfide minerals to sulfuric acid in meteoric water followed by weathering of sodium, magnesium, and calcium silicates or alumino-silicates.

SELENIUM TRANSPORT MECHANISMS

• **Selenium is available for transport by runoff.** Even though creeks during non-storm periods contain low amounts of selenium, runoff, in the flushing events of winter, shows elevated selenium. Concentrations of selenium in runoff sampled in the Panoche

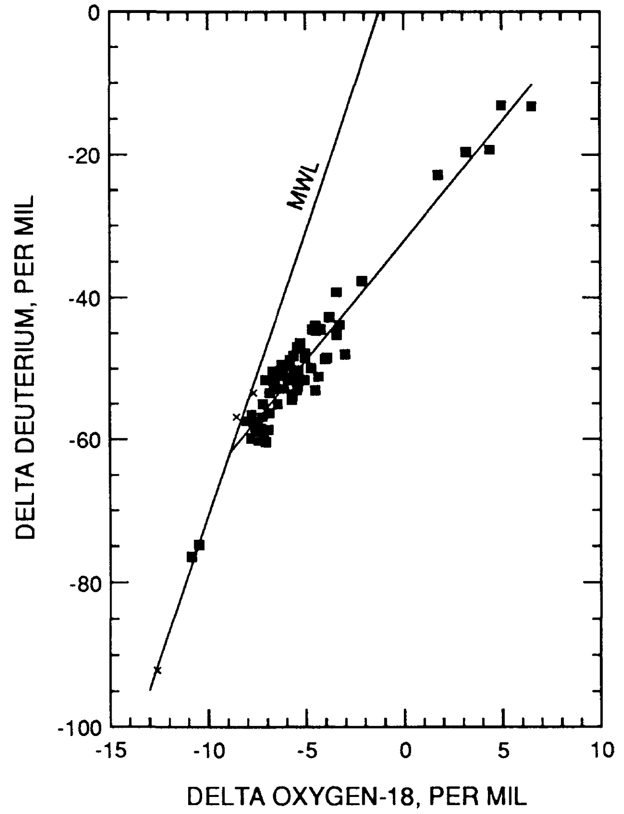


Figure 8. Relation of delta deuterium and delta oxygen-18 for waters in the study area. X denotes locally derived meteoric waters (analyses by L.D. White and Mark Huebner, U.S. Geological Survey, Menlo Park, California). MWL denotes meteoric water line.

Creek/Silver Creek drainages range from 44 to 57 µg/L selenium (table 10). A Stiff plot of the analysis of the runoff water containing the highest selenium is given in figure 7*C*. Only two events were measured because of drought conditions in the latter part of the study. Discharge measurements at Panoche Creek near its terminus on the valley floor at highway I-5 (site 58) were 25 ft^3/s (cubic feet per second) for a lesser event on 10/29/87 and 85 ft^3/s for a greater event on 1/17/88. Selenium data for these samples show that the lesser event contained less selenium, 44 µg/L, than the greater event, 56 µg/L selenium. In addition, for the 1/17/88 event, the selenium and discharge of Silver Creek above its confluence with Panoche Creek (at Panoche Road, site 59) is approximately the same as that measured in Panoche Creek at highway I-5, but the sulfate is lower. Assuming that upper Panoche Creek is flowing, this suggests that the water at highway I-5 is not diluted in selenium by Panoche Creek water, but rather that there is a source of selenium on Panoche Creek above or near the confluence of Panoche and Silver Creeks. In the confluence area, the Moreno Formation is dominant; the Kreyenhagen Formation is present in the drainage of lower Panoche Creek.

Eleven days after the peak of the 10/29/87 storm-runoff hydrograph with no subsequent precipitation event, at the higher elevations of Silver Creek, a rain pool contained 69 µg/L selenium and Silver Creek flow averaged 18.5 µg/L selenium (table 10; sites 41 and 62) as compared with less than 2 µg/L at low flow (table 8; site 44). Isotopically the Silver Creek samples remain on the evaporative trend line.

One explanation for the elevated concentration of selenium in runoff as compared with low flow is derived from findings on the importance of subsurface flow or throughflow in the unsaturated zone in generating runoff in response to precipitation events. Precipitation/runoff modeling efforts and isotopic studies (Pearce and others, 1986; Kennedy and others, 1986; Siegenthaler, 1979; Fontes, 1980) have shown that hydrographs can be dominated by water derived from subsurface sources. Because the runoff waters in the study area are especially high in suspended solids, measuring close to 10 percent (91,500 mg/L), subsurface flow coupled with mass wasting could be a mechanism contributing selenium to streams.

- **Mass wasting is extensive.** Limited field studies of hillslope processes have been done in either humid (Kirkby, 1978) or semiarid/arid climates (badland topography) (Bryan and Yair, 1982). However, some general concepts can be applied to this study. One conclusion drawn by Chorley and others (1984) is that erosional and depositional landforms in semiarid regions are susceptible to rapid and measurable systematic changes, especially those developed on shale outcrops. "Quick clays" also could be present in the study area. They are platy, open-structured marine clays whose strength has been decreased by leaching of salt and by other weathering processes. These clays are subject to liquefaction on slopes as low as 4° after subsequent increases in water content and pore water pressure. Failure of the "quick clays" is in the form of a thick sludge. Besides causing weathering by surficial runoff, rainfall can infiltrate and move to the water table or move beneath the hillslope surface as interflow or throughflow (Chorley and others, 1984). This subsurface flow can trigger massive soil slips and can form extensive piping features (narrow conduits or tunnels formed by erosion in the subsoil by percolating water through which soluble or granular material is moved) (Atkinson, 1978).

In the study area, both the characteristic instability associated with steeply dipping marine shales and the physical weathering occurring at the surface, at the near surface, and at depths greater than 10 meters results in large slope failures, near vertical escarpments, and numerous and frequent debris flows. Features of mass wasting in the study area were noted from field observations, geologic maps, and air photos. Throughout the Panoche and Silver Creek drainages, the Moreno Formation is especially characterized by landslides, slumps, piping, and deeply incised gullies. The material in the interfan area at the foot of Monocline Ridge was observed to be wholly comprised of debris flows or landslide deposits. Debris flows can occur on a yearly basis when heavy rainfall occurs on dry hills early in the winter (Bull, 1964a). In the study area it also was observed that, in unstable landscapes marked by landslides, seeps are characteristically acid, dominated by sodium-sulfate, and contain up to 420 µg/L selenium (table 4). In more stable landscapes of the study area, seeps are typically neutral to slightly alkaline with low selenium concentrations (table 6).

A mudflow in the Silver Creek drainage was sampled after a precipitation event (table 10). The analysis of the water associated with this mudflow is represented in a Stiff plot in figure *7C*. The water is a sodium-sulfate type with a selenium content of 7 µg/L. Low concentrations of trace metals are transported by this mudflow water as shown in table 11. The salt accompanying this mudflow is thenardite that contains 14 ppm selenium. The mudflow material itself contains 4.3 ppm selenium, a value that is comparable with the highest selenium concentration found on the valley floor in the 1986 sampling, 4.5 ppm selenium (Tidball and others, 1989).

Additional evidence that mass wasting, surface runoff and subsurface flow are significant mechanisms for transport lies in the fact that, if one takes the average concentrations of selenium (52 µg/L) and sulfate (2,800 mg/L) in the runoff water analyzed (table 10) and computes the selenium/sulfate ratio, it is equal to that of a sulfate salt containing 12.5 ppm selenium, a concentration that is seen in salts in the Coast Ranges and on the valley floor.

- **Selenium is redistributed in hillslope positions.** In typical hillslope situations developed on the Moreno, Kreyenhagen and Tumey Formations, selenium concentrations in soils and rock material show a distinct pattern of distribution. In addition to the effects of widespread mass wasting, subsurface water movement and solute transport appear to effectively redistribute selenium.

On shoulder/summit slope positions which have comparatively well developed soil profiles, selenium concentrations have a median value of 12 ppm (table 18). Relatively high evapotranspiration rates that occur here are due to well established vegetation and exposure to solar insolation and winds. Effects associated with evapotranspiration predominate over those associated with throughflow from the limited infiltration of direct precipitation and contribute to the retention of selenium in the soil profile over time.

Through midslope/backslope positions, selenium concentrations are relatively depleted, with a median of 4.4 ppm (table 18). Selenium concentrations in midslope/backslope positions were found to differ significantly (95 percent confidence level) from shoulder/summit slope positions (P=0.0146) using the Mann-Whitney two sample rank test. The midslope/backslope position receives direct precipitation, limited surface runoff, and throughflow from upslope positions, contributing to increased volumes of water moving through the soil horizon, as well as to accelerated surface erosion rates. The near surface processes of infiltration and evapotranspiration, while being more nearly balanced than on the summit, will vary substantially depending on soil development, vegetation, and the aspect of exposure (the south and west being more barren and more susceptible to landslides). These and other factors overprinted on the throughflow contribute to a high degree of variability in midslope/backslope selenium soil concentrations.

Selenium concentrations in toeslope/footslope positions, which can extend into the adjacent alluvial deposits, have a median of 8.2 ppm (table 18). This position contains extensive piping features and evaporative salt crusts. The toeslopes, as opposed to the summit and midslopes, are the most hydrologically active part of the hillslope system, making selenium available in precipitation-derived events through subsurface flow and mass wasting from above.

- **Selenium in stream sediments shows that contamination from the Coast Ranges is episodic.** Sediments (fig. 4 and table 15) in ephemeral streams emerging from the foothills of the Coast Ranges were sampled in the summer of 1986, near where they discharge onto the alluvial fans. The median is 2.8 ppm from areas in close downslope proximity (0 to 5 mi) from the Moreno Formation (parental material median = 6.5 ppm). These samples were observed to include recent debris flow materials identified by the presence of rough shale fragments up to 6 inches in diameter and the lack of evidence for subsequent disturbance or compaction. In areas downslope from Monocline

Ridge (2 to 3 mi) which is dominated by the Kreyenhagen Formation, the median is 0.8 ppm (parental material median = 8.9 ppm).

In addition, channel sediment samples were collected along a longitudinal transect of the San Carlos/Silver/lower Panoche Creek drainage system (fig. 4) and analyzed for selenium. A schematic diagram of this transect showing the selenium data plotted with the contributing geologic formations adjacent to the stream channel sites is displayed in figure 9. Sample data for the 1987 collection are incorporated in tables 2-10 while those from 1988 are shown only on the figure.

The September 1987 sampling of channel bed sediments for selenium preceded the runoff events of 1987-88. The concentrations at these sites (fig. 9) range from 0.1 to 3.8 ppm selenium with a median value of 1.2 ppm. Only one site has a concentration greater than 2 ppm selenium. This site appears to be subject to observed reducing conditions in stream sediments associated with a watershed that contains up to 141 µg/L selenium (table 7, site 32). The remainder of the sites show a uniform background of between 1 and 2 ppm regardless of the adjacent formation (note Moreno and Kreyenhagen Formations in lower reaches of Silver and Panoche Creeks) and of increasing size of drainage downstream. Analyses of samples of sediment following precipitation and runoff of 1987-88 showed selenium concentrations ranging from 1.7 to 2.9 ppm, with a median of 2.4 ppm. Selenium concentration in bed sediment in ephemeral drainages tributary to the main channel located in Moreno shale-derived materials are also shown in figure 9. Concentrations of these samples range from 3.6 to 8.5 ppm selenium with a median of 6.8 ppm, representing a significant reservoir of readily transportable materials.

Sequential extractions of selected samples of residual deposits of suspended load material at the head of Panoche Creek alluvial fan show that 95 percent of the selenium is in a form that is resistant to solubilization, needing a mixture of strong acids to liberate the selenium from the matrix.

These data suggest that the contamination from the Coast Ranges is episodic. Pulses of selenium from recently deposited parent material occur as the soluble forms of selenium are removed during infrequent streamflow events. Selenium is not concentrated in stream sediments but rather a background residual fraction is then mixed and diluted with sediments derived from formations comparatively low in selenium.

- **Development of concentrated selenium pulses is enhanced in an intermittently open system.** As described by Bull (1964b), alluvial fan deposition has been rapid in the area of the Coast Ranges bordered by Little Panoche Creek and Cantua Creek. In this area, factors contributing to a high sediment deposition on a seasonal basis are little vegetation on steep, poorly consolidated slopes and a range of effective precipitation (10 to 14 in. per year) in the higher hills that produce maximum sediment yield. Precipitation amounts below or above this range cause either a deficiency of runoff or an increase in vegetation resulting in decreased runoff. Bull (1964b) also concludes that mudflows reach the alluvial fans more now than in the past because channels are now narrower and more confining and the steep banks provide additional debris. On a broader scale, during the 50 or 100 year flood, transport rates are accelerated and the maximum material is deposited (Barnes, 1986).

Base line data from several sources for solid phase transport of selenium from the Coast Ranges can now be considered. From Shacklette and Boerngen (1984), for surficial materials of the conterminous United States, the geometric mean is 0.26 ppm selenium. From Tidball and others (1989): for soils of the San Joaquin Valley, the geometric mean is 0.14 ppm selenium; for soils on the Panoche Fan itself, the geometric mean is 0.7 ppm selenium; for soils in the area containing the highest selenium concentrations in the valley (between Panoche and Cantua Creeks), the median is 1.8 ppm selenium. From Roger Fujii (U.S. Geological Survey, oral commun., 1989): in irrigated soils from the San Joaquin Valley that have been leached, the median is 0.8 ppm selenium. From this report within the study area: for non-seleniferous formations, the median is 0.8 ppm selenium; and for seleniferous formations, the median is 7.3 ppm selenium; for hillslope positions within these seleniferous formations, median values are 12 ppm selenium for summit slopes, 4.2 ppm selenium for midslopes and 8.2 ppm selenium for toe slopes; for stream sediments in the San Carlos/Silver/lower Panoche Creek drainage, the median is 1.2 ppm selenium with an increase to 2.4 ppm selenium after a rainfall event; for stream sediments in ephemeral streams between the foothills of the Coast Ranges and the alluvial fans, the median

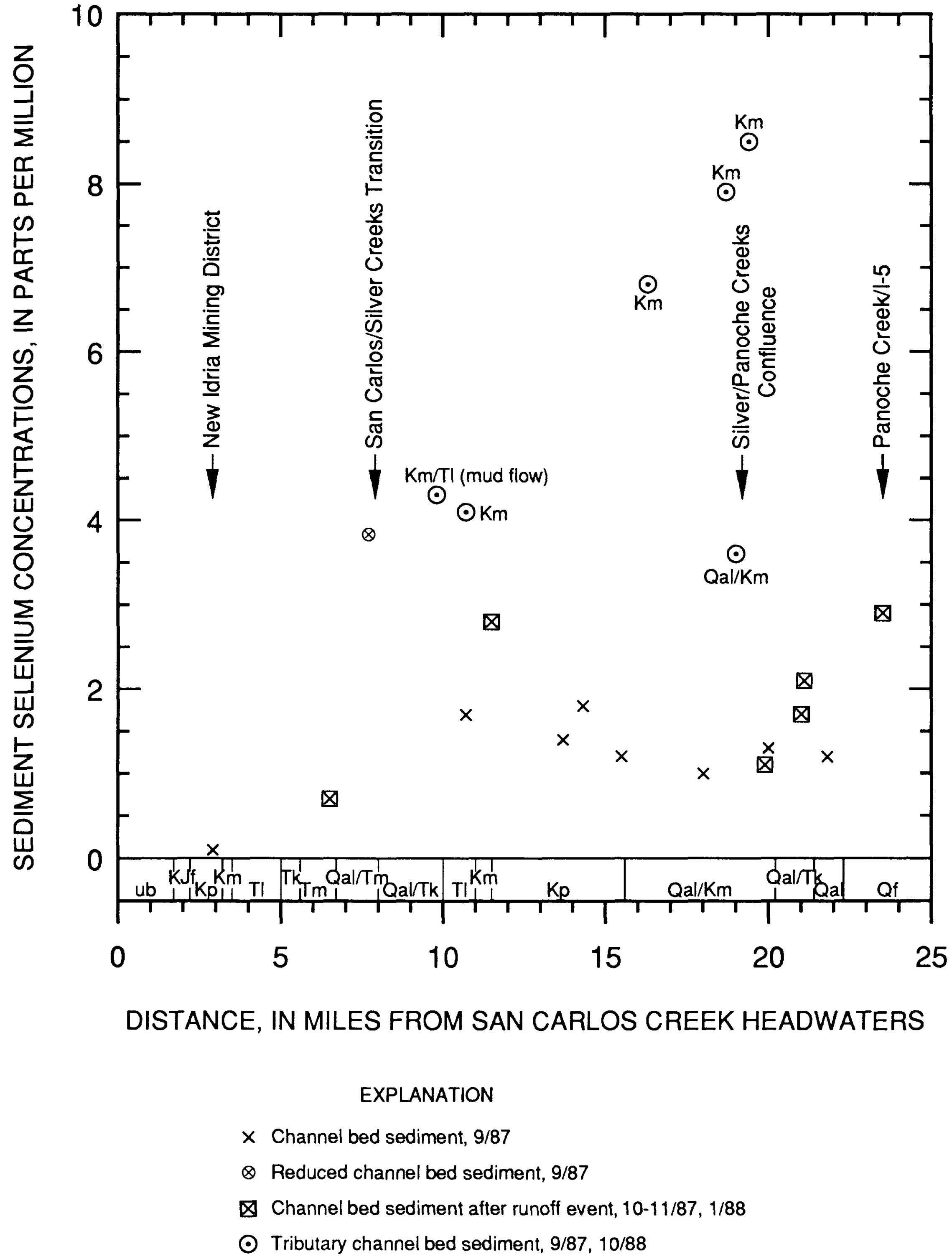


Figure 9. Concentrations of selenium in stream sediments from a longitudinal profile of the San Carlos Creek/Silver Creek/lower Panoche Creek drainage and selected tributaries. Channel bank geology denoted along profile. Abbreviations used for geologic formations are as follows: KJf, Franciscan assemblage; Km, Moreno Formation; Kp, Panoche Formation; Qal, Quaternary alluvium; Qf, Quaternary alluvial-fan deposits; Tk, Kreyenhagen Formation; Tl, Lodo Formation; Tm, Monterey Formation; ub, ultrabasic intrusive rocks.

downslope from the Moreno Formation is 2.8 ppm selenium (observed to include recent debris flow material) and downslope from the Kreyenhagen Formation, 0.8 ppm selenium; for ephemeral drainage bed sediment from or in source formations, the median is 6.8 ppm selenium.

The highest selenium concentrations occur in the dynamic parts of the drainage originating in the Moreno Formation. For parent materials this is in the summit and toeslopes, for stream sediments, this is in the recent debris flow deposits and bed sediments of ephemeral streams. Otherwise, the limits associated with stream sediment movement are not exceptional. Accelerated mass wasting of this material takes place, but salts are also being alternately moved to the surface by capillary action and then stripped during small rainfall events. Evaporative concentration would accentuate this mechanism, producing concentrated pulses of selenium contamination during infrequent large hydrologic events. These flows rarely reach the valley floor, making this a mainly closed evaporative system, that is, one only intermittently open to deliver selenium during large storms.

- **Regional ground water is a significant source of selenium.** Regional ground-water flow, as indicated by headwater seeps, was found associated with structural synclines in the upper reaches of Panoche Creek drainage (table 7). The waters thus represent integrated watershed samples encompassing the geologic section from Jurassic to Miocene with the Eocene-Oligocene Kreyenhagen and Miocene Monterey Formations being the dominant strata represented. These contributions of ground water to streamflow contain up to 153 µg/L selenium at the head of Griswold Creek (confluence of Vallecitos and Pimental Creeks) and up to 141 µg/L at the head of Silver Creek (fig. 5 and table 7). Thus, this system represents a significant source of selenium from the subsurface saturated zone. The waters are of the sodium-sulfate or mixed sodium-magnesium-sulfate type. An analysis for the headwater seep sample at Silver Creek is plotted in figure 7. The trace element analysis of the water from an earlier collection is given in table 11.

Waters from deeper wells (approximately 400 ft), shown by the isotope data to be evaporatively concentrated only to a small extent, also indicate a ground-water reservoir of selenium (up to 58 µg/L) (table 9). Waters from shallower wells (approximately 100 ft) contain lower concentrations of selenium (less than 8 µg/L).

- **Alluvial ground-water system is low in selenium.** The alluvial ground-water system, represented by headcuts, channel seeps and contact seeps (table 8), is low in selenium (3 µg/L or less). Two exceptions to this are a seep and pool traversing the Moreno Formation along the strike as opposed to the other cases which drain perpendicular to the strike; these sites contain 17 and 14 µg/L selenium, respectively. All alluvial ground-water samples are sodium- or sodium-magnesium-sulfate waters except two seep samples from Salt Creek which contain chloride as a major component.

During low flow conditions, surface water in Silver Creek is usually derived from ground water entering the stream alluvium. Selenium was found not to be conservative in the Silver Creek drainage because it decreases from a concentration of 141 µg/L in the headwater seep water (table 7) to less than 2 µg/L in the seep water in Silver Creek near the confluence with Panoche Creek (table 8). This is not due to dilution because concentrations of dissolved solids increase from 3,580 to 10,432 mg/L and sulfate from 1,900 to 5,800 mg/L as the water is evaporatively concentrated between these sampling points. The decrease in selenium in the Silver Creek drainage may be a function of ground waters interacting under reducing conditions to form insoluble selenium compounds. Reducing conditions were evident in channel muds at several localities. Anaerobic bacterial intervention in these processes is postulated (Shrift, 1964; National Academy of Sciences, 1976; Brierley and others, 1981; Oremland and others, 1989).

- **A biological marsh provides a reductive and bioaccumulative environment.** Reductive reactions were seen in the KNWR wetlands (Presser and Ohlendorf, 1987) and are seen in inferred historical marshlands in the Tulare Basin (Swain, 1988) and at the contact between reduced Sierran sediments and oxidized Coast Range alluvium on the valley floor (Dubrovsky and others, 1988). All these sites have elevated selenium in reduced sediments (up to 210 ppm at KNWR). The concentration of selenium has resulted from the transport of a water-soluble selenium into a poorly drained organic reducing basin (Lakin, 1961a). The processes at KNWR are summarized as follows from Presser and Ohlendorf (1987) and Lemly and Smith (1987). Reductive mechanisms can incorporate selenium directly into the food chain via plant uptake of selenate and subsequent reduction within its tissues or indirectly via chemically or microbially mediated selenate reduction and subsequent incorporation into sediments that are then digested by benthic organisms. Bioaccumulative mechanisms by aquatic plants, insects, and other animals include uptake of water and food containing selenium and replacement of sulfur by selenium in sulfur-containing amino acids. Bioaccumulation and biomagnification of selenium in organs of the food chain organisms can lead to impaired reproduction in birds and fish. Toxicity studies of cells of higher organisms show impaired reproduction, inhibition of growth, mutagenesis, and suppression of the immune system.

In 1986, the State of California declared the reservoir at KNWR to be a toxic waste dump. The reservoir was subsequently drained, filled, and graded in 1989 (National Research Council, 1989).

- **Selenium is biogeochemically cycled in the Coast Ranges and KNWR.** A diagrammatic view of the entire selenium cycle is shown in figure 10. This model is a combination of the Coast Range processes and those taking place on the valley floor. Although the model shows only a single iteration of cycling in the Coast Ranges, the arid climate presupposes concentrating mechanisms through many evaporative concentration/dissolution cycles on semiarid slopes. Chemical recycling occurs as weathered Coast Range material is reduced or KNWR sediment is oxidized. It can be concluded that the biogeochemical cycling of selenium has been at work both over geologic time in the Coast Ranges and their alluvial fans and, on a smaller time scale but in a more complex way, with the addition of the food chain, in KNWR.

SUMMARY AND CONCLUSIONS

Conditions necessary for the Coast Range geohydrologic system to issue selenium in elevated amounts are as follows.

In the study area, elevated concentrations of selenium are seen in the extensive surficial exposures of the Upper Cretaceous-Paleocene Moreno and Eocene-Oligocene Kreyenhagen Formations which provide the primary sources of selenium to the west-central valley. These formations are not as extensively exposed to the north or to the south of the area implicated to be the source of selenium at KNWR. Alternative source materials investigated, including Cretaceous and Tertiary sandstones, Pliocene-Pleistocene continental deposits, acid mine drainage from the New Idria Mercury Mining District, and waters from the eugeosynclinal Franciscan assemblage and serpentinites are comparatively barren of selenium.

Selenium is mobilized by oxidative weathering of pyritic shales. It is postulated that the characteristic acid (pH 4) seeps and soils are surface expressions of the transition points in which the sulfur in pyritic shales is oxidized to sulfate, the selenium being oxidized with it. In the seeps, both selenium and heavy metals are elevated. The buffering capacity of the existing bicarbonate regimes of the Panoche and Lodo Formations and the Franciscan assemblage provide alkaline oxidative conditions ensuring the concentration and mobility of selenium as selenate. Heavy metals are not transported, however, in these alkaline waters.

A sulfate chemical regime dominates the Coast Ranges waters that drain into the west-central San Joaquin Valley. These stream, seep, and spring waters, along with the chemistry of the San Luis Drain and KNWR waters, imply that the complex array and interrelation of soluble sulfate evaporative minerals are important factors in the study of selenium sources. Thirteen sodium and magnesium sulfate minerals, containing selenium in the selenate state, were identified, that act as temporary geologic sinks for selenium. Theoretically, the open lattice structures of these hydrous minerals could incorporate the selenate (SeO_4^{2-}) anion into the sulfate (SO_4^{2-}) space.

Elevated concentrations of Se, indicating a hydrologic reservoir of selenium to be transported, can be found in four water sources: (1) ephemeral streams in which fractional crystallization and evaporative concentration can create a sodium-sulfate fluid that exceeds the U.S. Environmental Protection Agency selenium criterion for a toxic waste; (2) runoff waters from the flushing events of winter in which the surficial selenium held in evaporative minerals is readily remobilized; (3) throughflow in the unsaturated zone in which a sustained release of selenium is seen; (4) ground water in wells and as indicated by seeps associated with structural synclines in which the integrated watershed represents a significant source of selenium in the subsurface saturated zone.

Two mechanisms are inferred for the transport of selenium from the Coast Ranges to the San Joaquin Valley floor. One mechanism involves the movement

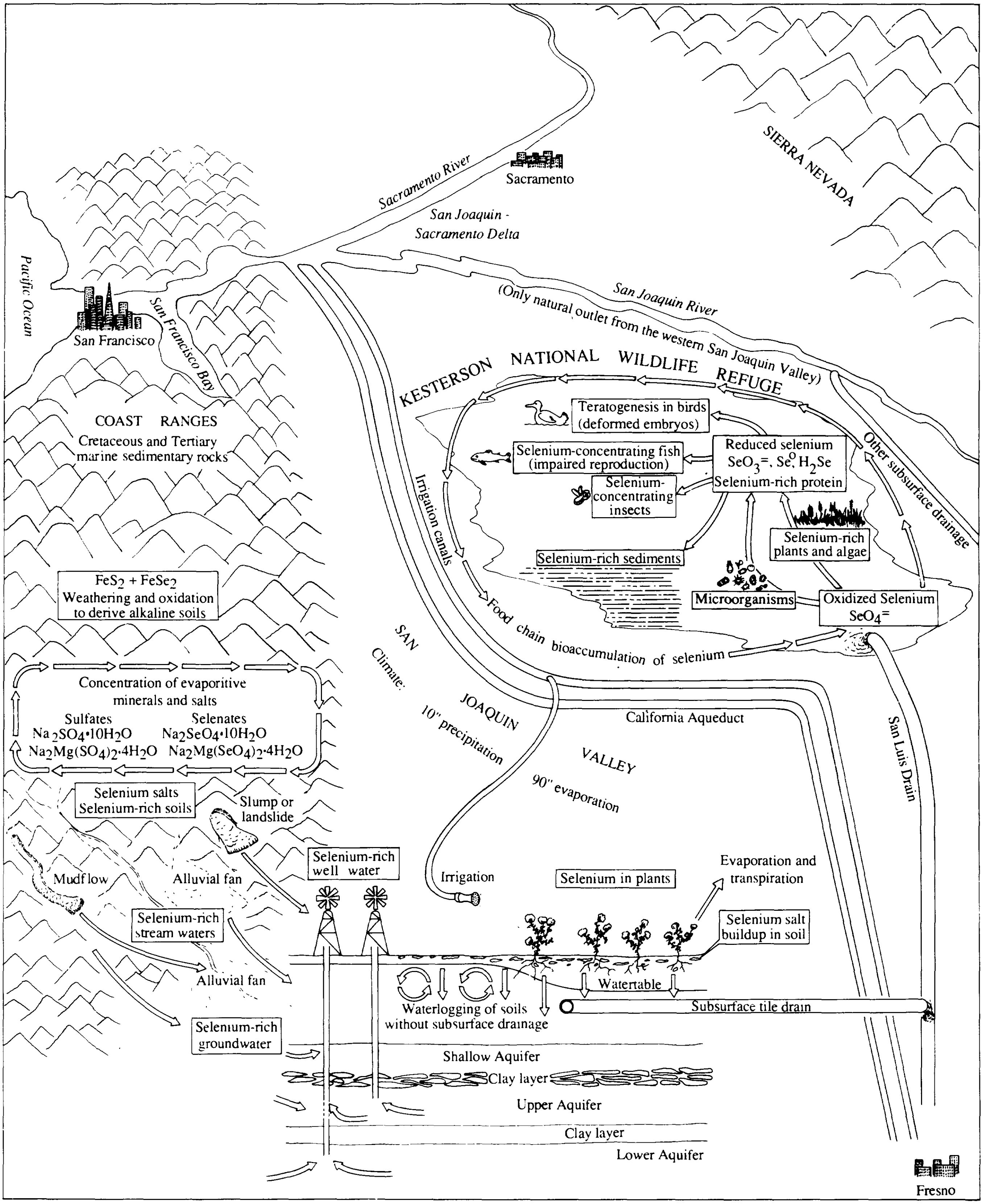


Figure 10. Biogeochemical cycling of selenium in the Coast Ranges, the San Joaquin Valley, and Kesterson National Wildlife Refuge.

of selenium already oxidized to selenate in soluble salts from erosional and depositional shale landforms. These salt crusts, formed on surface exposures of shales, are enriched in selenium when compared with those shales. The weathering profiles on summit slopes, where salts are concentrated in the capillary fringe by evaporation, and on toeslopes of landslides, where extensive salt layering forms due to down-gradient throughflow, are sources of soluble selenium for runoff and transport to the valley floor. The second mechanism involves movement of selenium in a residual insoluble fraction as exemplified by residual deposits of suspended load material found at the head of Panoche Creek alluvial fan. The steeply dipping marine shales, in areas of reduced rainfall and little vegetation, are subject to accelerated erosion and throughflow. Extensive mass wasting in the form of landslides, slumps, and mudflows causes mechanical disintegration of the parent geologic materials, producing increased finer-grained material that can be carried, deposited and reacted with during hydrologic events. This material, in addition to that eroded from channel banks and beds, can transport residual insoluble particulate selenium downstream, delivering relatively high sediment volumes to the alluvial fans. Any salts that are present are also transported downstream.

Highest selenium concentrations in stream sediments are in the dynamic parts of the drainage originating in the Moreno Formation, such as recent debris flow deposits and bed sediments in short ephemeral streams. Seasonality and infrequent flood events provide a framework for episodes or pulses of both soluble and insoluble selenium contamination to take place. Subsequent cycling of wetting and drying events and evaporation in an arid climate lead to accumulation of selenium instead of the constant low mobilization and transport afforded by areas of higher, regular rainfall and more humid conditions. These transport processes point out the relative importance of this type of system, one that acts as almost a closed basin only intermittently open (that is, infrequently transporting water and selenium downstream to the valley floor) during large storm and runoff events, in developing the elevated levels of selenium delivered to the fans and especially to the interfans. Reductive mechanisms in the selenium biogeochemical cycle can intervene to immobilize selenium, but transport of selenium remains high enough to pose a threat in the San Joaquin Valley to water quality and hence to the wildlife, fish, human health, and beneficial use supported by that water.

REFERENCES CITED

Anderson, R., and Pack, R.W., 1915, Geology and oil resources of the west border of the San Joaquin Valley north of Coalinga, California: U.S. Geological Survey Bulletin 603, 220 p.

Atkinson, T.C., 1978, Techniques for measuring subsurface flow on hillslopes, *in* Kirkby, M.J.,ed., Hillslope Hydrology: New York, Wiley-Interscience, p. 73-120.

Atwill, E.R., 1935, Oligocene Tumey Formation of California: Bulletin of the American Association of Petroleum Geologists, v. 19, p. 1192-1204.

Bailey, E.H., Irwin, W.P., and Jones, D.L., 1964, Franciscan and related rocks, and their significance in the geology of western California: California Division of Mines and Geology Bulletin 183, 177 p.

Barnes, Ivan, 1986, Sources of selenium, *in* Howard, Alice, ed., Selenium and Agricultural Drainage: implications for San Francisco Bay and the California Environment, Proceedings of the Second Selenium Symposium March 23, 1985, Berkeley, California: The Bay Institute of San Francisco, Tiburon, California, p. 41-51.

Barnes, Ivan, Hinkle, M.E., Rapp, J.B. Heropoulos, Chris and Vaughn, W.W., 1973a, Chemical composition of naturally occurring fluids in relation to mercury deposits of north-central California: U.S. Geological Survey Bulletin 1382-A, p. A1-A19.

Barnes, Ivan, Irwin, W.P., and Gibson, H.A., 1975, Geologic map showing springs rich in carbon dioxide or chloride in California: U.S. Geological Survey Water-Resources Investigations Open-File Map.

Barnes, Ivan, LaMarche, V.C., Jr., and Himmelberg, Glen, 1967, Geochemical evidence of present-day serpentinization: Science, v. 156, p. 830-832.

Barnes, Ivan, and O'Neil, J.R., 1969, The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, Western United States: Geological Society of America Bulletin, v. 80, p. 1947-1960.

Barnes, Ivan, O'Neil, J.R., Rapp, J.B., and White, D.E., 1973b, Silica-carbonate alteration of serpentine: wall rock alteration in mercury deposits of the California Coast Ranges: Economic Geology, v. 68, p. 388-398.

Bartow, J.A., 1988a, Preliminary geologic map of the Lillis Ranch quadrangle, California: U.S. Geological Survey Open-File Report 88-49, 1 sheet, scale 1:24,000.

-----1988b, Preliminary geologic map of the Monocline Ridge quadrangle, California: U.S. Geological Survey Open-File Report 88-528, 1 sheet, scale, 1:24,000.

Belitz, Kenneth, and Heimes, F.J., 1990, Character and evolution of the ground-water flow system in the central part of the western San Joaquin Valley, California: U.S. Geological Survey Water-Supply Paper 2348, 28 p.

Berkstresser, C.F., 1968, Data for springs in the southern coast, Transverse and Peninsular Ranges of California: U.S. Geological Survey Open-File Report 68-10, 32 p.

Berner, R.A, 1984, Sedimentary pyrite formation: an update: Geochimica et Cosmochimica Acta, v. 48, p. 605-615.

Bodine, M.W., Jr., and Jones, B.F., 1986, THE SALT NORM: a quantitative chemical-mineralogical characterization of natural waters: U.S. Geological Survey Water-Resources Investigations Report 86-4086, 134 p.

Boctor, N.Z., Shieh, Y.N., and Kullerud, G., 1987, Mercury ores from the New Idria Mining District, California: geochemical and stable isotope studies: Economic Geology, v. 51, p. 1705-1715.

Brierley, C.L., and Brierley, J.A., 1981, Contamination of ground and surface waters due to uranium mining and milling: biological processes for concentrating trace elements from uranium mine waters: Socorro, New Mexico, New Mexico Bureau of Mines and Mineral Resources, v. 1, 102 p.

Briggs, L.I., Jr., 1953, Geology of the Ortigalita Peak quadrange, California: California Division of Mines Bulletin 167, 61 p.

Briggs, P.H., and Crock, J.G., 1986, Automated determination of total selenium in rocks, soils and plants: U.S. Geological Survey Open-File Report 86- 40, 20 p.

Brown, Randy, 1985, Selenium in the Sacramento-San Joaquin Estuary: a summary of available data: U.S. Fish and Wildlife Service Interagency Ecological Studies Program Annual Workshop, Sacramento, California, 5 p.

Bryan, Rorke, and Yair, Aaron, eds., 1982, Badland geomorphology and piping: Norwich, England, Geo Books, 408 p.

Bull, W.B., 1964a, Alluvial Fans and near-surface subsidence in western Fresno: County, California: U.S. Geological Professional Paper 437-A, 71 p.

-----1964b, Geomorphology of segmented alluvial fans in western Fresno county: U.S. Geological Survey Professional Paper 352-E, p. 89-129.

Byers, H.G., 1935, Selenium occurrence in certain soils in the U.S. with a discussion of related topics: U.S. Department of Agriculture Technical Bulletin 482, 47 p.

-----1936, Selenium occurrence in certain soils in the U.S. with a discussion of related topics: second report: U.S. Department of Agriculture Technical Bulletin 530, 79 p.

Byers, H.G., Miller, J.T., Williams, K.T., and Lakin, H.W., 1938, Selenium occurrence in certain soils in the U.S. with a discussion of related topics: third report: U.S. Department of Agriculture Technical Bulletin 601, 75 p.

California Department of Water Resources, 1988, San Joaquin Valley Drainage Monitoring Program, 1986: Sacramento, California, California Department of Water Resources, 146 p.

California Regional Water Quality Control Board, 1988, Water and sediment quality in evaporation basins used for the disposal of agricultural subsurface drainage water in the San Joaquin Valley, California: Sacramento, California, California Regional Water Quality Control Board, 50 p.

California State Water Resources Control Board, 1985, Hearing order WQ 85-1: Sacramento, California, California State Water Resources Control Board, 65 p.

Chorley, R.J., Schumm, S.A., and Sugden, D.E., 1984, Geomorphology: New York, Methuen, 605 p.

Coleman, R.G., and Delevaux, M., 1957, Occurrence of selenium in sulfides from some sedimentary rocks of the Western United States: Economic Geology, v. 52, p. 499-527.

Craig, H., 1961, Isotopic variations in meteoric waters: Science, v. 133, p. 1702-1703.

Cutter, G.A., 1978, Species determination of selenium in natural waters: Analytica Chimica Acta, v.98, p. 59-66.

Davidson, D.F., 1963, Selenium in some oxidized sandstone-type uranium deposits: U.S. Geological Survey Bulletin 1162-C, p. C1-C33.

Davidson, D.F., and Lakin, H.W., 1961, Metal content of some black shales of the Western United States: U.S. Geological Survey Professional Paper 424, p. 329-331.

Davidson, D.F., and Powers, H.A., 1959, Selenium content of some volcanic rocks from western United States and Hawaiian Islands, U.S. Geological Survey Bulletin 1084-C, 81 p.

Davis, G.H., 1961, Geologic control of mineral composition of stream waters of the eastern slope of the southern Coast Ranges, California: Geochemistry of water: U.S. Geological Survey Water-Supply Paper 1535-B, p. B1-B30.

Davis, G.H., Green, J.H., Olmsted, F.H., and Brown, D.W., 1959, Ground-water conditions and storage capacity in the San Joaquin Valley, California: U.S. Geological Survey Water-Supply Paper 1469, 287 p.

Desborough, G.A., Poole, F.G., Hose, R.K., and Green, G.N., 1984, Metalliferous oil shale in the Upper Devonian Gibellini Facies of the Woodruff Formation, southern Fish Creek Range, Nevada: U.S. Geological Survey Bulletin 1694, p. 93-104.

Deverel, S.J., Gilliom, R.J., Fujii, Roger, Izbicki, J.A. and Fields, J.C., 1984, Areal distribution of selenium and other inorganic constituents in shallow ground water of the San Luis Drain Service Area, San Joaquin Valley, California: A preliminary study: U.S. Geological Survey Water-Resources Investigations Report 84-4319, 67 p.

Dibblee, T.W., 1971, U.S. Geologic maps of seventeen 15-minute quadrangles U.S. Geological Survey Map.

-----1973, Stratigraphy of the Southern Coast Ranges near the San Andreas Fault from Cholame to Maricopa, California: U.S. Geological Survey Professional Paper 764, 45 p.

-----1975, Geologic map of the Pacheco Pass, Hollister, Quien Sabe, Ortigalita Peak, San Benito, Panoche Valley and Tumey Hills quadrangles, San Benito, Santa Clara, Merced, and Fresno Counties, California. U.S. Geological Survey Open-File Report 75-0394.

Driessen, P.M., and Schoorl, R., 1973, Mineralogy and morphology of salt efflorescences on saline soils in the Great Konya Basin, Turkey: Journal of Soil Science, v. 24, p. 437-443.

Dubrovsky, N.M., Neil, J.M., and Fujii, Roger, 1988, Possible redox control of selenium transport in a complex setting in the San Joaquin Valley, California: Eos Transactions of the American Geophysical Union, Abstract, v. 69, p. 1181.

Eckel, E.B., and Myers, W.B., 1946, Quicksilver deposits of the New Idria District, San Benito and Fresno Counties, California: State Mineralogist's Report, California Journal of Mines and Geology, v. 42, no. 2, p. 81-124.

Emmerich, W., Rubin, B., and Wilcock, R.J., 1977, Low pressure solubility of gases in liquid water: Chemical Reviews, v. 77, p. 219-262.

Evangelou, V.P., Whittig, L.D., and Tanji, K.K., 1984, Dissolved mineral salts derived from Mancos Shale: Journal of Environmental Quality, v. 13, p. 146-150.

Fleischer, M., 1970, New Mineral Names: American Mineralogist v. 55, p. 317- 321.

Fontes, J.C., 1980, Environmental isotopes in groundwater hydrology, *in* Fritz, P., and Fontes J.C., eds. Handbook of environmental isotope geochemistry v. 1: Amsterdam, Elsevier, p. 75-140.

Garrels, R.M. and Lerman, A., 1981, Phanerozoic cycles of sedimentary carbon and sulfur: Proceedings of the National Academy of Sciences, v. 78, p. 4652-4656.

Geering, H.R., Carey, E.E., Jones, L.H.P., and Allaway, W.H., 1968, Solubility and redox criteria for the possible forms of selenium in soils: Soil Science Society of America Proceedings, v. 32, p. 35-40.

Gilliom, R.J., and others, 1989, Preliminary assessment of sources, distribution, and mobility of selenium in the San Joaquin Valley, California: U.S. Geological Survey Water-Resources Investigations Report 88-4186, 129 p.

Gilmer, D.S., Miller, M.R., Bauer, R.D., and LeDonne, J.R, 1982, California's Central Valley wintering waterfowl: concerns and challenges: Transactions of the North American Wildlife and Natural Resources Conference, v. 47, p. 441-452.

Greenberg, A.J., and Kopec, D., 1986, Decline of Bay-Delta fisheries and increased selenium loading: possible correlation, *in* Howard, Alice ed., Selenium in agricultural drainage: implications for the San Francisco Bay and the California environment, Proceedings of the Second Selenium Symposium March 23, 1985: Berkeley, California. The Bay Institute of San Francisco Tiburon, California, p. 69-81.

Gunn, A.M, 1981, The determination of arsenic and selenium in raw and potable waters by hydride generation/atomic absorption spectrometry-a review: Technical Report TR169, Medmenham, Marlow, Bucks, Great Britain, WRC Environmental Protection, 76 p.

Hawley, J.E., and Nichol, Ian, 1959, Selenium in some Canadian sulfides: Economic Geology, v. 54, p. 608-628.

Hoffman, D.J., Rattner, B.A., Sileo, L, Docherty, D., and Kubiak, T.J., 1987, Embryotoxicity, teratogenicity, and aryl hydrocarbon hydroxylase activity in Forster's terns on Green Bay, Lake Michigan: Environmental Research, v. 42, p. 176-184.

Howard, J.H., 1977, Geochemistry of selenium: formation of ferroselite and selenium behavior in the vicinity of oxidizing sulfide and uranium deposits: Geochimica et Cosmochimica Acta, v. 41, p. 1665-1678.

Irwin, W.P., and Barnes, Ivan, 1975, Effect of geologic structure and metamorphic fluids on seismic behavior of the San Andreas fault system in central and northern California: Geology, v. 3, p. 713-716.

Kennedy, V.C., Kendall, C., Zellweger, G.W., Wyerman, T.A., and Avanzino, R.J., 1986, Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River Basin, California: Journal of Hydrology, v. 84, p. 107-140.

Kharaka Y.K., and Barnes, Ivan, 1973, SOLMNEQ: solution mineral equilibrium computations: U.S. Geological Survey Computer Contribution WRD-73-002 (NTIS PB-215-899), 82 p.

Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H., and DeBraal, J.D., 1988, SOLMNEQ.88: a computer program for geochemical modeling for water-rock interactions: U.S. Geological Water-Resources Investigations Report 88-4227, 420 p.

Kirkby, M.J., ed., 1978, Hillslope hydrology: New York, Wiley and Sons, 389 p.

Knapton, J.R., Jones W.E., and Sutphin, J.W., 1988, Reconnaissance investigation of water quality, bottom sediment and biota associated with irrigation drainage in the Sun River Area, west-central Montana, 1986-87: U.S. Geological Water-Resources Investigations Report 87-4244, 78 p.

Konetzka, W.A., 1977, Microbiology of metal transformations, *in* Weinberg E.D., ed., Microorganisms and minerals: New York, Marcel Dekker, p. 317-342.

Krauskopf, K.B., 1955, Sedimentary deposits of rare metals, *in* Bateman, A.M., ed., Fiftieth Anniversary Volume 1905-1955, Economic Geology: Lancaster, Pennsylvania, Economic Publishing Company, p. 411-462.

-----1967, Introduction to geochemistry: San Francisco, McGraw-Hill, 721 p.

Lakin, H.W., 1961a, Geochemistry of selenium in relation to agriculture. *in* Anderson, M.S., Lakin, H.W., Beeson, K.C., Smith, F.F., and Thacker, E., eds., Selenium in agriculture: Washington, D.C., U.S. Department of Agriculture Handbook 200, p. 3-12.

-----1961b, Vertical and lateral distribution of selenium in sedimentary rocks of Western United States, *in* Anderson, M.S., Lakin, H.W., Beeson, K.C., Smith, F.F., and Thacker, E., eds., Selenium in agriculture: Washington, D.C., U.S. Department of Agriculture Handbook 200, p. 12-24.

-----1973, Selenium in our environment, *in* Kothny, E.L., ed., Advances in chemistry, Series 123: American Chemical Society, Washington D.C., p. 96-111.

Lakin, H.W., and Byers, H.G., 1941, Selenium occurrence in certain soils in the U.S. with a discussion of related topics: sixth report: U.S. Department of Agriculture Technical Bulletin 783 p. 1-27.

Lemly, D.A., and Smith, G.J., 1987, Aquatic cycling of selenium: implications for fish and wildlife: U.S. Fish and Wildlife Leaflet 12, 12 p.

Lettis, W.R., 1982, Late Cenozoic stratigraphy and structure of the western margin of the central San Joaquin Valley, California: U.S. Geological Survey Open-File Report 82-526. 203 p.

Linn, R.K., 1968, New Idria Mining District, *in* Ridge, J.D., ed., Ore deposits of the United States, 1933-1967, The Graton-Sales Volume: New York, The American Institute of Mining, Metallurgical and Petroleum Engineers Inc., p. 1624-1649.

Murata, K.J., 1977, Occurrence of bloedite and related minerals in marine shale of Diablo and Temblor Ranges, California: U.S. Geological Survey Journal of Research, v. 5, no. 5, p., 637-642.

Nakahara, T., 1983, Applications of hydride generation techniques in atomic absorption, atomic fluorescence, and plasma atomic emission spectroscopy: Progress in Analytical Atomic Spectroscopy, v. 6, no. 3, p. 163-223.

National Academy of Sciences, 1976, Selenium: Medical and Biologic Effects of Environmental Pollutants: Washington, D.C., National Academy of Sciences, 203 p.

National Research Council, 1989, Irrigation-induced Water Quality Problems: Washington, D.C., National Academy Press, 157 p.

Nichols, F.H., Cloern, J.E., Luoma, S.N., and Peterson, D.H., 1986, The modification of an estuary: Science, v. 231, p. 567-573.

Norris, R.M., and Webb, R.W., 1976, Geology of California: New York, John Wiley, 365 p.

Ohlendorf, H.M., and Skorupa, J.P., 1990 (in press), Selenium in relation to wildlife and agricultural drainage water, *in* Proceedings of the Fourth International Symposium on Uses of Selenium and Tellurium: Banff, Alberta, May 7-10, 1989.

Oremland, R.S., Hollibaugh, J.T., Maest, A.S., Presser, T.S., Miller, L.G., and, Culbertson, C.W., 1989, Selenate reduction to elemental selenium by anaerobic bacteria in sediments and culture: biogeochemical significance of a novel, sulfate-independent respiration, Applied and Environmental Microbiology, v. 55, no. 9, p. 2333-2343.

Page, B.M., 1966, Geology of the Coast Ranges of California, *in* Bailey, Edgar, ed., Geology of northern California, Bulletin 190: San Francisco, California, California Division of Mines and Geology, p. 255-276.

Payne, M.B., 1951, Type Moreno Formation and overlying Eocene strata on the west side of the San Joaquin Valley, Fresno and Merced counties, California: California Division of Mines Special Report 9, 29 p.

Pearce, A.J., Stewart, M.K., and Sklash, M.G., 1986, Storm runoff in humid headwater catchments: where does the water come from?: Water Resources Research, v. 22, no. 8, p. 1263-1272.

Pelczar, M.J., Chan, E.C.S., and Krieg, N.R., 1986, Microbiology (5th ed.): San Francisco, McGraw-Hill, p. 557-559.

Pierce, F.D., and Brown, H.R., 1977, Comparison of inorganic interferences in atomic absorption spectrometric determination of arsenic and selenium: Analytical Chemistry, v. 49, no. 9, p. 1417-1422.

Presser T.S., and Barnes, Ivan, 1984, Selenium concentrations in waters tributary to and in the vicinity of Kesterson National Wildlife Refuge, Fresno and Merced counties, California: U.S. Geological Survey Water-Resources Investigations Report 84-4122, 26 p.

-----1985, Dissolved constituents including selenium in waters in the vicinity of Kesterson National Wildlife Refuge and the west Grassland, Fresno and Merced counties, California: U.S. Geological Survey Water-Resources Investigations Report 85-4220, 73 p.

Presser, T.S. and Ohlendorf, H.M., 1987, Biogeochemical cycling of selenium in the San Joaquin Valley, California: Environmental Management, v. 11, p. 805-821.

Rantz, S.E., 1969, Map of the mean annual precipitation in the California Region: U.S. Geological Survey Open-File Report, 2 sheets, scale 1,000,000.

Schroeder, R.A, Palawski, D.U., and Skorupa, J.P., 1988, Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in the Tulare Lake Bed area, southern San Joaquin Valley, California, 1986-1987: U.S. Geological Water-Resources Investigations Report 88-4001, 86 p.

Shacklette, H.T., and Boerngen, J.G., 1984, Element concentrations in soils and other surficial material of the conterminous United States: U.S. Geological Survey Professional Paper 1270, 105 p.

Shayan, A., and Lancucki, C.J., 1984, Konyaite in salt efflorescence from a Tertiary marine deposit near Geelong, Victoria, Australia: Soil Science Society of America Journal, v. 48, p. 939-942.

Shrift, A., 1964, A selenium cycle in nature?: Nature, v. 201, p. 1304-1305.

Siegenthaler, U., 1979, Stable hydrogen and oxygen isotopes in the water cycle, *in* Jaeger E. and Hunziker, J.C., eds., Lectures in Isotope Geology: Berlin, Springer-Verlag, p. 264-273.

Skorupa, J.P., and Ohlendorf, H.M., 1989, Drainwater contaminants in eggs related to deformities in Tulare Basin waterbirds: U.S. Fish and Wildlife Service Research Information Bulletin 89-04, 2 p.

Stiff, H.A., Jr., 1951, The interpretation of chemical water analysis by means of patterns: Journal of Petroleum Technology, v .3, no. 10, p. 15-17.

Stumm, Werner, and Morgan, J.J., 1981, Aquatic chemistry: an introduction emphasizing chemical equilibrium in natural waters, 2d ed.: New York, John Wiley, p. 469-471.

Sullivan, P.J., Sposito, Garrison, Strathouse, S.M., and Hansen, C.L., 1979, Geologic nitrogen and the occurrence of high nitrate soils in the western San Joaquin Valley, California: Hilgardia, v. 47, p. 15-49.

Swain, W.C., 1988, Characteristics of shallow ground water and subsurface drainage in the Tulare Basin, California: Eos Transactions of the American Geophysical Union, Abstract, v. 69, p. 1181.

Sylvester, M.A., and Wilber, W.G., 1989, Irrigation drainage in the West, *in* Howard, Alice, ed., Selenium and agricultural drainage: implications for San Francisco Bay and the California environment, Proceedings of the Third Selenium Symposium March 15, 1986: Berkeley, California, The Bay Institute of San Francisco, Tiburon, California, p. 129-134.

Sylvester, M.A., Deason, J.P., Feltz, H.R., and Engberg, R.A., 1988, Preliminary results of the Department of the Interior's Irrigation Drainage Studies, *in* Proceedings on planning now for irrigation and drainage, July 18-21, 1988, Lincoln, Nebraska: Irrigation Division, American Society of Civil Engineers, p. 665-677.

Taliaferro, N.L., 1951, Geology of the San Francisco Bay counties, *in* Geologic guidebook of the San Francisco Bay counties: California Division of Mines Bulletin 154, p. 117-150.

Tidball, R.R., Severson, R.C., Gent, C.A., and Riddle, G.O., 1986, Element associations in soils of the San Joaquin Valley, California: U.S. Geological Survey Open-File Report 86-583, 15 p.

Tidball, R.R., Severson, R.C., McNeal, J.M., and Wilson, S.A., 1989, Distribution of selenium, mercury, and other elements in soils of the San Joaquin Valley and parts of the San Luis Drain Service Area, California, *in* Howard, Alice, ed., Selenium and agricultural drainage: implications for San Francisco Bay and the California environment, Proceedings of the Third Selenium Symposium, March 15, 1986: Berkeley, California, The Bay Institute of San Francisco, Tiburon, California, p. 71-82.

Trelease, S.F., and Beath, O.A., 1949, Selenium, its geological occurrence and its biological effects in relation to botany, chemistry, agriculture, nutrition, and medicine: Burlington, Vermont, Champlain Printers, 292 p.

U.S. Bureau of Reclamation, 1984, San Luis Unit, Central Valley Project, California: U.S. Bureau of Reclamation Information Bulletins 1, 2, 3, and 4, 48 p.

U.S. Bureau of Reclamation, 1987, Water quality analyses, west side-San Joaquin Valley, California: Sacramento, California, U.S. Bureau of Reclamation, Mid-Pacific Region, p. 115-117.

U.S. Department of the Interior (Task Group on Irrigation Drainage), 1985, Preliminary evaluation of selenium concentrations in ground and surface water, soils, sediment, and biota from selected areas in the Western U.S: Washington, D.C., U.S. Department of the Interior, Office of the Secretary, 126 p.

U.S. Environmental Protection Agency, 1979, Water related environmental fate of 129 priority pollutants, volume I: Washington, D.C., U.S. Environmental Protection Agency report EPA-440/4-79-029a, p. 16-1 to 16-13.

-----1980, Hazardous waste management system, Federal Register, v. 45, no. 98, p. 33063-33285.

-----1987, Ambient water quality criteria for selenium: Washington, D.C., U.S. Environmental Protection Agency report EPA-440/5-87-006, 121 p.

van Doesburg, J.D.J., Vergouwen, L., and van der Plas, L., 1982, Konyaite, $Na_2Mg(SO_4)_2 \bullet 5H_20$, a new mineral from the Great Konya Basin, Turkey: American Mineralogist, v. 67, p. 1035-1038.

Vine, J.D., and Tourtelot, E.B., 1970, Geochemistry of black shale deposits--a summary report: Economic Geology, v. 65, p. 253-272.

Wagenet, R.J., and Jurinak, J.J., 1978, Spatial variability of soluble salt content in a Mancos Shale watershed: Soil Science, v. 126, p. 342-349.

Wedepohl, K.H., 1970, Handbook of Geochemistry: New York, Springer-Verlag, 92 chapters.

Whittig, L.D., Deyo, A.E., and Tanji, K.K., 1982, Evaporite mineral species in Mancos Shale and salt efflorescence, upper Colorado River basin: Soil Science Society of America Journal, v. 46, p. 645-651.

Williams, K.T., Lakin, H.W., and Byers, H.G., 1940, Selenium occurrence in certain soils in the U.S. with a discussion of related topics: fourth report: U.S. Department of Agriculture Technical Bulletin 702, 60 p.

-----1941, Selenium occurrence in certain soils in the U.S. with a discussion of related topics: fifth report: U.S. Department of Agriculture Technical Bulletin 758, 70 p.

page 35 follows

Table 1. Efflorescent sulfate minerals identified in the study area

Name	Formula
Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Thenardite	Na_2SO_4
Bloedite	$MgNa_2(SO_4)_2 \cdot 4H_2O$
Konyaite	$MgNa_2(SO_4)_2 \cdot 5H_2O$
Loeweite	$MgNa_2(SO_4)_2 \cdot 2\frac{1}{2}H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Starkeyite	$MgSO_4 \cdot 4H_2O$
Pentahydrite	$MgSO_4 \cdot 5H_2O$
Hexahydrite	$MgSO_4 \cdot 6H_2O$
Epsomite	$MgSO_4 \cdot 7H_2O$
Ferrohexahydrite	$FeSO_4 \cdot 6H_2O$
Glauberite	$Na_2Ca(SO_4)_2$
Hydroglauberite	$Na_{10}Ca_3(SO_4)_8 \cdot 6H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Bassanite	$CaSO_4 \cdot \frac{1}{2}H_2O$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Alunite	$KAl_3(SO_4)_2(OH)_6$
Burkeite	$Na_6CO_3(SO_4)_2$

Table 2a. Locations of creek sampling sites and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: bl, bloedite; gp, gypsum; ky, konyaite; th, thenardite. Analyses of selenium concentrations at transect sites by T. Fries, USGS, Branch of Geochemistry, Menlo Park, California]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
1	Little Panoche Creek	Lat 36°45′19″, long 120°50′56″, in NE1/4 sec.35 T13S R10E, Fresno County	4/84 11/84		no salt no salt		
2	Mine Creek	Lat 36°44′51″, long 120°51′47″, in NE1/4 sec.3 T14S R10E, Fresno County	11/84		no salt		
3	Griswold Creek above confluence with Panoche Creek	Lat 36°33′38″, long 120°50′18″, in NW1/4 sec.12 T16S R10E, San Benito County	4/84 6/84 11/84	0.8	ky,th,bl no salt no salt		
4	San Carlos at Silver Creek	Lat 36°27′24″, long 120°40′51″, in NW1/4 sec.17 T17S R12E, San Benito County	4/88		no salt		
5	Clear Creek at San Benito River	Lat 36°21′31″, long 120°47′08″, in SE1/4 sec.17 T18S R11E, San Benito County	4/88		no salt		
6	Larious Creek	Lat 36°27′35″, long 120°42′02″, in SW1/4 sec.7 T17S R12E, San Benito County	4/84		no salt		
7	Silver Creek	Lat 36°28′35″, long 120°41′38″, in SE1/4 sec.31 T15S R12E, San Benito County	12/84		no salt	0.4	1.7
8	Panoche Creek	Lat 36°37′02″, long 120°40′26″, in NW1/4 sec.21 T15S R12E, Fresno County	11/84	.65 .20	bl,th bl,gp		
9	Cantua Creek	Lat 36°24′25″, long 120°26′46″, in NE1/4 sec.33 T17S R14E, Fresno County	5/87		no salt		

Table 2b. Selenium concentrations and water chemistry of creek samples

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
1	<2	Na-HCO_3 Cl	8.66	15	881	140	2.1	71	29	110	145	345	17	3.8
	<2	Na-Cl HCO_3	8.61	14	1,104	200	2.8	88	34	120	240	367	18	5.8
2	<2	NaCaMg-HCO_3	8.16	15	881	110	4.4	75	42	155	60	398	19	2.9
3	20	Na-SO_4	8.33	21	4,467	860	7.9	290	170	2,600	180	311	7.2	7.1
	7	Na-SO_4	8.1	25	5,056	1,000	10	320	180	2,900	200	365	26	9.5
	12	Na-SO_4	7.98	14	5,453	1,100	13	230	225	3,200	210	406	17	8.8
4	3	Mg-SO_4	8.26	22	5,728	420	24	440	605	3,850	180	203	6.4	10
5	<2	Mg-HCO_3	8.33	15	987	29	1.4	17	135	63	26	708	7.2	<1
6	3	Mg-HCO_3	9.36	21	1,531	61	2.3	12	220	150	38	1,035	3.1	1.6
7	2	NaMg-SO_4	8.21	9	9,146	1,550	23	315	670	5,050	670	760	15	16
8	5	NaMg-SO_4	8.34	13	7,878	1,350	12	410	510	8,080	1,260	521	20	13
9	6	Mg-SO_4HCO_3	8.65	24	1,794	215	5	38	170	590	50	726	16	1.4

Table 3a. Locations of spring sampling sites and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: bl, bloedite; hl, halite; hx, hexahydrite; ky, konyaite; th, thenardite. Analyses of selenium concentrations at transect sites by T. Fries, USGS, Branch of Geochemistry, Menlo Park, California]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
10	Mercey Hot Spring	Lat 36°42′12″, long 120°51′34″, in SE1/4 sec.15 T14S R10E, Fresno County	4/84		no salt		
11	Harris Spring	Lat 36°22′47″, long 120°31′17″, in NE1/4 sec.11 T18S R13E, Fresno County	5/87	0.2	th		
12	Greenwater Spring	Lat 36°22′44″, long 120°28′40″, in NW1/4 sec.8 T18S R14E, Fresno County	5/87	.9	bl,hl,th		
13	Developed spring at Salt Creek	Lat 36°22′30″, long 120°25′53″, in SE1/4 sec.10 T18S R14E, Fresno County	5/87		carbonate		
14	Ciervo Spring	Lat 36°28′52″, long 120°33′24″, in NE1/4 sec.4 T17S R13E, Fresno County	5/86		no salt		
15	Larious Spring	Lat 36°26′35″, long 120°44′20″ in NW1/4 sec.23 T17S R11E, San Benito County	9/87	.5	hx,ky	1.0	

Table 3b. Selenium concentrations and water chemistry of spring samples

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
10	<2	Na-Cl	8.95	44	2,388	830	5.9	40	<1	4	1,300	58	70	14
11	<2	Na-HCO_3	8.75	19	844	235	1	4	4	160	7	433	16	<1
12	<2	Na-SO_4	7.6	19	4,776	1,100	12	130	170	2,350	130	884	22	4.0
13	<2	Na-SO_4	7.85	25	3,828	745	13	135	180	1,300	320	1,135	23	5.3
14	<2	NaMgCa-SO_4	7.2	--	1,683	295	11	145	89	810	34	252	49	1.0
15	<2	Na-SO_4	8.6	21	1,925	455	33	54	43	615	23	702	18	1.2

Table 4a. Locations of acid water sampling sites and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: bl, bloedite; ep, epsomite; gp, gypsum; hg, Hydroglauberite; hx, hexahydrite; ky, konyaite; lw, loeweite; st, starkeyite; th, thenardite. Analyses of selenium concentrations at transect sites by T. Fries, USGS, Branch of Geochemistry, Menlo Park, California]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
		Acid seeps in Moreno Formation					
16	at Arroyo Hondo	Lat 36°24′50″, long 120°34′06″,	5/87	12	bl,th	4.4	3.3
		in SW1/4 sec.28 T17S R13E,	10/87	5.5	bl,th	4.1	9.8
		Fresno County	4/88		no salt	6.3	3.8
	at Tumey Gulch tributary	Lat 36°32′11″, long 120°38′01″,					
		in SW1/4 sec.14 T16S R12E,					
		Fresno County					
17	seep I		5/86	4.0	th[1]		
				.7	th[2]		
			5/87	15	th		
				14	hg		
17	seep II		5/88	2.4	lw,bl,th		
	seep III						
17	seep		5/88	.1	th		
17	pool		5/88				
18	at Escapardo Canyon	Lat 36°38′27″, long 120°41′28″,	5/88	1.1	bl,lw		
		in NW1/4 sec.8 T15S R12E,					
		Fresno County					
	at confluence area of Panoche and Silver Creeks	Lat 36°35′59″, long 120°41′33″,					
		in NW1/4 sec.29 T15S R12E,					
		Fresno County					
19	upper seep		10/88	25	bl,gp		
19	lower seep		10/88	2.1	bl,ep		
20	at Moreno Gulch acid mine drainage	Lat 36°43′20″, long 120°44′35″,	1/89	1.8	ky,lw,st,hx		
		in SW1/4 sec.11 T14S R11E,					
		Fresno County					
		Acid mine drainage from New Idria mercury mine					
21	at San Carlos Creek	Lat 36°24′56″, long 120°40′13″,	4/84	.7	bl		
		in NW1/4 sec.29 T17S R12E,	9/87	.1	bl,hx,ep	<.1	.6
		San Benito County	4/88		no salt		

---

[1] Powder.

[2] Compact.

Table 4b. Selenium concentrations and water chemistry of acid water samples

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total acidity as hydrogen	Silica	Boron
Acid seeps in Moreno Formation														
16	298	Na-SO_4	4.35	21	13,417	2,950	47	370	590	9,350	110	9.4	96	7.8
	320	Na-SO_4	4.40	24	14,329	3,150	49	365	640	10,000	125	6.2	72	7.8
	420	Na-SO_4	4.38	16	17,901	3,850	50	394	895	12,500	150	10	61	8.0
17	211	Na-SO_4	3.95		71,567	15,000	76	170	4,550	50,000	1,700	67	120	28
	107	Na-SO_4	3.85	24	32,449	6,900	30	171	1,950	22,500	820	37	95	12
17	197	Na-SO_4	3.83	15	49,744	9,850	35	470	3,700	34,500	1,100	16	89	13
17	6	Na-SO_4	3.90	16	22,111	4,800	27	380	1,100	15,200	500	11	104	11
17	5	Na-SO_4	4.03	14	27,732	6,100	36	415	1,500	19,000	610	11	71	13
18	42	MgNa-SO_4	3.60	16	28,332	4,200	28	410	2,650	20,500	425	31	119	10
19	28	Mg-SO_4	4.47	24	29,461	4,100	46	410	2,650	22,000	235	7.5	42	13
19	38	Mg-SO_4	4.15	27	37,358	5,400	59	435	3,350	27,500	293	9.2	48	16
20	87	Mg-SO_4	4.24	5	21,159	1,350	30	360	3,250	16,000	200	4.1	62	10
Acid mine drainage from New Idria mercury mine														
21	<2	FeMg-SO_4[1]	3.98	18	9,553	495	52	380	555	6,700	210	57	37	15
	<2		3.5	19	5,465	520	65	315	315	4,000	250	26	42	22
	<2	FeMg-SO_4[2]	3.02	18	6,349	530	72	325	350	4,700	300	36	46	22

[1] Iron (Fe) = 1,000 mg/L.
[2] Iron (Fe) = 640 mg/L.

Table 5a. Locations of ephemeral stream sampling sites and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: bk, burkeite; bl, bloedite; ep, epsomite; gp, gypsum; hl, halite; hg, hydroglauberite; lw, loeweite; th, thenardite; tr, trona. Analyses of selenium concentrations at transect sites by T. Fries, USGS, Branch of Geochemistry, Menlo Park, California]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
22	at Tumey Gulch I	Lat 36°31′28″, long 120°37′14″,	5/86	[1]7	th,lw		
		in SW1/4 sec.24 T16S R12E,		8	th		
		Fresno County	5/87	[2]11	bl,hl		
			4/88	11	th,bl,lw		
23	at Tumey Gulch II	Lat 36°33′13″, long 120°37′35″, in NE1/4 sec.11 T16S R12E, Fresno County	4/88	8.8	th,hg,gp		
24	at Tumey Gulch III	Lat 36°31′08″, long 120°37′20″, in SW1/4 sec.24 T16S R12E, Fresno County	5/87	2.4	th,hl		
25	at Vallecitos Creek	Lat 36°29′17″, long 120°47′44″,	9/85	1.9	th		
		in SW1/4 sec.32 T16S R11E,		7.8	th,bk,tr		
		San Benito County	1/89	11	th		
26	at Los Pinos Creek	Lat 36°28′35″, long 120°46′20″, in SW1/4 sec.4 T17S R11E, San Benito County	11/84	1.9	th,ep	1.5	0.8

[1] Salts precipitated in laboratory water sample.

[2] Precipitated salts floating on water surface at sampling site.

Table 5b. Selenium concentrations and water chemistry of ephemeral stream samples

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
22	2,100	Na-SO_4	8.40	--	108,539	33,000	72	520	4,450	58,000	11,500	993	16	71
	2,850	Na-SO_4	8.74	38	139,360	37,000	88	680	6,450	79,000	15,000	1,135	22	89
	3,500	Na-SO_4	8.59	25	159,811	44,000	200	635	7,550	88,000	18,200	1,415	20	67
23	14	Na-ClSO_4	8.94	29	94,344	30,000	98	680	2,800	33,000	27,000	763	10	115
24	<2	Na-ClHCO_3	9.10	29	16,353	5,600	36	11	51	980	4,250	5,426	10	45
25	12	Na-SO_4	8.19	14	2,976	750	6.5	70	79	1,150	170	751	21	6.2
	20	Na-SO_4	8.91	12	2,916	730	6.2	61	59	1,100	180	708	36	6.3
26	24	Na-SO_4	8.79	14	5,411	1,300	5.0	160	160	3,050	160	477	13	15

Table 6a. Locations of seep sampling sites in the Moreno, Kreyenhagen, and Panoche Formations and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: bl, bloedite; ep, epsomite; hl, halite; ky, konyaite; lw, loeweite; mb; mirabilite; st, starkeyite; th, thenardite]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
Alkaline seeps in Moreno Formation							
	near confluence of Silver and Panoche Creeks	Lat 36°35'41", long 120°41'21", SW1/4 sec.29 T15S R12E, Fresno County					
27	upper seep		10/88	0.6	bl,st		
27	lower seep		10/88	.1	ky,bl		
Seeps on Monocline Ridge (Kreyenhagen Formation)							
	South group						
28	upper seep	Lat 36°31'51", long 120°34'08", SE1/4 sec.17 T16S R13E, Fresno County	1/89	3.1	ep,th,mb		
28	middle seep	Lat 36°32'02", long 120°34'05", SE1/4 sec.17 T16S R13E, Fresno County	1/89				
28	lower seep	Lat 36°32'07", long 120°34'00", SW1/4 sec.16 T16S R13E, Fresno County	1/89				
	North group						
29	upper seep	Lat 36°32'08", long 120°34'18", SE1/4 sec.17 T16S R13E, Fresno County	1/89				
29	lower seep	Lat 36°32'10", long 120°34'10", SE1/4 sec.17 T16S R13E, Fresno County	1/89				
Alkaline seeps in Panoche Formation (Moreno Gulch)							
30	Secondary drainage	Lat 36°45'45", long 120°43'11", SW1/4 sec.10 T14S R11E, Fresno County	4/89	[1].1 .8	lw ky		

[1] Precipitate in water sample.

Table 6b. Selenium concentrations and water chemistry of seep samples from the Moreno, Kreyenhagen, and Panoche Formations

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
Alkaline seeps in Moreno Formation														
27	4	MgNa-SO_4	8.34	20	40,970	5,550	86	460	3,800	30,000	250	735	2.8	15
27	7	MgNa-SO_4	7.85	20	59,744	8,400	109	405	5,550	44,000	350	817	16	17
Seeps on Monocline Ridge (Kreyenhagen Formation)														
28	48	Na-SO_4	6.84	3	15,994	4,000	33	355	525	9,600	440	984	23	6.0
28	28	Na-SO_4	5.87	0	14,320	3,250	35	355	750	9,500	360	--	30	7.0
28	10	Na-SO_4	7.74	4	14,889	3,050	54	390	760	9,700	400	469	23	7.5
29	9	NaMg-SO_4	6.38	3	8,794	1,400	34	415	620	5,900	90	275	34	3.8
29	52	NaMg-SO_4	6.34	1	13,182	1,900	49	405	1,250	9,200	120	192	33	5.4
Alkaline seeps in Panoche Formation (Moreno Gulch)														
30	<2	Mg-SO_4	6.93	20	421,409	41,000	515	170	56,000	318,000	3,500	787	18	248

Table 6a. Locations of seep sampling sites in the Moreno, Kreyenhagen, and Panoche Formations and selenium concentrations in identified evaporative salts and transect samples--Continued

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
		Alkaline seeps in Panoche Formation (Moreno Gulch)--Continued					
31	Main drainage seep I	Lat 36°45′20″, long 120°42′46″, NW1/4 sec.15 T14S R11E, Fresno County	4/89	0.9	ky		
31	pool	Lat 36°45′14″, long 120°42′47″, NE1/4 sec.15 T14S R11E, Fresno County	4/89		hl		
31	spring	Lat 36°45′14″, long 120°42′48″, NE1/4 sec.15 T14S R11E, Fresno County	4/89		hl		
31	seep II	Lat 36°45′10″, long 120°42′52″, NE1/4 sec.15 T14S R11E, Fresno County	4/89	.9	hl		

Table 6b. Selenium concentrations and water chemistry of seep samples from the Moreno, Kreyenhagen, and Panoche Formations--Continued

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
Alkaline seeps in Panoche Formation (Moreno Gulch)--Continued														
31	<2	Na-Cl	7.30	26	84,122	23,500	52	875	3,950	16,000	38,500	259	8	171
31	<2	Na-Cl	8.05	28	31,301	7,850	22	905	1,650	6,900	13,000	537	<2	76
31	<2	Na-Cl	8.05	17	12,986	935	7	200	25	1,050	1,000	235	12	16
31	<2	Na-Cl	7.68	27	28,442	6,700	24	2,850	515	1,900	15,500	162	<2	138

Table 7a. Locations of integrated watershed sampling sites and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: bl, bloedite; ep, epsomite; hl, halite; hx, hexahydrite; ky, konyaite; th, thenardite. Analyses of selenium concentrations at transect sites by T. Fries, USGS, Branch of Geochemistry, Menlo Park, California]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
32	Silver Creek headwaters seep	Lat 36°28′03″, long 120°41′02″, in NW1/4 sec.8 T17S R12E, San Benito County	9/85	0.4	ep,hx		
			9/87	.1	ep,bl,hx	3.7	0.6
			4/88		no salt		
			1/89				
			2/89				
33	upstream of headwater seep	Lat 36°27′50″, long 120°41′04″, in SW1/4 sec.8 T17S R12E, San Benito County	2/89	5.6	ky		
34	Larious Creek at Silver Creek	Lat 36°27′58″, long 120°41′09″, in NW1/4 sec.8 T17S R12E, San Benito County	2/89	1.5	th		
35	Griswold Creek below confluence of Vallecitos and Pimental Creeks	Lat 36°31′06″, long 120°49′56″, in SW1/4 sec.24 T16S R10E, San Benito County	10/88		no salt		
			2/89		no salt		
36	confluence of Vallecitos and Pimental Creeks	Lat 36°31′01″, long 120°49′56″, in SW1/4 sec.24 T16S R10E, San Benito County	2/89	2.9	th,ky,bl		
37	sulfur seep	Lat 36°31′23″, long 120°49′57″, in SW1/4 sec.24 T16S R10E, San Benito County	4/84	7.5	bl,hx		
			6/84	14	ky,bl,ep,hx,hl		
			6/84				

Table 7b. Selenium concentrations and water chemistry of integrated watershed samples

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
32	24	MgNa-SO_4	8.03	23	4,437	470	9.8	290	400	2,700	100	467	24	6.2
	77	MgNa-SO_4	8.30	21	3,697	445	6	230	335	2,300	65	316	30	6.0
	83	MgNa-SO_4	7.60	18	4,413	475	12	275	405	2,700	115	411	20	7.3
	126	NaMg-SO_4	8.06	15	3,347	570	5.8	163	255	2,000	82	210	25	6.3
	141	NaMg-SO_4	7.68	16	3,580	577	6.0	160	245	1,900	80	555	26	5.5
33	88	NaMg-SO_4	7.50	20	5,100	795	7.0	235	357	2,900	120	616	24	8.0
34	89	Na-SO_4	8.99	21	3,068	620	4.1	90	170	1,600	150	379	17	6.7
35	39	Na-SO_4	8.00	14	5,071	775	8.5	270	135	2,050	190	668	28	8.7
	55	Na-SO_4	7.88	15	4,274	845	6.7	250	165	2,300	190	465	4.0	8.5
36	153	Na-SO_4	7.96	15	4,356	920	6.9	185	145	2,350	250	438	6.0	9.7
37	40	Na-SO_4	8.17	19	3,741	655	6.4	300	150	2,100	110	371	19	5.0
	28	Na-SO_4	7.92	28	3,863	650	6.0	300	160	2,300	90	309	21	4.5
	23	Na-SO_4	8.00	30	3,782	670	6.6	290	150	2,200	105	310	20	5.1

Table 8a. Locations of creekbed headcut, channel seep, and contact seep sampling sites and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: bl, bloedite; ep, epsomite; fhx, ferrohexahydrite; gp, gypsum; hg, hydroglauberite; hl, halite; hx, hexahydrite; ky, konyaite; ks, kieserite; th, thenardite. Analyses of selenium concentrations at transect sites by T. Fries, USGS, Branch of Geochemistry, Menlo Park, California]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
		Parallel to dip					
	Salt Creek						
38	headcut in tributary	Lat 36°22′04″, long 120°28′22″, in NW1/4 sec.17 T18S R14E, Fresno County	5/87	0.2	th,bl		
39	seep I	Lat 36°22′21″, long 120°26′12″, in SE1/4 sec.10 T18S R14E, Fresno County	5/87	.2	th,ky,bl,hl,gp		
13	seep II	Lat 36°22′30″, long 120°25′53″, in SE1/4 sec.10 T18S R14E, Fresno County	5/87	.5	th,hl		
40	seep III	Lat 36°22′32″, long 120°25′19″, in NE1/4 sec.11 T18S R14E, Fresno County	5/87	.3	th,hl		
	Silver Creek						
41	seep at Lodo landslide	Lat 36°30′30″, long 120°41′22″, in NW1/4 sec.29 T16S R12E, San Benito County	9/87	.5	hx,ky,bl,fhx	1.6 4.1	1.1 3.9
41	seep in tributary at Lodo landslide	Lat 36°30′31″, long 120°41′19″, in NW1/4 sec.29 T16S R12E, San Benito County	9/87	3.1	bl,th,hg	4.1	2.2
42	Moreno-Lodo drainage	Lat 36°30′46″, long 120°42′26″, in NE1/4 sec.30 T16S R12E, San Benito County	11/87	.8	th		
43	headcut	Lat 36°34′22″, long 120°41′58″, in NE1/4 sec.6 T16S R12E, Fresno County	9/87	.6	hx,ky,gp	1.2	2.1
44	seep near confluence with Panoche Creek	Lat 36°34′44″, long 120°41′32″, in SW1/4 sec.32 T15S R12E, Fresno County	9/85	2.7	bl,hl,ks	6.8	8.4

Table 8b. Selenium concentrations and water chemistry of headcut, channel seep, and contact seep samples from creek beds

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
						Parallel to dip								
38	3	Na-SO$_4$	8.15	26	3,328	655	6	190	160	1,500	275	542	7.4	3.5
39	2	Na-SO$_4$	8.10	24	9,616	2,700	11	180	250	3,900	2,000	575	7.2	27
13	2	Na-Cl	8.55	24	8,479	2,900	31	25	43	530	3,100	1,850	3.6	50
40	2	Na-ClSO$_4$	8.00	19	17,819	5,400	55	195	420	3,100	2,400	749	2.0	64
41	<2	NaMg-SO$_4$	8.2	22	7,128	1,200	34	230	530	4,150	260	724	3.2	11
41	<2	Na-SO$_4$	7.9	21	7,442	1,600	15	500	200	4,500	160	467	27	11
42	<2	Na-SO$_4$	8.4	15	7,190	2,150	4	100	160	3,500	360	916	21	3.8
43	<2	NaMg-SO$_4$	8.4	29	11,923	2,050	19	285	985	7,200	840	544	<1	23
44	<2	Na-SO$_4$	8.12	24	10,432	1,950	19	330	700	5,800	870	763	22	21

Table 8a. Locations of creekbed headcut, channel seep, and contact seep sampling sites and selenium concentrations in identified evaporative salts and transect samples--Continued

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
		Parallel to dip--Continued					
8	Panoche Creek seep I	Lat 36°37′02″, long 120°40′26″, in NW1/4 sec.21 T15S R12E, Fresno County	9/87	0.2	bl,th	1.1	1.0
						1.2	1.0
45	seep II	Lat 36°37′22″, long 120°39′53″, in SE1/4 sec.16 T15S R12E, Fresno County	10/88	.3	bl		
				1.2	ky,hx,ep,bl,hl		
46	Griswold Creek headcut	Lat 36°32′29″, long 120°50′02″, in SW1/4 sec.13 T16S R10E, San Benito County	10/88	3.9	th,bl		
47	Cantua Creek seep	Lat 36°23′44″, long 120°32′59″, in NW1/4 sec.3 T18S R13E, Fresno County	5/87	8.5	bl,th		
				.9	bl,th		
		Perpendicular to dip					
48	Silver Creek headcut	Lat 36°33′00″, long 120°42′41″, in SE1/4 sec.12 T16S R11E, San Benito County	9/87	1.4	hx,bl,ky, hl,gp	1.4	1.8
						1.8	.7
49	Salt Creek seep in tributary	Lat 36°22′08″, long 120°26′28″, in NW1/4 sec.15 T18S R14E, Fresno County	5/87	1.9	ky,th,bl,hl		
50	pool	Lat 36°22′15″, long 120°27′28″, in SW1/4 sec.9 T18S R14E, Fresno County	5/87	1.1	bl,hl		

Table 8b. Selenium concentrations and water chemistry of headcut, channel seep, and contact seep samples from creek beds--Continued

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
					Parallel to dip--Continued									
8	<2	Na-SO_4	8.1	27	13,901	2,900	19	360	830	8,100	1,250	442	2.8	29
45	<2	Na-SO_4	7.80	16	18,461	3,400	24	475	1,250	10,500	2,150	632	4.0	26
46	<2	Na-SO_4	7.35	14	7,084	1,400	12	410	265	4,000	250	641	26	14
47	<2	Na-SO_4	7.82	24	18,204	4,150	21	355	860	12,000	270	548	<1	7.0
					Perpendicular to dip									
48	<2	NaMg-SO_4	8.0	20	7,473	1,150	15	290	600	4,500	440	478	4.0	16
49	17	Na-SO_4	7.95	19	5,925	1,350	8	260	235	2,900	740	430	19	7.4
50	14	Na-SO_4	7.95	19	7,635	1,450	10	400	380	4,500	450	445	14	4.9

Table 9a. Locations of well sampling sites and selenium concentrations in identifed evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
	Panoche Valley						
51	domestic at 400 feet	Lat 36°35'34", long 120°46'58", in SE1/4 sec.29 T15S R11E, San Benito County	9/87 11/87		no salt no salt		
52	livestock at 400 feet	Lat 36°35'16", long 120°46'53", in SE1/4 sec.29 T15S R11E, San Benito County	11/87		no salt		
53	domestic at 100 feet	Lat 36°36'06", long 120°50'40", in NE1/4 sec.26 T15S R11E, San Benito County	10/88		no salt		
54	domestic	Lat 36°35'44", long 120°47'45", in NW1/4 sec.29 T15S R10E, San Benito County	9/87		no salt		
55	domestic	Lat 36°36'28", long 120°51'32", in SE1/4 sec.22 T15S R10E, San Benito County	9/87		no salt		
56	domestic	Lat 36°36'58", long 120°56'32", in SE1/4 sec.24 T15S R9E, San Benito County	9/87		no salt		
32	at Silver Creek headwater seep	Lat 36°28'03", long 120°41'02", in NW1/4 sec.8 T17S R12E, San Benito County	1/89 2/89		no salt no salt		
57	at Panoche Creek above confluence with Silver Creek	Lat 36°36'54", long 120°51'28", in NW1/4 sec.23 T15S R9E, San Benito County	2/89		no salt		

Table 9b. Selenium concentrations and water chemistry of well samples

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
51	56	CaMgNa-SO_4	7.2	20	3,003	295	4	360	195	1,650	270	219	38	4.0
	49	CaMgNa-SO_4	7.6	--	3,029	295	4	370	215	1,500	410	235	41	6.3
52	58	NaMgCa-SO_4	7.6	--	2,987	405	5	265	180	1,700	200	232	30	4.2
53	7	MgNaCa-SO_4	8.22	23	1,026	98	4.5	80	71	380	37	309	44	1.2
54[1]	8	MgNaCa-SO_4	7.4	29	893	102	2.4	88	59	295	134	188	--	1.7
55[1]	<2	NaCaMg-SO_4	7.4	24	1,040	126	4.0	90	52	530	41	151	--	1.4
56[1]	4	MgNaCa-SO_4	7.4	27	684	84	1.7	58	50	239	47	243	--	.7
32	19	Mg-SO_4	7.60	15	3,863	280	7.6	270	405	2,400	90	352	29	4.6
	25	Mg-SO_4	7.22	16	3,922	290	7.7	274	407	2,450	80	356	29	4.8
57	5	CaMgNa-HCO_3SO_4	7.73	9.5	817	69	1.5	93	38	190	42	352	20	.6

---

[1] California Department of Water Resources data.

Table 10a. Locations of runoff sampling sites and selenium concentrations in identified evaporative salts and transect samples

[Map number refers to figure 5. Selenium concentrations in parts per million. Salt type: ep, epsomite; gp, gypsum; hx, hexahydrite; th, thenardite. Analyses of selenium concentrations at transect sites by T. Fries, USGS, Branch of Geochemistry, Menlo Park, California]

Map number	Name	Location	Date	Selenium concentration in salts	Salt type	Selenium concentrations at transect sites	
						Channel bed	Bank
		At peak of hydrograph					
58	Panoche Creek at highway I-5	Lat 36°39′03″, long 120°37′55″, in SW1/4 sec.2 T15S R12E, Fresno County	9/29/87			1.2	1.3
			10/29/87		no salt		
			11/9/87			2.9	
			1/17/88		no salt		
59	Silver Creek at Panoche Road	Lat 36°35′40″, long 120°41′01″, in SE1/4 sec.29 T15S R12E, Fresno County	1/17/88		no salt		
		Eleven days after peak					
60	Silver Creek rainpool	Lat 36°28′08″, long 120°40′56″, in NW1/4 sec.8 T17S R12E, San Benito County	11/10/87		no salt		
61	at mudflow	Lat 36°30′06″, long 120°40′47″, in SE1/4 sec.29 T16S R12E, San Benito County	11/10/87	14	th,gp	4.3	
41	at Lodo landslide	Lat 36°30′30″, long 120°41′22″, in NW1/4 sec.29 T16S R12E, San Benito County	11/10/87		no salt		
62	at Moreno landslide	Lat 36°30′47″, long 120°41′38″, in NE1/4 sec.30 T16S R12E, San Benito County	11//10/87		no salt	2.9	4.2
41	Tributary at Lodo landslide headwaters	Lat 36°30′30″, long 120°41′19″, in NW1/4 sec.29 T16S R12E, San Benito County	11/10/87		no salt		
41	at confluence with Silver Creek	Lat 36°30′31″, long 120°41′19″, in NW1/4 sec.29 T16S R12E, San Benito County	11/10/87		no salt		
4	San Carlos Creek at Silver Creek	Lat 36°27′24″, long 120°40′51″, in NW1/4 sec.17 T17S R12E, San Benito County	11/10/87	.6	ep,hx	.7	

Table 10b. Selenium concentrations and water chemistry of runoff samples

[Map number refers to figure 5. µg/L, micrograms per liter; constituents in milligrams per liter; pH in standard units; water temperature in degrees Celsius (°C); <, value is less than actual value shown]

Map number	Selenium (µg/L)	Water type	pH	Water temperature	Dissolved solids, calculated	Sodium	Potassium	Calcium	Magnesium	Sulfate	Chloride	Total alkalinity as bicarbonate	Silica	Boron
At peak of hydrograph														
58[1]	44	CaNaMg-SO_4	--	--	3,392	360	24	470	115	2,200	84	155	--	1.6
	57	NaCaMg-SO_4	7.9	--	3,710	495	17	410	170	2,400	125	151	--	2.0
59[1]	55	NaMgCa-SO_4	7.8	--	6,190	845	19	475	300	3,700	95	205	--	3.0
Eleven days after peak														
60	69	Ca-SO_4	6.6	--	3,344	200	17	575	160	2,300	45	47	19	1.5
61	7	Na-SO_4	8.0	11	10,925	3,100	12	190	210	6,000	610	803	19	4.8
41	19	NaMg-SO_4	8.1	13	6,356	1,000	15	255	500	3,800	240	546	11	9.5
62	18	NaMg-SO_4	8.2	--	6,493	1,000	15	275	490	3,950	240	523	12	10
41	4	$\text{Na-HCO}_3\text{SO}_4$	8.2	--	3,839	885	7	195	78	1,700	155	819	16	11
41	3	Na-SO_4	8.4	11	2,668	660	5	115	31	640	170	1,047	16	14
4	2	Mg-SO_4	5	--	5,731	470	16	475	570	4,000	200	[2].3	9.6	12

---

[1] California Department of Water Resources data except for selenium.

[2] Milligrams per liter hydrogen.

Table 11. Trace element concentrations for acid and alkaline samples[1,2]

[Abbreviations: µg/L, micrograms per liter; mg/L, milligrams per liter. pH in standard units. <, less than value shown]

	pH	Se	As	Hg	Fe	Al	Mn	Ni	Co	Cu	Cd	Zn	Cr	Be	Ti
		µg/L			mg/L										
Acid samples															
Arroyo Hondo	4.4	420	<1	<0.1	0.3	72	31	6.0	0.8	<0.03	0.08	9	<0.04	0.038	0.06
Tumey Gulch tributary seep II	3.8	197	<1	<.1	.4	106	95	8.3	1.2	.08	.09	11	<.04	.039	.09
Escapardo Canyon	3.6	42	2	<.1	.4	188	88	8.8	1.7	.05	.03	13	.03	.070	.09
New Idria mine drainage	3.0	<2	4	<.1	640	88	10	1.4	.6	<.03	.10	3	.07	<.003	<.03
Rainpool	5.5	69	<1	-	<.1	<.3	2	.2	<.1	.03	<.03	.1	<.04	<.003	<.03
Alkaline samples															
Tumey Gulch I	8.6	3,500	8	--	0.1	<0.3	1	0.6	<0.1	0.4	<0.03	<0.1	<0.04	<0.003	<0.03
Mercey Hot Springs	9.0	<2	<1	0.1	<.1	<.3	<1	<.1	<.1	<.03	<.03	<.1	<.04	<.003	<.03
Mudflow	8.0	7	<1	--	<.1	<.3	<1	<.1	<.1	<.03	<.03	<.1	<.04	<.003	<.03
Silver Creek headwater seep	7.6	83	<1	--	<.1	<.3	2	<.1	<.1	<.03	<.03	<.1	<.04	<.003	<.03

[1] Pb and Mo concentrations were all <0.3 mg/L.

[2] V concentrations were all <0.04 mg/L.

Table 12. Gas chemistry of acid seep headspace samples

[Samples analyzed by W.C. Evans, U.S. Geological Survey, Menlo Park, California. Abbreviations: °C, degrees Celsius; µg/L, micrograms per liter; µmoles/kg, micromoles per kilogram; atm., atmosphere; mg/L, milligrams per liter. <, less than value shown]

	Water temperature (°C)	Selenium (µg/L)	N_2	O_2	Ar	CH_4	CO_2	N_2O	pCO_2 (atm.)	H_2CO_3 (mg/L)
			µmoles/kg solution							
Tumey Gulch Tributary										
pool III	16	5	649	303	17.9	0.06	638	<0.1	0.0165	40
seep III	14	6	685	20.2	15.1	<.06	2,740	14.9	.0722	173
San Carlos Creek at New Idria	22	<2	848	.2	21.4	<.06	30.6	<.1	.0206	19.6
Escapardo Canyon	16	42	760	327	19.9	<.06	197	6.5	.0053	12.4
Arroyo Hondo										
lower seep	16	420	932	380	21.3	<.06	469	18.3	.0122	29.5
upper seep	16	420	719	584	19.3	<.08	1,290	94.1	.0182	80.4
Air saturated water at sea level at 15 °C[1]	15	--	587	315	15.4	--	14.7	--	0.0003	--

[1] Based on data from Emmerich and others (1977).

Table 13. Locations and selenium concentrations of geologic samples, by formation, collected by the U.S. Geological Survey

[Analysis by S.A. Wilson and staff, U.S. Geological Survey, Branch of Geochemistry, Denver, Colorado. Selenium concentrations in parts per million]

Sample No.	Location	Area	Member/type	Selenium
		Panoche Formation		
1	Lat 36°23′35″, long 120°33′44″, Fresno County	Cantua Creek	clayshale	1.3
2	Lat 36°23′35″, long 120°33′44″, Fresno County	Cantua Creek	clayshale	.08
		Moreno Formation		
3	Lat 36°24′33″, long 120°33′42″, Fresno County	Cantua Creek	sandstone	12
4	Lat 36°24′20″, long 120°33′35″, Fresno County	Cantua Creek	sandstone	16
5	Lat 36°24′51″, long 120°34′05″, Fresno County	Arroyo Hondo	shale	3.9
6	Lat 36°24′33″, long 120°33′42″, Fresno County	Cantua Creek	shale	3.1
7	Lat 36°31′06″, long 120°37′28″, Fresno County	Tumey Gulch	shale	15
8	Lat 36°31′12″, long 120°37′22″, Fresno County	Tumey Gulch	shale	23
9	Lat 36°32′14″, long 120°37′58″, Fresno County	Tumey Gulch	Dos Palos shale	1.4
10	Lat 36°32′18″, long 120°38′27″, Fresno County	Tumey Hills	shale	1.4
11	Lat 36°31′14″, long 120°39′24″, San Benito County	Tumey Hills	shale	18
12	Lat 36°31′05″, long 120°39′58″, San Benito County	Tumey Hills	soil (0-8″ depth), clayshale	2.4
13	Lat 36°31′11″, long 120°39′48″, San Bentio County	Tumey Hills	clayshale, efflorescence	2.6
14	Lat 36°31′11″, long 120°39′48″, San Benito County	Tumey Hills	clayshale, efflorescence	1.6
15	Lat 36°34′59″, long 120°41′42″, Fresno County	Silver Creek	shale	2.8
16	Lat 36°35′01″, long 120°41′40″, Fresno County	Silver Creek	sandstone and shale	.8
17	Lat 36°34′59″, long 120°41′37″, Fresno County	Silver Creek	soil and salt	35
92[1]	Lat 36°37′22″, long 120°41′11″, Fresno County	Silver/Panoche confluence	shale	8.5
93[1]	Lat 36°37′33″, long 120°41′33″, Fresno County	Silver/Panoche confluence	shale	7.8
94[1]	Lat 36°37′27″, long 120°41′38″, Fresno County	Silver/Panoche confluence	shale	6.5
95[1]	Lat 36°35′58″, long 120°41′34″, Fresno County	Silver/Panoche confluence	shale	7.9
96[1]	Lat 36°35′58″, long 120°41′34″, Fresno County	Silver/Panoche confluence	shale	7.5
		Lodo Formation		
18	Lat 36°25′12″, long 120°34′17″, Fresno County	Arroyo Hondo	Cantua sandstone	0.9
19	Lat 36°25′37″, long 120°34′36″, Fresno County	Arroyo Hondo	Cantua sandstone	.8
20	Lat 36°25′59″, long 120°31′02″, Fresno County	Arroyo Hondo	claystone (undifferentiated)	.8
21	Lat 36°26′16″, long 120°31′11″, Fresno County	Arroyo Hondo	claystone (undifferentiated)	.4
22	Lat 36°33′00″, long 120°38′11″, Fresno County	Tumey Gulch		.3
23	Lat 36°32′31″, long 120°37′36″, Fresno County	Tumey Gulch		1.8
24	Lat 36°32′17″, long 120°37′31″, Fresno County	Tumey Gulch	Cantua sandstone	.2
25	Lat 36°32′17″, long 120°37′31″, Fresno County	Tumey Gulch	Cantua sandstone	.6
26	Lat 36°32′14″, long 120°37′53″, Fresno County	Tumey Gulch	Cantua sandstone	3.4
27	Lat 36°35′04″, long 120°40′02″, Fresno County	Tumey Hills	claystone (undifferentiated)	6.5
28	Lat 36°34′38″, long 120°39′53″, Fresno County	Tumey Hills	claystone (undifferentiated)	1.0
29	Lat 36°33′14″, long 120°38′25″, Fresno County	Tumey Hills	claystone (undifferentiated)	4.4
30	Lat 36°32′35″, long 120°38′23″, Fresno County	Tumey Hills	claystone (undifferentiated)	.6
31	Lat 36°35′23″, long 120°41′52″, Fresno County	Silver Creek	35 - 49″ depth	1.3

[1] Supplemental samples analyzed by Bill Walker, University of California, Davis, California.

Table 13. Locations and selenium concentrations of geologic samples, by formation, collected by the U.S. Geological Survey--Continued

Sample No.	Location	Area	Member/type	Selenium
		Domengine Formation		
32	Lat 36°33′09″, long 120°37′45″, Fresno County	Tumey Gulch	sandstone	0.4
		Kreyenhagen Formation		
33	Lat 36°31′03″, long 120°35′45″, Fresno County	Monocline Ridge	shale	13
34	Lat 36°31′00″, long 120°35′45″, Fresno County	Monocline Ridge	shale	2.2
35	Lat 36°30′11″, long 120°34′56″, Fresno County	Monocline Ridge	shale	26
36	Lat 36°31′52″, long 120°35′28″, Fresno County	Monocline Ridge	shale	.8
37	Lat 36°31′50″, long 120°35′33″, Fresno County	Monocline Ridge	shale	20
40	Lat 36°32′12″, long 120°34′11″, Fresno County	Monocline Ridge	semi-siliceous and clayey shale	4.4
41	Lat 36°32′11″, long 120°34′24″, Fresno County	Monocline Ridge	semi-siliceous and clayey shale	3.2
42	Lat 36°32′11″, long 120°34′24″, Fresno County	Monocline Ridge	semi-siliceous and clayey shale	11
43	Lat 36°32′11″, long 120°34′30″, Fresno County	Monocline Ridge	semi-siliceous and clayey shale	.7
44	Lat 36°32′11″, long 120°34′30″, Fresno County	Monocline Ridge	semi-siliceous and clayey shale	13
45	Lat 36°32′11″, long 120°34′30″, Fresno County	Monocline Ridge	semi-siliceous and clayey shale	16
46	Lat 36°32′12″, long 120°34′11″, Fresno County	Monocline Ridge	semi-siliceous and clayey shale	8.9
47	Lat 36°32′13″, long 120°34′04″, Fresno County	Monocline Ridge	semi-siliceous shale	6.7
48	Lat 36°32′13″, long 120°34′04″, Fresno County	Monocline Ridge	semi-siliceous shale	.6
49	Lat 36°32′13″, long 120°34′04″, Fresno County	Monocline Ridge	semi-siliceous shale	10
50	Lat 36°32′02″, long 120°33′45″, Fresno County	Monocline Ridge	semi-siliceous shale	8.5
51	Lat 36°32′02″, long 120°33′45″, Fresno County	Monocline Ridge	semi-siliceous shale	5.8
52	Lat 36°34′21″, long 120°39′18″, Fresno County	Tumey Hills	clayey shale	45
53	Lat 36°36′45″, long 120°39′38″, Fresno County	Tumey Hills	semi-siliceous and clayey shale	29
54	Lat 36°37′23″, long 120°39′30″, Fresno County	Tumey Hills	semi-siliceous shale	9.4
57	Lat 36°28′49″, long 120°33′34″, Fresno County	Ciervo Hills	shale (gypsum and jarosite)	22
58	Lat 36°27′29″, long 120°35′41″, Fresno County	Ciervo Hills	soil (0 - 8″ depth)	2.2
		Tumey Formation		
59	Lat 36°32′23″, long 120°33′19″, Fresno County	Monocline Ridge	semi-siliceous shale	12
60	Lat 36°32′23″, long 120°33′19″, Fresno County	Monocline Ridge	semi-siliceous shale	1.1
61	Lat 36°32′23″, long 120°33′19″, Fresno County	Monocline Ridge	semi-siliceous shale	10
62	Lat 36°32′23″, long 120°33′19″, Fresno County	Monocline Ridge	semi-siliceous shale	
63	Lat 36°32′15″, long 120°33′12″, Fresno County	Monocline Ridge	semi-siliceous shale	2.5
64	Lat 36°32′15″, long 120°33′12″, Fresno County	Monocline Ridge	semi-siliceous shale	7.3
		Tulare Formation		
65	Lat 36°33′00″, long 120°31′09″, Fresno County	Monocline Ridge		0.8
66	Lat 36°32′55″, long 120°31′27″, Fresno County	Monocline Ridge		.5
67	Lat 36°32′50″, long 120°31′50″, Fresno County	Monocline Ridge		1.2
68	Lat 36°32′50″, long 120°31′50″, Fresno County	Monocline Ridge		.5
69	Lat 36°32′56″, long 120°32′34″, Fresno County	Monocline Ridge		1.2
70	Lat 36°32′47″, long 120°32′15″, Fresno County	Monocline Ridge		1.3
71	Lat 36°32′47″, long 120°32′15″, Fresno County	Monocline Ridge		1.8
72	Lat 36°32′46″, long 120°32′02″, Fresno County	Monocline Ridge		2.6

Table 13. Locations and selenium concentrations of geologic samples, by formation, collected by the U.S. Geological Survey--Continued

Sample No.	Location	Area	Member/type	Selenium
Tulare Formation--Continued				
73	Lat 36°36′14″, long 120°39′48″, Fresno County	Tumey Hills		0.7
74	Lat 36°35′55″, long 120°39′59″, Fresno County	Tumey Hills		.5
75	Lat 36°34′49″, long 120°39′26″, Fresno County	Tumey Hills		1.2
Non-marine units				
76	Lat 36°32′36″, long 120°33′27″, Fresno County	Monocline Ridge	clay, minor sand	0.4
77	Lat 36°32′36″, long 120°33′27″, Fresno County	Monocline Ridge	clay, minor sand	1.1
78	Lat 36°32′15″, long 120°32′44″, Fresno County	Monocline Ridge	clay, minor sand	.5
79	Lat 36°32′15″, long 120°32′44″, Fresno County	Monocline Ridge	clay, minor sand	.4
80	Lat 36°32′26″, long 120°32′39″, Fresno County	Monocline Ridge	clay, minor sand	4.2
81	Lat 36°32′26″, long 120°32′39″, Fresno County	Monocline Ridge	clay, minor sand	1.5
82	Lat 36°32′26″, long 120°32′39″, Fresno County	Monocline Ridge	clay, minor sand	.3
83	Lat 36°33′03″, long 120°33′26″, Fresno County	Monocline Ridge	sand, gravel and clay	.1
84	Lat 36°33′03″, long 120°33′26″, Fresno County	Monocline Ridge	sand, gravel and clay	1.0
85	Lat 36°33′03″, long 120°33′26″, Fresno County	Monocline Ridge	sand, gravel and clay	.5
86	Lat 36°33′03″, long 120°33′26″, Fresno County	Monocline Ridge	sand, gravel and clay	.7
87	Lat 36°32′57″, long 120°33′18″, Fresno County	Monocline Ridge	sand, gravel and clay	2.2
88	Lat 36°32′46″, long 120°33′20″, Fresno County	Monocline Ridge	sand, gravel and clay	15
89	Lat 36°32′35″, long 120°32′34″, Fresno County	Monocline Ridge	sand, gravel and clay	.3
90	Lat 36°32′35″, long 120°32′34″, Fresno County	Monocline Ridge	sand, gravel and clay	.8
91	Lat 36°26′42″, long 120°25′57″, Fresno County	Ciervo Hills	sand (39-45″ depth)	.6

Table 14. Locations and selenium concentrations of geologic materials, by formation, and chemical type and pH of soil solutions in samples collected by the U.S. Soil Conservation Service

[Analysis by the Soil Conservation Service (SCS), Hanford, Califonia. Selenium concentration in parts per million. pH in standard units. Abbreviations: Km, Moreno Formation; Tl, Lodo Formation; Tk, Kreyenhagen Formation; Ttu, Tumey Formation; Tt, Temblor Formation; Tun, non-marine units; QTt, Tulare Formation; Qoa, older alluvium; Qa, alluvium]

SCS No.	Location	Area	Formation	Selenium[1]	Soil solution	
					Chemical type	pH
0786	Lat 36°33′51″, long 120°41′02″, Fresno County	Silver Creek	Km	25	Ca-ClSO$_4$	4.1
0886	Lat 36°43′50″, long 120°44′04″, Fresno County	Moreno Gulch	Km	4.8	Ca-SO$_4$	3.9
1286	Lat 36°39′34″, long 120°42′11″, Fresno County	Dosados Canyon	Km	9.2	Ca-SO$_4$	4.3
1686	Lat 36°35′50″, long 120°40′32″, Fresno County	Silver/Panoche Creeks confluence	Tl	.5	Na-HCO$_3$	7.5
1786	Lat 36°34′35″, long 120°37′55″, Fresno County	Tumey Hills	Tk	12	Ca-SO$_4$	3.9
1986	Lat 36°32′30″, long 120°37′30″, Fresno County	Tumey Hills	Tk	2.7	Ca-HCO$_3$	6.0
1386	Lat 36°36′49″, long 120°39′49″, Fresno County	Panoche Creek below confluence with Silver Creek	Tk	14	Mg-SO$_4$	5.5
2286	Lat 36°32′03″, long 120°33′50″, Fresno County	Monocline Ridge	Tk	8.4	Ca-SO$_4$	4.0
0184	Lat 36°32′14″, long 120°33′43″, Fresno County	Monocline Ridge	Ttu	.2	Ca-SO$_4$	7.7
1284	Lat 36°29′04″, long 120°33′53″, Fresno County	Arroyo Ciervo	Tt	.1	Ca-HCO$_3$	7.8
2086	Lat 36°34′16″, long 120°36′29″, Fresno County	Tumey Hills	Tun	.7	NaCa-SO$_4$	7.5
1886	Lat 36°34′25″, long 120°37′57″, Fresno County	Tumey Hills	Tun/QTt	.7	Ca-HCO$_3$	7.0
1086	Lat 36°41′18″, long 120°40′54″, Fresno County	Escapardo Canyon	QTt	.9	Ca-SO$_4$	7.7
1486	Lat 36°35′17″, long 120°39′39″, Fresno County	Silver/Panoche Creeks confluence	QTt	1.2	Ca-SO$_4$	7.6
1186	Lat 36°36′18″, long 120°40′05″, Fresno County	Silver/Panoche Creeks confluence	QTt	2.3	Na-SO$_4$	7.5
0686	Lat 36°34′55″, long 120°41′16″, Fresno County	Silver/Panoche Creeks confluence	Qoa	1.2	NaCa-SO$_4$	7.5
0586	Lat 36°35′03″, long 120°40′56″, Fresno County	Silver/Panoche Creeks confluence	Qoa	1.3	Na-SO$_4$	6.5
0186	Lat 36°37′21″, long 120°39′48″, Fresno County	Panoche Creek below confluence with Silver Creek	Qa	1.3	Na-ClSO$_4$	7.6
0286	Lat 36°37′50″, long 120°39′53″, Fresno County	Panoche Creek below confluence with Silver Creek	Qa	1.2	Ca-HCO$_3$	7.5
0386	Lat 36°37′51″, long 120°39′54″, Fresno County	Panoche Creek below confluence with Silver Creek	Qa	1.4	NaMg-SO$_4$	8.5
0486	Lat 36°37′02″, long 120°40′17″, Fresno County	Panoche Creek below confluence with Silver Creek	Qa	2.7	Na-SO$_4$Cl	8.2

[1] Maximum value.

Table 15. Locations and selenium concentrations of stream sediments

[Analysis by S.A. Wilson and staff, U.S. Geological Survey, Branch of Geochemistry, Denver, Colorado. Selenium concentrations in parts per million]

Sample No.	Location	Area	Selenium
SS1	Lat 36°34′31″, long 120°35′42″, Fresno County	Monocline Ridge	1.5
SS2	Lat 36°34′24″, long 120°34′52″, Fresno County	Monocline Ridge	1.8
SS3	Lat 36°33′52″, long 120°34′20″, Fresno County	Monocline Ridge	1.9
SS4	Lat 36°33′33″, long 120°33′54″, Fresno County	Monocline Ridge	.4
SS5	Lat 36°33′31″, long 120°32′47″, Fresno County	Monocline Ridge	.8
SS6	Lat 36°33′25″, long 120°32′08″, Fresno County	Monocline Ridge	2.6
SS7	Lat 36°32′57″, long 120°31′07″, Fresno County	Monocline Ridge	.9
SS8	Lat 36°32′43″, long 120°30′47″, Fresno County	Monocline Ridge	.4
SS9	Lat 36°32′36″, long 120°30′30″, Fresno County	Monocline Ridge	.9
SS10	Lat 36°32′22″, long 120°30′12″, Fresno County	Monocline Ridge	1.2
SS11	Lat 36°31′59″, long 120°29′39″, Fresno County	Ciervo Hills	2.9
SS12	Lat 36°31′33″, long 120°28′58″, Fresno County	Ciervo Hills	.7
SS13	Lat 36°31′12″, long 120°28′32″, Fresno County	Ciervo Hills	.7
SS14	Lat 36°30′17″, long 120°27′36″, Fresno County	Ciervo Hills	1.7
SS14a	Lat 36°29′32″, long 120°27′18″, Fresno County	Ciervo Hills	1.0
SS15	Lat 36°28′09″, long 120°27′12″, Fresno County	Ciervo Hills	.3
SS16	Lat 36°27′36″, long 120°26′40″, Fresno County	Ciervo Hills	.6
SS17	Lat 36°25′18″, long 120°25′37″, Fresno County	Ciervo Hills	.6
SS18	Lat 36°25′28″, long 120°25′39″, Fresno County	Ciervo Hills	.5
SS19	Lat 36°25′14″, long 120°24′46″, Fresno County	Ciervo Hills	.9
SS20	Lat 36°26′14″, long 120°25′17″, Fresno County	Ciervo Hills	.2
SS21	Lat 36°26′50″, long 120°25′56″, Fresno County	Ciervo Hills	.3
SS22	Lat 36°35′34″, long 120°37′31″, Fresno County	Tumey Gulch	.7
SS23	Lat 36°35′23″, long 120°37′29″, Fresno County	Tumey Gulch	.8
SS24	Lat 36°35′04″, long 120°36′44″, Fresno County	Tumey Gulch	.6
SS25	Lat 36°34′57″, long 120°36′37″, Fresno County	Tumey Gulch	1.0
SS26	Lat 36°38′32″, long 120°40′42″, Fresno County	Panoche Hills	2.9
SS27	Lat 36°38′26″, long 120°40′35″, Fresno County	Panoche Hills	.5
SS28	Lat 36°38′44″, long 120°41′03″, Fresno County	Panoche Hills	1.7
SS29	Lat 36°39′31″, long 120°41′47″, Fresno County	Panoche Hills	4.0
SS30	Lat 36°39′52″, long 120°42′02″, Fresno County	Panoche Hills	1.6
SS31	Lat 36°39′52″, long 120°42′02″, Fresno County	Panoche Hills	2.6
SS32	Lat 36°40′16″, long 120°42′14″, Fresno County	Panoche Hills	3.3
SS33	Lat 36°40′16″, long 120°42′14″, Fresno County	Panoche Hills	3.8
SS34	Lat 36°40′54″, long 120°41′56″, Fresno County	Panoche Hills	2.7
SS35	Lat 36°40′38″, long 120°42′14″, Fresno County	Panoche Hills	9.5
SS36	Lat 36°41′28″, long 120°42′24″, Fresno County	Panoche Hills	4.8
SS37	Lat 36°42′23″, long 120°42′12″, Fresno County	Panoche Hills	1.3
SS38	Lat 36°42′23″, long 120°42′52″, Fresno County	Panoche Hills	2.9
SS39	Lat 36°42′23″, long 120°42′52″, Fresno County	Panoche Hills	4.0
SS40	Lat 36°43′23″, long 120°42′55″, Fresno County	Panoche Hills	7.4
SS41	Lat 36°43′42″, long 120°43′00″, Fresno County	Panoche Hills	1.9
SS42	Lat 36°44′17″, long 120°43′35″, Fresno County	Panoche Hills	2.3
SS43	Lat 36°44′55″, long 120°44′14″, Fresno County	Panoche Hills	1.6
SS44[1]	Lat 36°37′30″, long 120°39′40″, Fresno County	Silver/Panoche Creeks confluence	1.7
SS45[1]	Lat 36°37′30″, long 120°39′40″, Fresno County	Silver/Panoche Creeks confluence	2.1
SS46[1]	Lat 36°36′55″, long 120°40′28″, Fresno County	Silver/Panoche Creeks confluence	1.1
SS47[1]	Lat 36°36′55″, long 120°40′28″, Fresno County	Silver/Panoche Creeks confluence	1.3
SS48[1]	Lat 36°36′44″, long 120°41′00″, Fresno County	Silver/Panoche Creeks confluence	3.6

---

[1] Supplemental samples analyzed by Bill Walker, University of California, Davis, California.

Table 16. Selenium concentrations of geologic materials, by formation, found in the study area

[Selenium concentrations in parts per million]

Formation	Number of samples	Mean selenium	Median selenium	Relative variability, Quartile range/ median
	Seleniferous Formations			
Moreno (Km)	27	9.1	6.5	1.40
Kreyenhagen (Tk)	27	11.1	8.9	1.17
Tumey (Ttu)	5	6.6	7.3	1.26
	59	8.9	7.3	1.33
	Non-Seleniferous Formations			
Panoche (Kp)	2	1.0	1.0	--
Lodo (Tl)	15	1.2	.8	2.47
Domengine (Td)	1	.4	.4	--
Tulare (QTt)	17	1.4	1.2	1.33
Non-marine units (Tun)	20	1.7	0.7	1.47
	55	1.1	0.8	--

Table 17. Selenium/sulfate ratios, thermodynamic properties, and normative salt percentages in water samples containing selenium

[Thermodynamic property (ΔG) is the difference in the Gibbs free energy, in kilocalories, between the actual state and the equilibrium state. ΔG greater than 0 indicates that the solution is supersaturated with respect to the solid phase; ΔG = 0 indicates equilibrium; and ΔG less than 0 indicates undersaturation. Selenium concentrations in micrograms per liter]

Selenium	Selenium/ sulfate ($\times 10^{-3}$)	ΔG				Percentage of salt in samples containing selenium					
		Calcite	Gypsum	Anhydrite	Mirabilite	Thenardite	Bloedite	Epsomite	Glauberite	Halite	Anhydrite
				Tumey Gulch I ephemeral stream							
3,500	0.067	+2.709	+0.435	+0.185	-1.445	--	51	11	--	34	--
2,850	.036	+2.767	+.645	+.576	-1.634	31	47	--	--	18	--
2,100	.036	+2.329	+.315	+.232	-1.890	40	38	--	--	18	--
				Arroyo Hondo seep							
420	.034	acid	-.022	-.424	-2.755	28	55	--	16	--	--
320	.032	acid	-.112	-.419	-3.625	31	49	--	18	--	--
298	.032	acid	-.105	-.450	-3.482	31	48	--	19	--	--
				Tumey Gulch tributary seep I							
211	.004	acid	-.297	-.584	-1.648	23	71	--	--	4	--
107	.005	acid	-.460	-.761	-2.617	25	67	--	--	4	--
				Tumey Gulch tributary seep II							
197	.006	acid	+.223	-.180	-1.539	10	80	--	6	--	--
				Vallecitos/Pimental Creeks confluence							
153	.065	+1.043	-.619	-1.112	-4.844	33	16	--	32	10	--

Table 17. Selenium/sulfate ratios, thermodynamic properties, and normative salt percentages in water samples containing selenium--Continued

Selenium	Selenium/ sulfate ($\times 10^{-3}$)	ΔG				Percentage of salt in samples containing selenium					
		Calcite	Gypsum	Anhydrite	Mirabilite	Thenardite	Bloedite	Epsomite	Glauberite	Halite	Anhydrite
Silver Creek headwater seep											
141	.074	+.803	-.769	-1.258	-5.505	8	42	--	33	4	--
126	.063	+.728	-.725	-1.219	-5.448	--	63	--	20	4	5
83	.031	+1.381	-.506	-.890	-5.741	--	53	12	--	--	21
77	.033	+1.561	-.642	-.990	-6.109	--	62	7	--	--	21
24	.009	+1.584	-.498	-.822	-6.185	--	55	10	--	--	22
Los Pinos Creek at Silver Creek											
89	.056	+1.943	-1.171	-1.605	-5.919	26	32	--	22	9	--
Moreno Gulch seep											
87	.005	acid	+.027	-.559	-3.286	--	35	58	--	--	5
Rainpool											
69	.030	-1.343	-.058	-.510	-6.222	--	29	8	--	--	56
Well 400 feet											
58	.034	+.625	-.603	-.963	-6.220	--	49	--	--	12	28
56	.034	+.249	-.461	-.821	-6.642	--	22	15	--	16	41
49	.032	+.850	-.507	-.868	-6.726	--	--	26	--	24	41
Runoff											
57	.024	+.756	-.126	-.668	-5.107	--	39	--	26	6	23
55	.015	+.558	+.015	-.527	-4.419	--	48	--	32	3	11
44	.020	+.940	-.050	-.593	-5.464	--	26	--	30	4	32
Below confluence of Vallecitos/Pimental Creeks											
55	.024	+1.154	-.464	-.957	-4.963	22	18	--	42	8	--
39	.019	+1.550	-.450	-.954	-5.014	27	--	--	50	8	--
Monocline Ridge seep (north lower)											
52	.006	-1.625	+.058	-.548	-2.791	--	77	8	--	2	9
Monocline Ridge seep (south upper)											
48	.005	-.190	-.018	-.622	-1.975	52	22	--	16	5	--
Escapardo Canyon seep											
42	.002	acid	+.052	-.348	-2.595	--	82	10	--	--	5
Griswold Creek sulfur seep											
40	.019	+1.615	-.473	-.845	-5.481	8	21	--	57	--	--
28	.012	+1.352	-.471	-.732	-6.208	--	28	--	56	--	--
23	.010	+1.486	-.508	-.742	-6.359	9	25	--	55	--	5
Tumey Gulch II ephemeral stream											
14	<.001	+2.758	+.212	-.016	-1.721	17	29	--	--	49	--
Mudflow											
7	.001	+1.116	-.534	-.993	-2.784	57	21	--	12	--	--
Tumey Gulch tributary III pool											
6	<.001	acid	-.022	-.422	-2.485	28	55	--	12	--	--
5	<.001	acid	+.058	-.357	-2.091	27	59	--	10	--	--
New Idria acid mine drainage											
<2		acid	-.149	-.531	-5.416	--	42	28	--	--	20
<2		acid	-.288	-.671	-5.402	--	53	9	--	--	20
<2		acid	-.244	-.627	-5.313	--	50	12	--	--	19

Table 18. Selenium concentrations of geologic samples collected from the Moreno, Kreyenhagen, and Tumey Formations by slope position

[Selenium concentrations in parts per million]

Formation	Shoulder/Summit slopes	Midslope/ Backslope	Toeslope/ Footslope
Moreno	23.0	3.9	15.0
	1.4	3.1	35.0
	18.0	1.4	8.5
	2.4	2.8	7.9
	2.6	.8	6.5
	1.6	10.3	7.5
	3.7	7.9	
	25.0	9.2	
	13.0	4.5	
	16.0		
	12.0		
Kreyenhagen	26.0	4.4	.8
	3.2	6.7	20.0
	11.0	0.6	8.5
	.7	10.0	5.8
	13.0	2.2	22.0
	16.0	14.0	2.6
	45.0	6.1	2.7
	29.0	4.3	8.4
	9.4	4.1	
	12.0	3.5	
		13.0	
		2.2	
Tumey		12.0	
		1.1	
		10.0	
		2.5	
		7.3	
Mean:	13.5	5.7	10.8
Median:	12.0	4.4	8.2
Variance:	128.0	15.6	86.5
Standard deviation:	11.3	3.9	9.3
Range:	0.7 to 45	0.6 to 14	0.8 to 35

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF THE INTERIOR
INT 413

U.S. DEPARTMENT OF THE INTERIOR
Geological Survey
345 Middlefield Road MS 435
Menlo Park, CA 94025

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE $300
SPECIAL 4TH CLASS BOOK RATE

Presser and others--GEOLOGIC SOURCES, MOBILIZATION, AND TRANSPORT OF SELENIUM, SAN JOAQUIN VALLEY, CALIFORNIA--USGS WRIR 90-4070