

# Detailed Study of Selenium and Other Constituents in Water, Bottom Sediment, Soil, Alfalfa, and Biota Associated with Irrigation Drainage in the Uncompahgre Project Area and in the Grand Valley, West-Central Colorado, 1991–93

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## CONVERSION FACTORS AND VERTICAL DATUM

	Multiply	By	To obtain
	acre	4,047	square meter
	acre	0.4047	hectare
	centimeter (cm)	0.3937	inch
	cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second
	foot (ft)	0.3048	meter
	foot per day (ft/d)	0.3048	meter per day
	foot per second (ft/s)	0.3048	meter per second
	gallon per minute (gal/min)	0.06309	liter per second
	inch (in.)	25.4	millimeter
	inch per year (in/yr)	25.4	millimeter per year
	kilogram (kg)	2.205	pound
	liter (L)	0.2642	gallon
	meter (m)	3.281	foot
	microgram per day (µg/d)	0.000000353	ounce per day
	micrometer (µm)	0.00003937	inch
	mile (mi)	1.609	kilometer
	milliliter (mL)	0.0610	cubic inch
	millimeter (mm)	0.03937	inch
	ounce (oz)	28.35	gram
	pound per day (lb/d)	0.4536	kilogram per day
	pound per day per 100 acres [(lb/d)/100 acres]	0.4536	kilogram per day per 100 acres
	ton per day (ton/d)	0.9067	metric ton per day
	ton per year (ton/yr)	0.9067	metric ton per year

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$^{\circ}\text{F} = 9/5 \text{ }^{\circ}\text{C} + 32$$

Degree Fahrenheit (°F) may be converted to degree Celsius (°C) by using the following equation:

$$^{\circ}\text{C} = 5/9 (\text{ }^{\circ}\text{F} - 32)$$

The following terms and abbreviations also are used in this report:

- microgram per gram (µg/g)
- microgram per kilogram (µg/kg)
- microgram per liter (µg/L)
- microgram per liter per year [(µg/L)/yr]
- millivolt (mV)
- milligram per kilogram (mg/kg)
- milligram per liter (mg/L)
- microsiemens per centimeter at 25 degrees Celsius (µS/cm)

**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.

For those who wish to convert dry-weight concentrations to wet-weight concentrations for biological samples, the equation is:

$$\text{wet weight} = \text{dry weight} [1 - (\text{percent moisture}/100)].$$

# Detailed Study of Selenium and Other Constituents in Water, Bottom Sediment, Soil, Alfalfa, and Biota Associated with Irrigation Drainage in the Uncompahgre Project Area and in the Grand Valley, West-Central Colorado, 1991–93

by David L. Butler, Winfield G. Wright, Kathleen C. Stewart, Barbara Campbell Osmundson, Richard P. Krueger, and Daniel W. Crabtree

## Abstract

In 1985, the U.S. Department of the Interior began a program to study the effects of irrigation drainage in the Western United States. These studies were done to determine whether irrigation drainage was causing problems related to human health, water quality, and fish and wildlife resources. Results of a study in 1991–93 of irrigation drainage associated with the Uncompahgre Project area, located in the lower Gunnison River Basin, and of the Grand Valley, located along the Colorado River, are described in this report. The focus of the report is on the sources, distribution, movement, and fate of selenium in the hydrologic and biological systems and the effects on biota. Generally, other trace-constituent concentrations in water and biota were not elevated or were not at levels of concern.

Soils in the Uncompahgre Project area that primarily were derived from Mancos Shale contained the highest concentrations of total and water-extractable selenium. Only 5 of 128 alfalfa samples had selenium concentrations that exceeded a recommended dietary limit for livestock. Selenium data for soil and alfalfa indicate that irrigation might be mobilizing and redistributing selenium in the Uncompahgre Project area.

Distribution of dissolved selenium in ground water is affected by the aqueous geochemical environment of the shallow ground-water

system. Selenium concentrations were as high as 1,300 micrograms per liter in water from shallow wells. The highest concentrations of dissolved selenium were in water from wells completed in alluvium overlying the Mancos Shale of Cretaceous age; selenium concentrations were lower in water from wells completed in Mancos Shale residuum. Selenium in the study area could be mobilized by oxidation of reduced selenium, desorption from aquifer sediments, ion exchange, and dissolution. Infiltration of irrigation water and, perhaps nitrate, provide oxidizing conditions for mobilization of selenium from alluvium and shale residuum and for transport to streams and irrigation drains that are tributary to the Gunnison, Uncompahgre, and Colorado Rivers.

Selenium concentrations in about 64 percent of water samples collected from the lower Gunnison River and about 50 percent of samples from the Colorado River near the Colorado-Utah State line exceeded the U.S. Environmental Protection Agency criterion of 5 micrograms per liter for protection of aquatic life. Almost all selenium concentrations in samples collected during the nonirrigation season from Mancos Shale areas exceeded the aquatic-life criterion. The maximum selenium concentrations in surface-water samples were 600 micrograms per liter in the Uncompahgre Project area and 380 micrograms per liter in the Grand Valley.

Irrigation drainage from the Uncompahgre Project and the Grand Valley might account for as much as 75 percent of the selenium load in the Colorado River near the Colorado-Utah State line. The primary source areas of selenium were the eastern side of the Uncompahgre Project and the western one-half of the Grand Valley, where there is extensive irrigation on soils derived from Mancos Shale. The largest mean selenium loads from tributary drainages were 14.0 pounds per day from Loutsenhizer Arroyo in the Uncompahgre Project and 12.8 pounds per day from Reed Wash in the Grand Valley. Positive correlations between selenium loads and dissolved-solids loads could indicate that salinity-control projects designed to decrease dissolved-solids loads also could decrease selenium loads from the irrigated areas. Selenium concentrations in irrigation drainage in the Grand Valley were much higher than concentrations predicted by simple evaporative concentration of irrigation source water. Selenium probably is removed from pond water by chemical and biological processes and incorporated into bottom sediment. The maximum selenium concentration in bottom sediment was 47 micrograms per gram from a pond on the eastern side of the Uncompahgre Project.

Selenium concentrations in some aquatic plants and aquatic invertebrates exceeded a dietary guideline of 3 micrograms per gram dry weight for protection of fish and wildlife resources. More than 75 percent of whole-body fish samples collected from rivers and tributaries throughout the study area had selenium concentrations that exceeded the 1984 National Contaminant Biomonitoring Program 85th-percentile concentration of 0.73 microgram per gram wet weight. Whole-body fish samples from the Gunnison River had significantly higher geometric mean selenium concentrations than fish samples from the Uncompahgre and Colorado Rivers.

Based on a risk assessment using selenium data for five Grand Valley streams, the selenate form of selenium could be a moderate risk to the

swim-up life stage (less than 99 days old) of the endangered Colorado squawfish and to three tested life stages of the endangered razorback sucker. Zinc concentrations in Adobe Creek, Leach Creek, and Indian Wash were in the high-risk category for the swim-up life stage of Colorado squawfish.

Selenium concentrations in food items of migratory birds collected at wetlands in the Uncompahgre Project area exceeded the dietary guideline for protection of consumer wildlife. Fathead minnows from ponds had high selenium concentrations, and the maximum concentration was 110 micrograms per gram dry weight. Selenium concentrations in bird eggs and livers generally were in the range of uncertainty regarding biological risk; however, some samples from the Uncompahgre Project area had selenium concentrations in the high-risk category. Of 65 bird eggs incubated, only one had any visual deformity. Five recently hatched birds and two embryos that were found dead at two ponds in the Uncompahgre Project area had selenium concentrations ranging from 19 to 43 micrograms per gram dry weight, but no abnormalities or deformities were observed.

Toxicity tests on irrigation-drainage water from five Grand Valley streams indicated no significant toxicity differences between control and test samples, except for the test on fathead minnows exposed to water from Leach Creek. Bioaccumulation of selenium from water to biota was significant in the study area, and the highest bioaccumulation factor was about 20,900 from water to bird livers. Selenium accumulates in fish and birds in the study area to levels that would limit human consumption if eaten on a daily basis. It is unlikely that fish and birds taken in the study area are consumed by humans on a daily basis.

## INTRODUCTION

High concentrations of selenium have been detected in irrigation drainage in the San Joaquin Valley in California. In 1983, incidences of mortality, abnormalities, and reproductive failure in waterfowl

were discovered by the U.S. Fish and Wildlife Service (FWS) at the Kesterson National Wildlife Refuge in the western San Joaquin Valley, California, where irrigation-drainage water was impounded. Because of the concern that problems related to selenium or other trace inorganic or organic constituents in irrigation drainage might not be limited to the Kesterson Reservoir area, the U.S. Department of the Interior (DOI) began a program in 1985 to determine whether irrigation-related problems existed at other DOI constructed or managed irrigation projects, national wildlife refuges, or other wetland areas for which the DOI has responsibility. About 600 irrigation projects and major wildlife resource areas have been constructed or are managed in 17 Western States by DOI bureaus. The program evolved into five phases (Deason, 1986): (1) Site identification, (2) reconnaissance investigations, (3) detailed studies, (4) planning, and (5) remediation. Activities in the first three phases are conducted by study teams consisting of scientists from the U.S. Geological Survey (USGS), the FWS, the Bureau of Reclamation (BOR), and the Bureau of Indian Affairs. A USGS scientist heads each study team. Phase 4 and phase 5 of the program are headed by the BOR.

The reconnaissance investigations are designed to determine whether irrigation drainage (1) has caused or has the potential to cause harmful effects on human health or on fish and wildlife or (2) might limit the suitability of water for beneficial uses. The duration of the reconnaissance investigations was about 2 years. Detailed studies were initiated if the reconnaissance investigations indicated that potentially serious water-quality problems were related to irrigation drainage. The purpose of detailed studies is to gather sufficient information to provide the scientific understanding needed for development of reasonable alternatives to mitigate or resolve identified problems. The purpose of planning is to develop coordinated action with appropriate Federal, State, and local agencies and water users for remediation of problem areas. The final phase involves implementation of remedial actions developed during planning.

A reconnaissance investigation of the Gunnison and Uncompahgre River Basins and of Sweitzer Lake (fig. 1) documented elevated concentrations of selenium in some water, bottom-sediment, and biota samples collected in 1987–88 (Butler and others, 1991). The reconnaissance report indicated that

irrigation drainage from the Uncompahgre Project, a BOR irrigation project, might be a primary source of selenium, dissolved solids, and other constituents to the Gunnison and Uncompahgre Rivers and to Sweitzer Lake. The extent of the irrigated area served by the Uncompahgre Project is shown in figure 1. The Uncompahgre Project area is defined as the irrigated area served by the Uncompahgre Project plus adjacent areas in the lower Gunnison River Basin, such as the Smith Fork, North Fork, and Tongue Creek Basins (fig. 1). Because of the limited scope of the reconnaissance studies, source areas and distribution of selenium in the Uncompahgre Project area were not determined, nor were effects to biota documented. Also, trace-element data for water and biota were not collected in other irrigated areas in the lower Gunnison River Basin. Because of these factors, a detailed study of the Uncompahgre Project area was initiated in 1991.

The Grand Valley was included with the Uncompahgre Project area in the detailed study. There are similarities of climate, physiography, agricultural crops, and geology between the Grand Valley and the Uncompahgre Project area. Also, the BOR identified irrigation drainage in the Grand Valley (fig. 1) as a large source of dissolved solids (salinity) to the upper Colorado River (Bureau of Reclamation, 1978). A marine shale, the Mancos Shale, was identified as the primary source of the salinity, and selenium problems have been documented in other Western States where marine shales are irrigated (See and others, 1992; Stephens and others, 1992). Historical selenium data for the Colorado and Gunnison Rivers also indicated that the Grand Valley might be a source area of selenium.

## **Purpose and Scope**

This report describes results of the detailed study of the Uncompahgre Project area and of the Grand Valley during 1991–93. The general objectives of the detailed study are (1) to determine the sources, distribution, movement, and fate of contaminants in the hydrologic and biologic systems; and (2) to measure contaminant concentrations, determine exposure pathways, and document effects on biota.

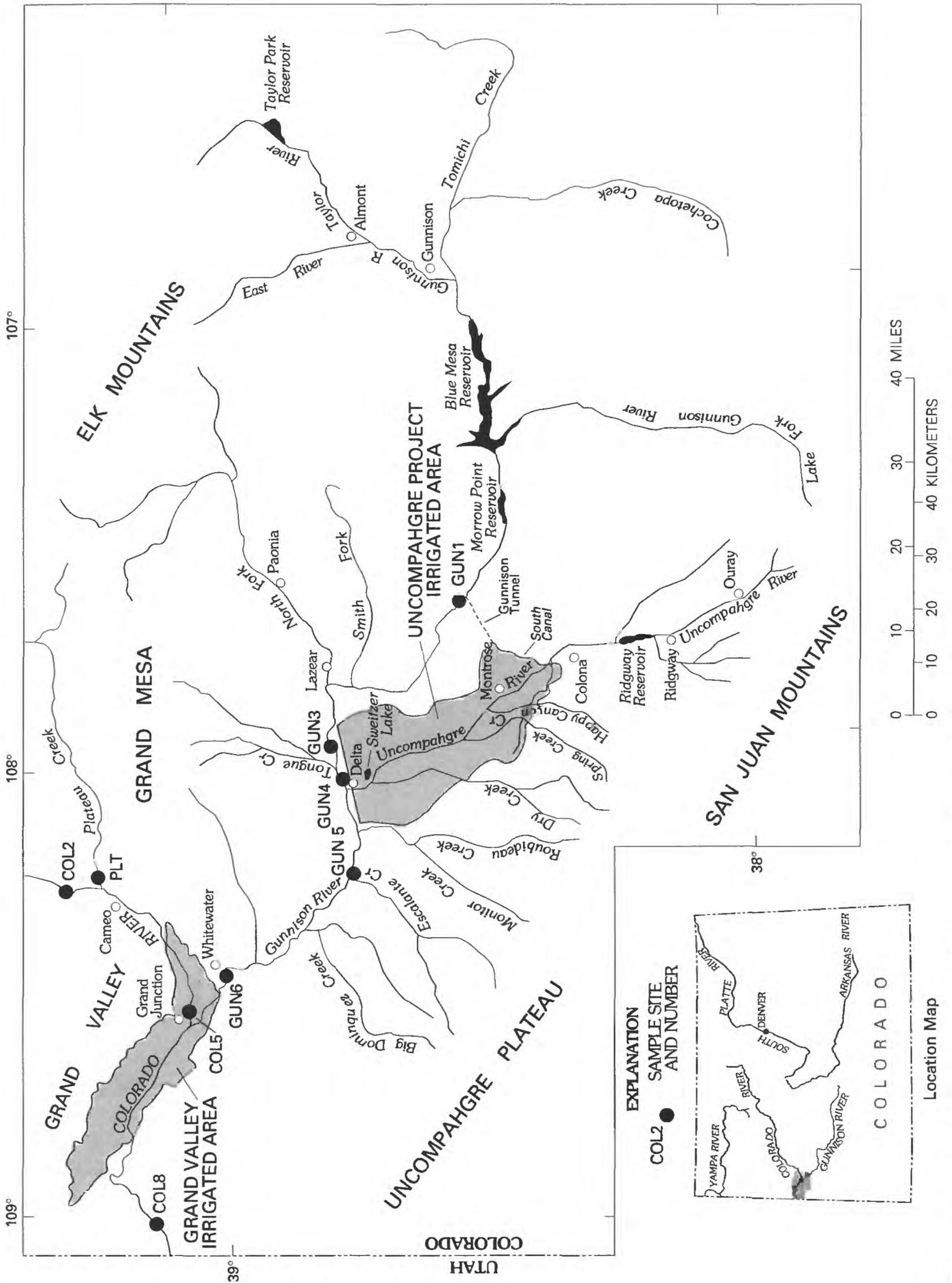


Figure 1. Location of the Uncompahgre Project area, the Grand Valley, and selected water-sampling sites on major streams.

Specific objectives of this report are to:

1. Describe concentrations and distribution of selenium and other trace constituents in soil and in alfalfa in irrigated areas of the Uncompahgre Project.
2. Describe the concentrations and distribution of selenium and other trace constituents in ground water in the Uncompahgre Project area and in the Grand Valley and the hydrochemical processes affecting selenium release and mobilization in ground water in irrigated areas on Mancos Shale terrain.
3. Discuss selenium concentrations and loads in the Gunnison and Colorado Rivers.
4. Describe distribution and variability of selenium concentrations in surface water and in bottom sediment in irrigated areas in the Uncompahgre Project area and in the Grand Valley.
5. Discuss selenium loads in streams, washes, and drains in the Uncompahgre Project area and in the Grand Valley and identify areas that are major sources of selenium to the Gunnison, Uncompahgre, and Colorado Rivers.
6. Describe concentrations and distribution of dissolved solids, major constituents, and selected trace constituents in surface water in the Uncompahgre Project area and in the Grand Valley and the relations of selenium to dissolved solids and selected constituents.
7. Describe concentrations and distribution of selenium and other trace constituents in fish, aquatic plants, and aquatic invertebrates in tributary streams and washes draining the Uncompahgre Project area and the Grand Valley.
8. Describe concentrations and distribution of selenium and other trace constituents in fish from the Gunnison, Uncompahgre, and Colorado Rivers and the potential effects of selenium on threatened and endangered fish.
9. Describe concentrations and distribution of selenium and other trace constituents in waterfowl and their effects on waterfowl reproduction in the Uncompahgre Project area and in the Grand Valley.
10. Discuss food-chain bioaccumulation of selenium.
11. Discuss implications of selenium concentrations to human health.

Soil, alfalfa, ground-water, mineralogic, surface-water, bottom-sediment, and biota samples were collected from March 1991 to August 1992 in the Uncompahgre Project area and in the Grand Valley. Selenium was the trace constituent of primary concern. Some water, bottom-sediment, and aquifer-sediment samples were analyzed for selenate and selenite selenium. Other trace elements were analyzed in water and biota samples collected in 1991. Also, streams and reservoirs outside the irrigated land served by the Uncompahgre Project (fig. 1) were sampled to determine if selenium and other trace-constituent concentrations were of concern in other irrigated areas in the lower Gunnison River Basin.

Soil and alfalfa samples were collected in irrigated areas of the Uncompahgre Project in June 1991. Soil samples were analyzed for total and extractable selenium, and trace constituents and alfalfa samples were analyzed for total selenium. Ground-water samples were collected in February and March 1992 to define ground-water quality during the nonirrigation season. Some ground-water samples were analyzed for hydrogen, oxygen, and sulfur isotopes. Samples of bedrock core, shale residuum, alluvium, and ground-water filtrate were collected for semiquantitative analyses of clay and bulk mineralogy.

Reconnaissance-level sampling of streams was done in 1991 in the Uncompahgre Project area and in the Grand Valley. Detailed synoptic sampling of streams, washes, and ditches draining irrigated areas in the Uncompahgre Project and in the Grand Valley was done during January through March 1992. Constituents analyzed in synoptic samples were selenium, boron, nitrite plus nitrate, dissolved solids, and major constituents. Selenium data were collected at selected surface-water sites in 1993 and were used for analyses of selenium distribution and loads in the study area. Bottom-sediment samples were collected from selected streams and ponds in 1992.

Biota samples collected in 1991 included aquatic plants and invertebrates, fish, birds, and bird eggs. Sample collection from March to September 1991 was designed to determine if other trace constituents or pesticides were of concern in the Uncompahgre Project and in the Grand Valley. Fish samples were collected from the Gunnison, Uncompahgre, and Colorado Rivers during March and April 1992 for selenium and selected trace-constituent analyses. Wetland sites were monitored for bird usage and nesting from April through July 1992. Birds and

bird-food items were collected at wetland sites. Bird eggs were collected and incubated. Bioassay samples were collected in March 1992 from five of the major streams in the Grand Valley and analyzed by the U.S. Environmental Protection Agency.

Water-quality, bottom-sediment, hydro-geologic, mineralogic, and biota data collected for the detailed study are listed in a report by Butler and others (1994). Selenium and other trace-constituent data for the soil and alfalfa samples collected in the Uncompahgre Project area are in a report by Crock and others (1994). Water-extractable data for selenium and other constituents for soil samples are discussed in Stewart and others (1993).

## Description of Study Area

The Uncompahgre Project area and the Grand Valley are located in west-central Colorado (fig. 1). The Uncompahgre Project is located along the Uncompahgre River in the lower Gunnison River Basin. The Uncompahgre Project extends about 34 mi between the towns of Colona and Delta (fig. 2). The irrigated part of the Grand Valley is located along the Colorado River, centered around Grand Junction (fig. 3). The confluence of the Gunnison and Colorado Rivers is at Grand Junction (fig. 3). Other communities in the Grand Valley include Palisade and Clifton, east of Grand Junction, and Fruita and Loma, west of Grand Junction.

## Physiography, Soils, Climate, and Land Uses

The Uncompahgre River Valley principally is an agricultural area where irrigation water is supplied by diversion from the Gunnison River through the Gunnison Tunnel (fig. 1) and by water from the Uncompahgre River and its tributaries. About two-thirds of the 86,000 irrigated acres of the Uncompahgre Project is located west of the Uncompahgre River on a series of terraces separated by small valleys that were eroded by tributaries of the Uncompahgre River. The terraces consist of stream deposits and outwash remnants that have relatively low soluble salt content (Bureau of Reclamation, 1984). Irrigated areas east of the Uncompahgre River compose about 34 percent of the project area and consist of soil formed primarily from weathered Mancos Shale. Soils derived from Mancos Shale commonly are referred to as adobe soils and are high

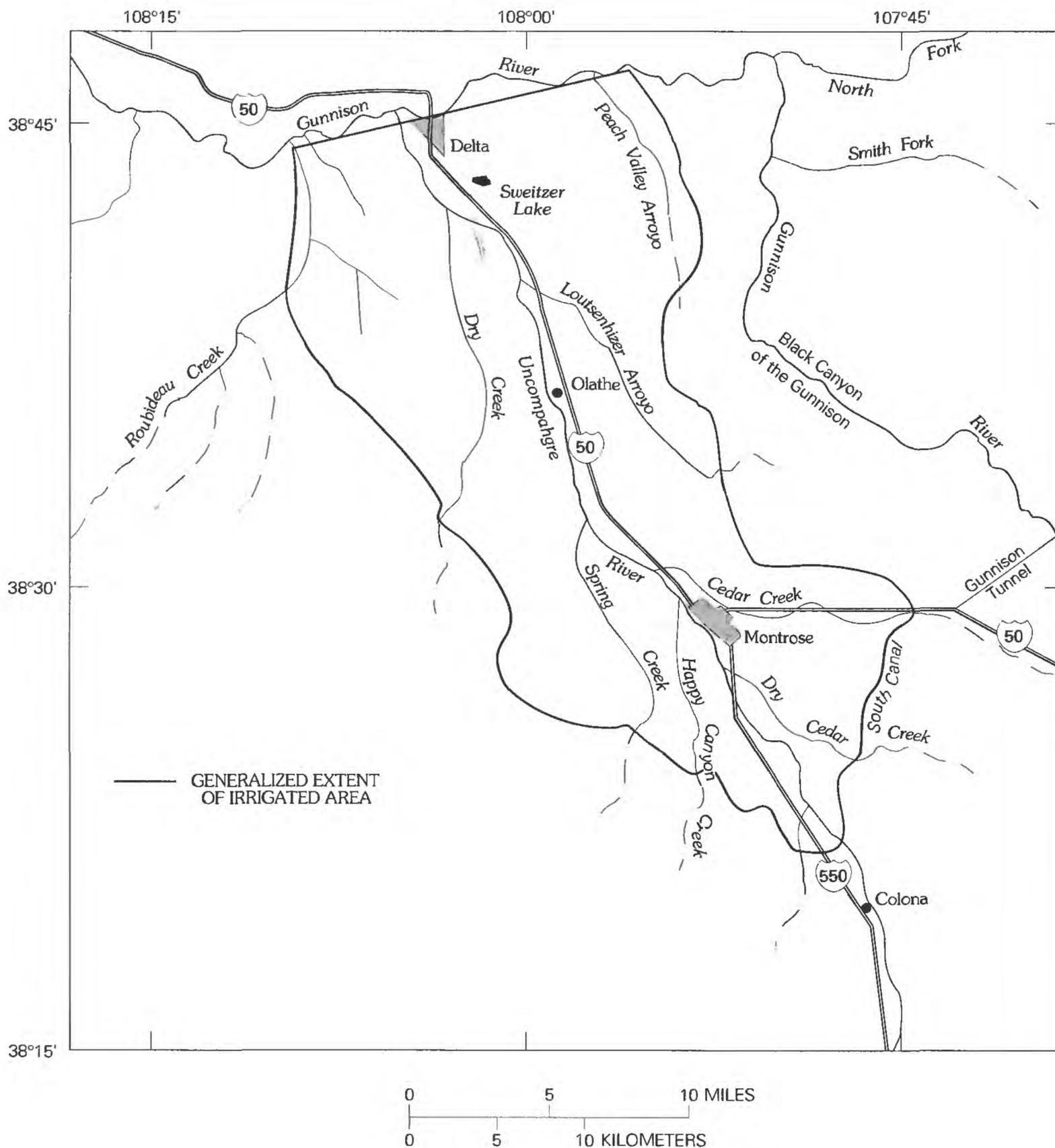
in salt content. Alluvial deposits derived primarily from Mancos Shale compose parts of the Cedar Creek and Loutsenhizer Arroyo Basins (fig. 2). Elevation of irrigated areas in the Uncompahgre Project ranges from about 4,900 ft at Delta to about 5,900 ft near Colona.

The approximately 70,000 acres of irrigated land in the Grand Valley are served by Federal and by private irrigation systems. The Federal system serves about 38,000 acres, and the remainder of the irrigated acreage is served by private systems. About 30,000 acres served by the Federal system is located on soils derived from Mancos Shale or from alluvium overlying Mancos Shale between the Colorado River and the Government Highline Canal (fig. 3). The remainder of the Federal system serves irrigated land on Orchard Mesa, a low alluvial terrace located in the southeast part of the Grand Valley (fig. 3). The Grand Valley is relatively flat and gradually slopes upward to the northeast to the Book Cliffs, which are about 1,500 ft above the valley floor. Elevation of irrigated areas in the Grand Valley ranges from about 4,400 to 4,800 ft. Numerous small streams and washes dissect the valley and discharge into the Colorado River.

The Uncompahgre Project area and the Grand Valley have an arid to semiarid climate characterized by cool to occasionally cold winters and hot summers. Annual precipitation ranges from about 8 in. at Grand Junction and Delta to 13 in. at Colona. Annual evaporation in both areas is about 50 to 70 in. In most years, snowfall is less than 30 in.

The length of the growing season is quite variable in the study area because of local climate variability. The growing season ranges from about 112 to 148 days in the Uncompahgre Project area and from about 150 to 190 days in the Grand Valley. Major crops produced are alfalfa, feed corn, hay, small grains, potatoes, beans, onions, fruit, sweet corn, melons, and soybeans. Cattle are wintered at many farms, and there are numerous small cattle-feeding operations and dairies.

Urban and residential areas in the Uncompahgre Project area are centered around Montrose, Olathe, and Delta. Considerable urban and residential areas are in the Grand Valley in the vicinity of Grand Junction and Clifton. Some agricultural land in both areas has been sold for rural-residential and commercial development. The conversion of agricultural land to nonagricultural uses has been increasing in the study area.



**Figure 2.** Selected features in the Uncompahgre Project area.

### Geologic Setting

Rocks exposed in the study area range in age from Precambrian to Upper Cretaceous. The Mancos Shale, the terrace deposits on the western side of the Uncompahgre Project, the valley-fill deposits in the eastern end of the Grand Valley (the cobble aquifer), and the alluvium overlying the Mancos Shale are the primary geologic units affected by irrigation in the study area. Other rocks in the

study area primarily are exposed on the outer edges of the irrigated valleys. The following descriptions of the geology of the study area were derived from Meeks (1950), Williams (1964), Lohman (1965), Craig (1971), Schneider (1975), Tweto and others (1976), Schwochow (1978), Cashion (1973), Bureau of Reclamation (1986a), and Steven and Hail (1989). Geologic maps of the irrigated parts of the study area are shown in figures 4 and 5.

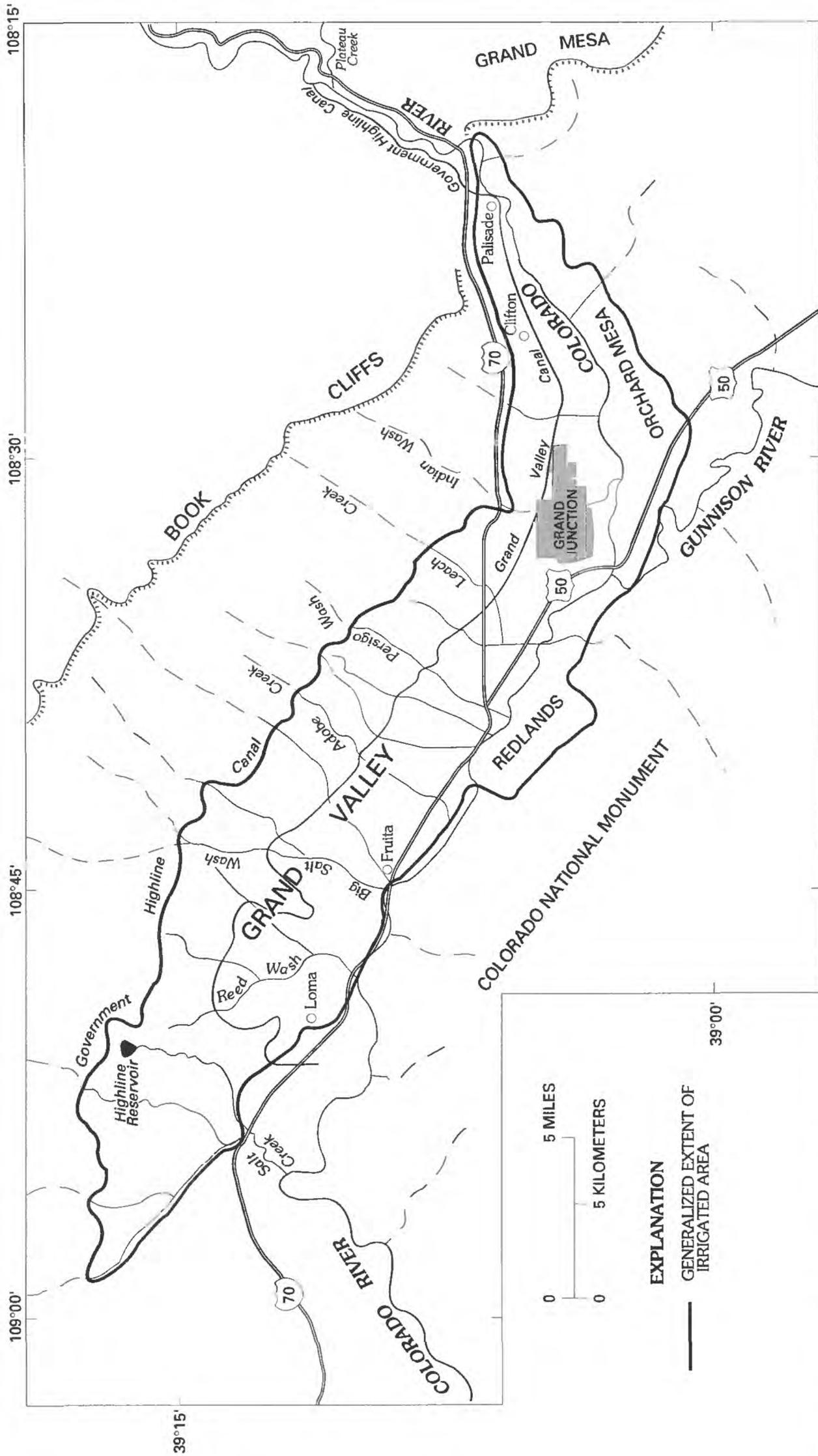
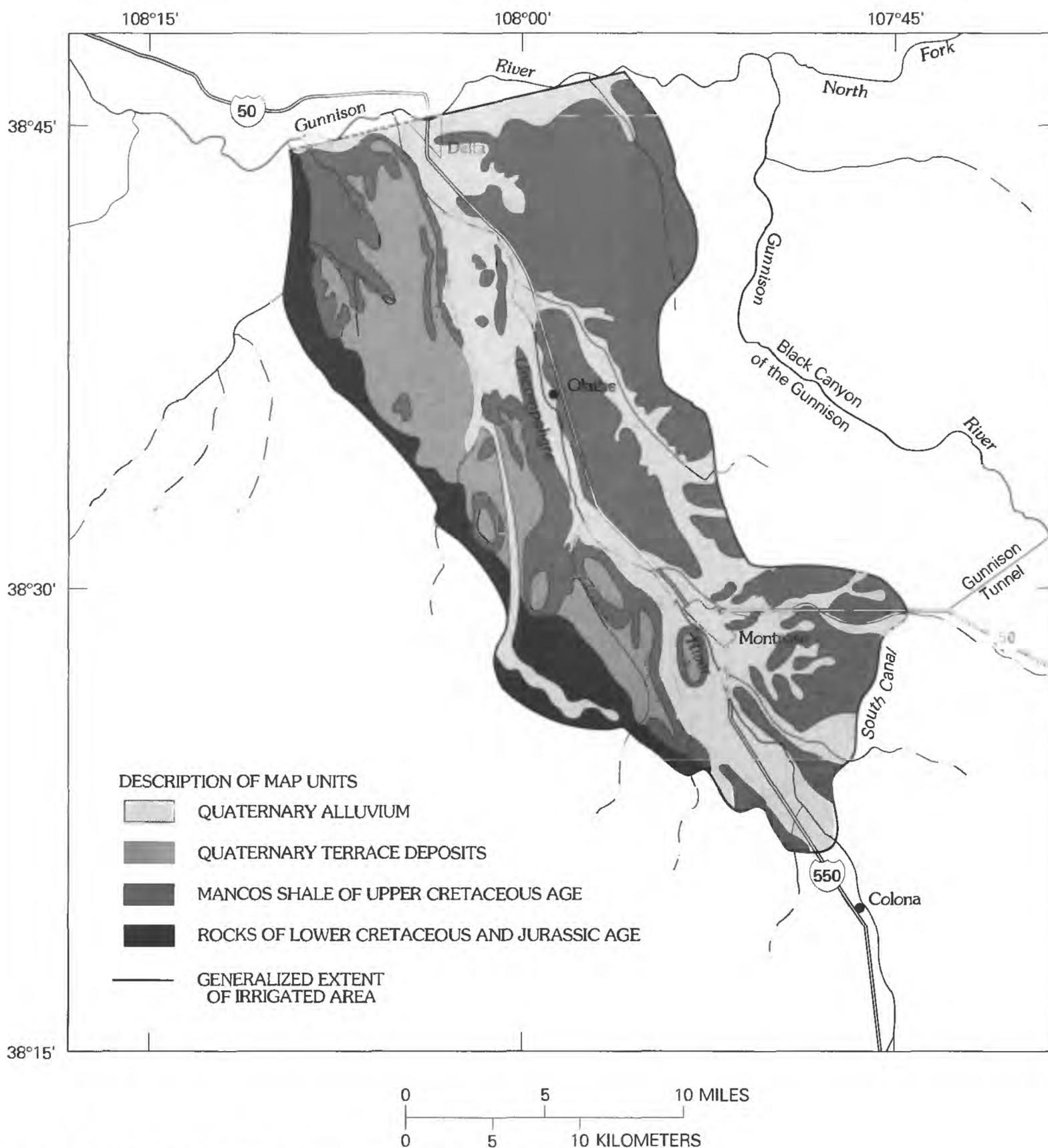


Figure 3. Selected features in the Grand Valley.

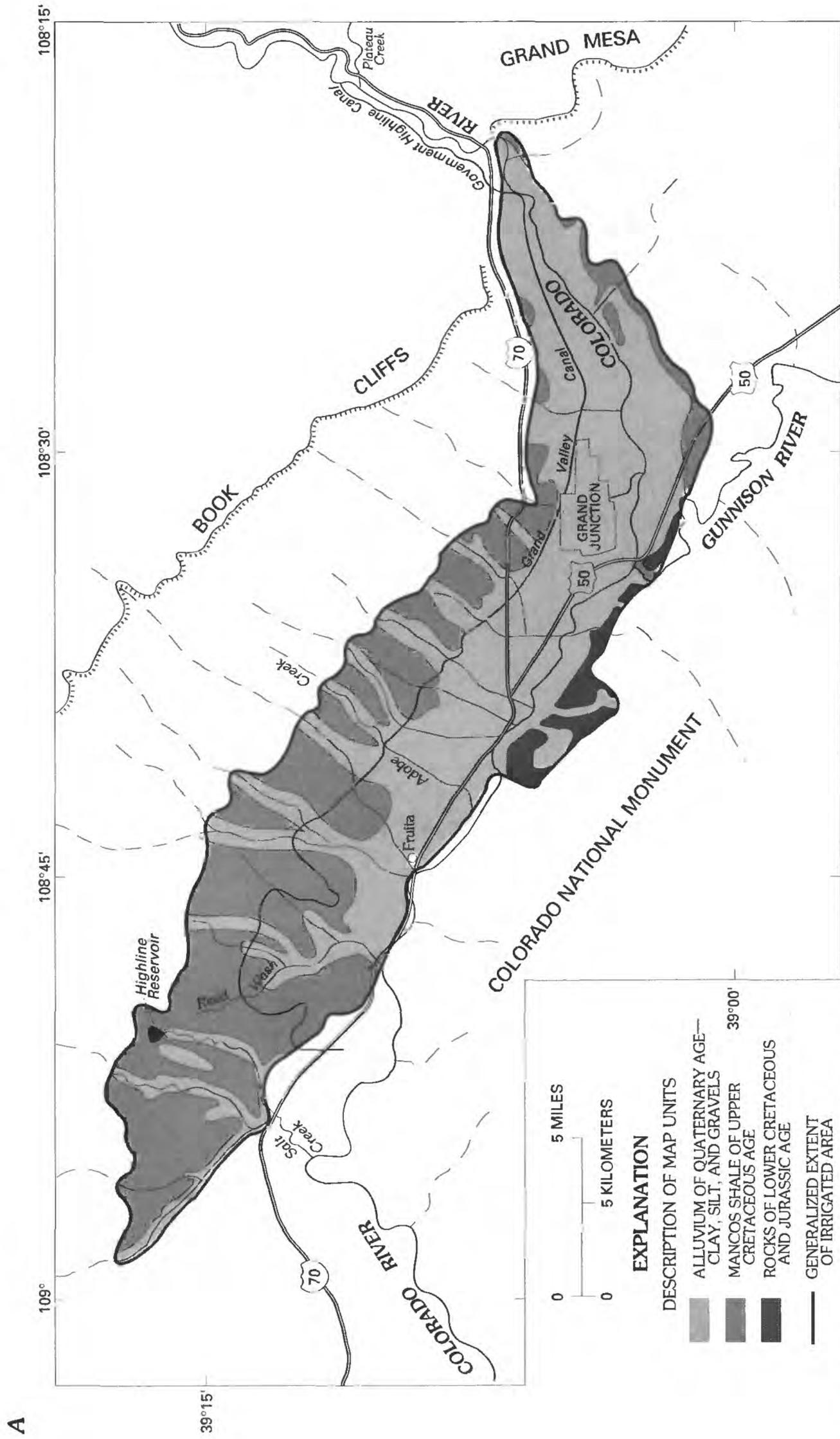


**Figure 4. Generalized surficial geology of the Uncompahgre Project**

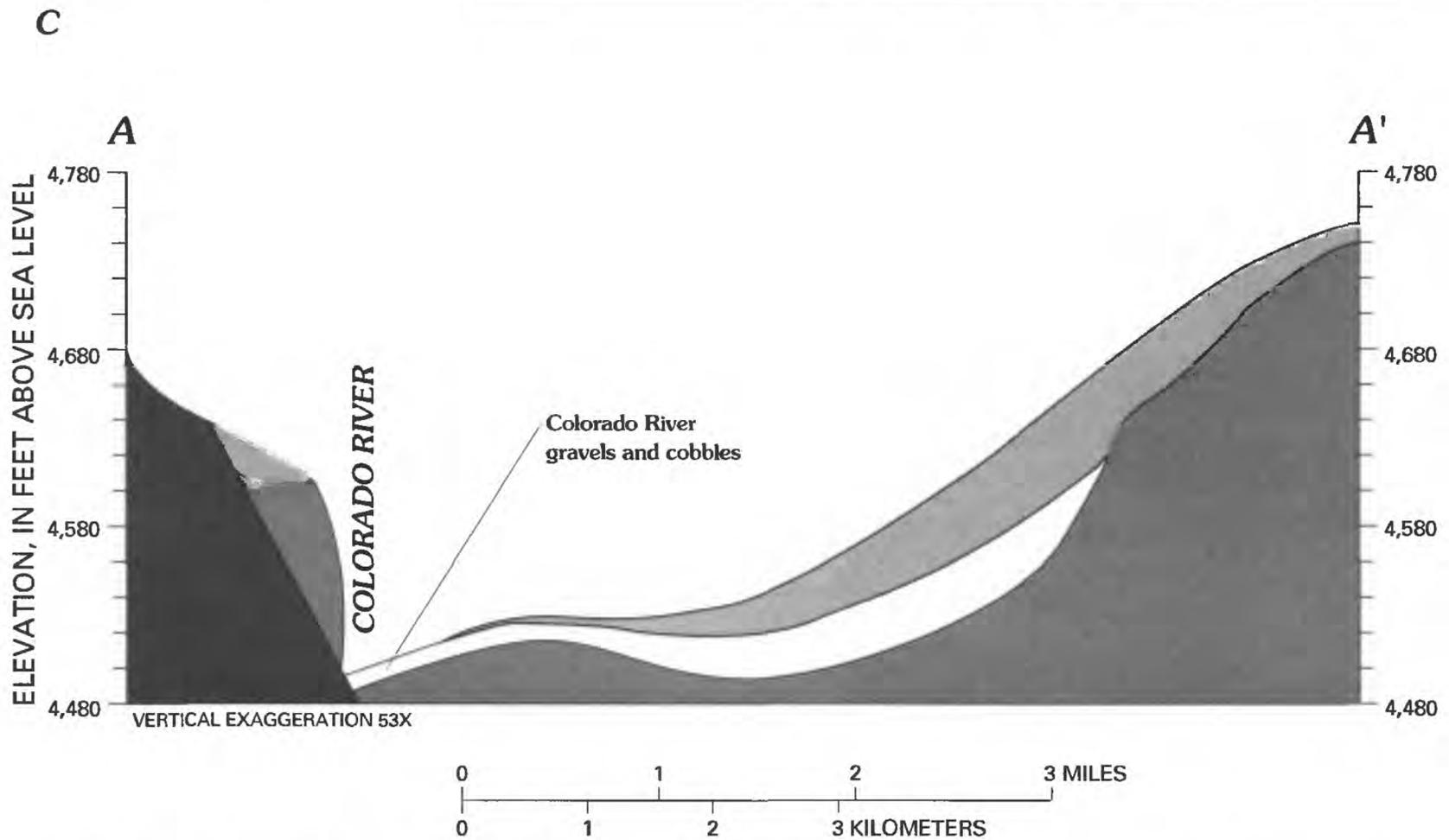
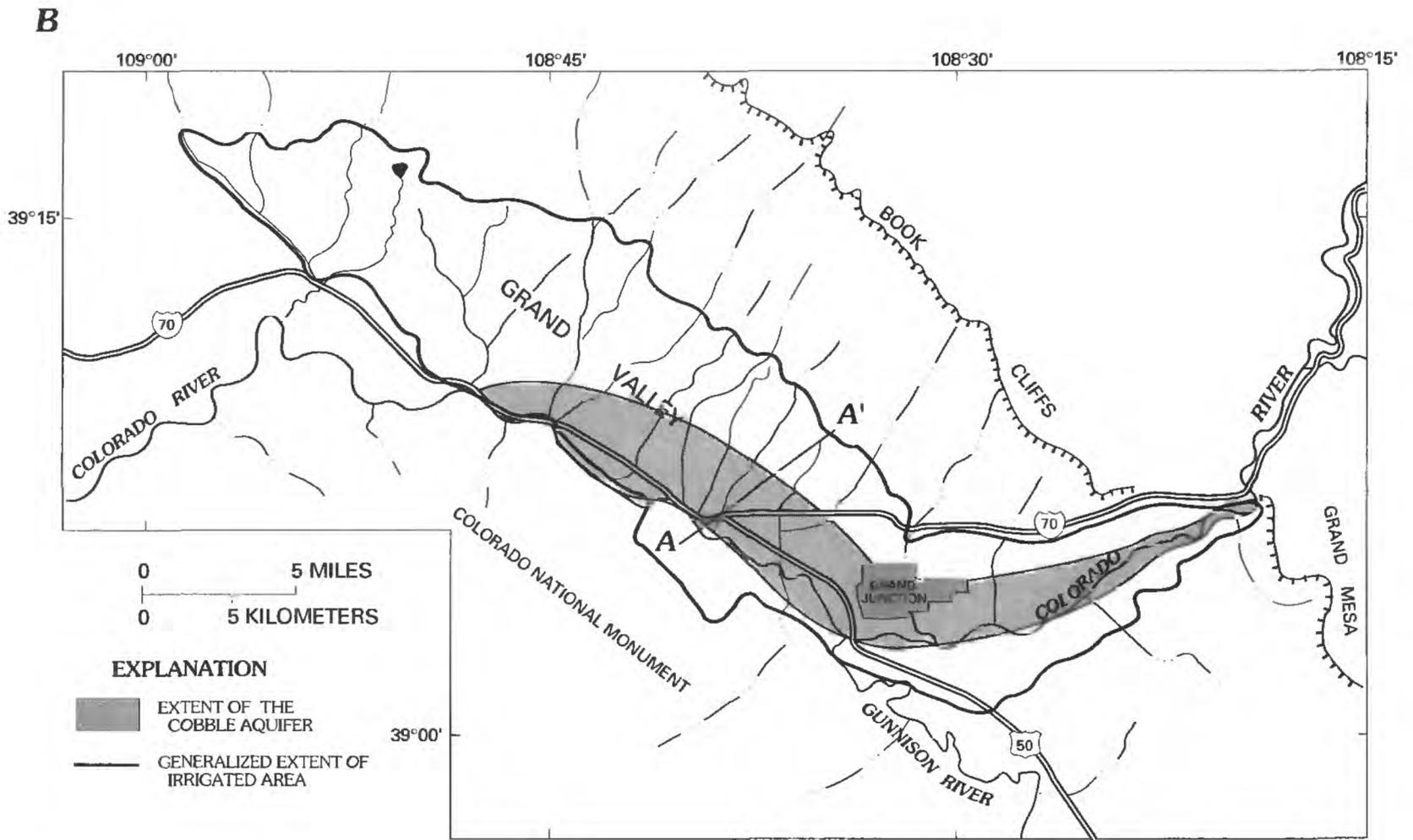
The Mancos Shale of Upper Cretaceous age underlies almost all of the Grand Valley, underlies the eastern one-half and part of the western one-half of the Uncompahgre Project area (figs. 4, 5A), and outcrops in many areas throughout western Colorado and Utah. The formation ranges in thickness from 2,000 to 3,000 ft and consists of massive, fossiliferous marine shale that contains interbedded sandstone, siltstone, and volcanic-ash layers. The Mancos Shale is the lateral equivalent

of the Niobrara Formation, Cody Shale, and Pierre Shale in Montana, Nebraska, South Dakota, and Wyoming.

The Mancos Shale is a regressive prodelta-plume complex genetically related to the deltaic systems active along the western interior seaway of Cretaceous age and is divided into the lower shale member, the Ferron Sandstone Member (or the Juana Lopez Member), the Mancos B Member, and the Buck Tongue Member (Cashion, 1973; Gill and Hail, 1975; Cole and Young, 1991).



**Figure 5. Grand Valley geology: (A) Surficial geology, (B) generalized extent of the cobble aquifer, and (C) generalized geologic section.**



**Figure 5.** Grand Valley geology: (A) Surficial geology, (B) generalized extent of the cobble aquifer, and (C) generalized geologic section—Continued.

The lower shale member contains massive and laminated silty-mudstone and sandy-siltstone parasequences that contain disseminated pyrite, lenticular kerogen and coal, and pyrite minerals associated with ash beds. Little information is available on the Ferron Sandstone Member. The Mancos B Member (called the Prairie Canyon Member by Cole and Young, 1991) is characterized by lenticular, cyclic, upward parasequences that range in thickness from 6 to 90 ft and consists of five main lithofacies: silty claystone, sandstone-claystone, sandy siltstone, bioturbated muddy sandstone, and sandy dolomite (as beds and concretions). Volcanic-ash layers occur as interbeds throughout the Mancos Shale and range in thickness from less than 1 in. to 2 ft. The ash layers in the study area could have originated from the Sevier Orogeny in central Utah. Volcanic ash could be the source of selenium and other trace constituents in the Mancos Shale.

The Mesaverde Formation of Upper Cretaceous age overlies the Mancos Shale (fig. 5) and forms the caprock for the Book Cliffs that border the northern edge of the Grand Valley. The formation consists of massive sandstone, gray shale, and coal, and ranges in thickness from 60 to 100 ft near the Book Cliffs, but is about 2,300 ft thick in areas north of the Grand Valley. The Mesaverde Formation has been eroded away and is not present in the Uncompahgre Project area.

Terrace deposits on the western side of the Uncompahgre Project area (fig. 4) consist of glacial outwash derived from the San Juan Mountains. These deposits range in thickness from 5 to 60 ft and are poorly sorted materials consisting of fine rock flour, sand, gravel, cobbles, and boulders. The parent material of terrace deposits generally consists of granite, rhyolite, and welded tuff mixed with weathered and transported detritus from the Dakota Sandstone and the Mancos Shale.

Valley-fill deposits in an ancient valley of the Colorado River are in the central and eastern parts of the Grand Valley (fig. 5B). The deposits were named the "cobble aquifer" (Bureau of Reclamation, 1986a), although the ground-water quality is poor and unacceptable for domestic, agricultural, and industrial uses. The cobble aquifer is late Holocene to Pleistocene in age, ranges in thickness from 10 to 65 ft, and consists of well-sorted pebbles, cobbles, and boulders in a sandy matrix. Alluvium and eolian sand may locally cover the gravels (part of the Quaternary clay, silt, and gravels shown in fig. 5A). Mudflows of

Mancos Shale mixed with detritus from the Mesaverde Formation overlies the cobble aquifer in some locations (part of the Quaternary clay, silt, and gravels shown in figure 5A).

Alluvium overlying the Mancos Shale consists of clay, silt, and gravel deposits of Holocene age. Alluvial deposits commonly are a combination of fluvial sediments and mudflows of Mancos Shale residuum. In the Grand Valley, the alluvium consists of Mancos Shale residuum mixed with detritus weathered from the Mesaverde Formation that forms the caprock for the Book Cliffs (fig. 5). In the Uncompahgre Project area, alluvium overlying the Mancos Shale in the eastern and southeastern parts of the area consists of Mancos Shale residuum mixed with detritus from the Dakota Sandstone, weathered ash-flow tuff, and andesite from the mountains east of the Uncompahgre Project area.

Mineral resources are rich in the areas surrounding the Uncompahgre Project area and the Grand Valley; however, little mineral resource development has occurred in the irrigated areas, except for limited natural gas exploration. Uranium and vanadium have been mined from the Morrison Formation west of the Uncompahgre Plateau; oil shale has been developed in the Green River Formation north and northeast of the Grand Valley; coal has been mined in the Mesaverde Formation and Dakota Sandstone; isolated deposits of copper, gold, molybdenum, beryllium, and titanium have been mined from granitic rocks near Unaweep Canyon south of the Grand Valley; bentonitic clays have been mined from the Morrison Formation; sulfur has been extracted from the Mancos Shale and alunite from the Morrison Formation in the upper Gunnison River Basin; and gypsum, halite, and potash have been mined in the Paradox and Sinbad Valleys along the southwestern edge of the Uncompahgre Plateau. Selenium occurs with many of these mineral deposits; however, the mineral resources development has not affected the irrigated areas on a large scale.

## **Irrigation Projects**

### **Uncompahgre Project**

Irrigation began in the 1880's in the Uncompahgre Valley, and by 1890 about 30,000 acres of land were irrigated by private systems that used water from five small diversion

dams along the Uncompahgre River. In 1901, the State of Colorado began building the 5.8-mi-long Gunnison Tunnel from the Gunnison River to supply more water to the Uncompahgre Valley. Because of insufficient funding, the State could not complete the tunnel, and the BOR completed construction of the Gunnison Tunnel in 1909 (fig. 1) and a diversion dam on the Gunnison River in 1912. The Uncompahgre Project, as it was called, included existing and new canals and laterals. Taylor Park Reservoir (fig. 1) was built in 1937 to supply the project with a dependable water supply. Operation and maintenance of the Uncompahgre Project was transferred to the Uncompahgre Valley Water Users Association in 1932.

The Uncompahgre Project supplies water for irrigation of about 86,000 acres in the lower Gunnison River Basin (figs. 1 and 2). About two-thirds of the irrigated land is west of the Uncompahgre River, where soils are more conducive to agriculture. Historically, diversion of water from the Gunnison River accounted for about two-thirds of the irrigation water for the project, and water from the Uncompahgre River accounted for the remainder of the irrigation water. The Gunnison Tunnel discharges into the South Canal near Highway 50 east of Montrose (fig. 1). Some water from the South Canal is used to irrigate land southeast of Montrose, but most of the water discharges into the Uncompahgre River to augment flows for downstream canal diversions. The irrigation season normally is from early April through October. Historically, water was diverted from the Uncompahgre River into canals during winter (hereinafter referred to as winter water) to provide water for livestock.

A part of the subsurface-irrigation drainage and surface-return flow discharges into the Uncompahgre River upstream from Delta. Much of the water diverted by canals downstream from Montrose consists of return flows (subsurface and surface) from upstream irrigated areas. Between Peach Valley Arroyo and Roubideau Creek (fig. 2), irrigation drainage and return flows from Uncompahgre Project land discharge into the Gunnison River through natural drainage pathways or manmade ditches. There is considerable irrigated land in the lower Gunnison River Basin upstream from Delta, such as in the Smith Fork, North Fork, and Tongue Creek Basins (fig. 1).

## **Grand Valley**

Settlement began in the Grand Valley in 1881, and the private Grand Valley Canal (fig. 3) was completed prior to 1910. The Grand Valley Canal irrigates approximately the southern one-half of the Grand Valley that is north of the Colorado River between Palisade and Loma (fig. 3). The Government Highline Canal (the Grand Valley Project) was completed in 1917. The Federal system provides water to areas between the Government Highline Canal and the Grand Valley Canal, to Orchard Mesa, and to some areas between Clifton and Palisade. The Grand Valley Water Users Association operates and maintains the Federal system north of the Colorado River, which serves about 30,000 acres. The remainder of the valley north of the Colorado River is served by the private Grand Valley Irrigation Company. Orchard Mesa is served by the Orchard Mesa Irrigation District, and the Redlands area (fig. 3) is served by the private Redlands Water and Power Company.

The Colorado River is the source of all irrigation water for the Grand Valley, except for the Redlands area, which uses water from the Gunnison River that is diverted about 2 mi upstream from the mouth of the Gunnison River. The Government Highline Canal diverts water from the Colorado River immediately upstream from the confluence with Plateau Creek (fig. 3), and the Grand Valley Canal diverts water near Palisade. Much of the subsurface-irrigation drainage and surface-return flow discharges into natural streams and washes that dissect the Grand Valley (fig. 3) and discharge into the Colorado River. In addition to natural drains, there is about 600 mi of man-made surface drains, many of which are in the private irrigation system.

## **Salinity-Control Projects**

In 1974, the Colorado River Basin Salinity Control Act (Public Law 93-320) was passed by the U.S. Congress. That law authorized various investigations and construction of projects with the objective of decreasing the salt (dissolved-solids) loading to the Colorado River. The Uncompahgre Project and the Grand Valley have been included in the salinity-control program.

The Lower Gunnison Basin Unit of BOR's Colorado River Water Quality Improvement Program includes the Uncompahgre Project and

other irrigated areas in the lower Gunnison River Basin. The BOR (1982, 1984) estimated that about 360,000 tons/yr of salt from irrigation-induced sources in the Uncompahgre Project is conveyed to the Uncompahgre and Gunnison Rivers, and the salt ultimately is discharged to the Colorado River. The salt loading is attributed to conveyance-system losses, on-farm seepage, and deep percolation of irrigation water into weathered and fractured shale of the Mancos Shale and into alluvium derived from shale. As this irrigation-induced ground water flows through the shale, salt is picked up and eventually is discharged to drains and rivers and, thus, into the Colorado River system.

The Winter Water Replacement Program of the Lower Gunnison Basin Unit (Bureau of Reclamation, 1987) provides a replacement winter-water supply for livestock operators who depended on Uncompahgre Project canals and laterals for their livestock watering needs during the winter. Winter canal flows were terminated, and replacement water supplies were provided by expanding the existing rural domestic-water systems. The replacement program was expected to decrease salt loading to the Colorado River by 74,000 tons/yr. As of October 1994, the replacement program was 95 percent complete.

The East Side Lateral Program of the Lower Gunnison Basin Unit is planned to replace about 195 mi of earthen irrigation laterals and about 7 mi of small canals east of the Uncompahgre River with underground pipeline. That program is planned to decrease salt loading from the Uncompahgre Project to the Colorado River by about 65,000 tons/yr. Implementation of the program was scheduled to begin in fiscal year 1995; however, as of early 1996, this project has not been started.

The Grand Valley Unit is a salinity-control project that consists of the Colorado River Valley between Palisade and the Colorado-Utah State line. The Grand Valley Unit contributes an estimated 580,000 tons/yr of salt to the Colorado River through deep percolation of water from canals, laterals, and on-farm irrigation (Bureau of Reclamation, 1983, 1985). Between 1980 and 1982, the BOR lined 7 mi of canal and placed 34 mi of earthen laterals in underground pipeline in the Reed Wash Basin (fig. 3) for a test program known as Stage One (Bureau of Reclamation, 1978). Post-construction monitoring indicated that Stage One improvements decreased the

annual salt loading to the Colorado River by 21,900 tons. The Stage Two program of the Grand Valley Unit presently (1996) is under construction and completion is scheduled in 1998 (Bureau of Reclamation, 1985, 1986b). Stage Two is planned to replace about 320 mi of laterals with underground pipeline and to line about 40 mi of canals, decreasing the salt loading to the Colorado River by an estimated 151,000 tons/yr.

The Natural Resources Conservation Service (NRCS), formerly the Soil Conservation Service of the U.S. Department of Agriculture, is conducting the on-farm parts of the salinity-control program in the Lower Gunnison Basin Unit and in the Grand Valley Unit. The total irrigated area in the Lower Gunnison Basin Unit that was studied by NRCS was 171,000 acres, which includes the Uncompahgre Project. The estimated total salt loading from irrigation sources in the Lower Gunnison Basin Unit (the 171,000 irrigated acres) was about 640,000 tons/yr (Bureau of Reclamation, 1984). The NRCS is improving the private on-farm irrigation water delivery and application systems through a volunteer cost-share program. Those improvements include leveling of irrigation land, underground and gated pipelines, sprinkler and drip-application systems, concrete-lined ditches, and associated irrigation water-management practices. The NRCS estimates that the total salt decrease attributed to on-farm improvements to be about 166,000 tons/yr in the Lower Gunnison Basin Unit and about 132,000 tons/yr in the Grand Valley Unit (Hedlund, 1994).

## Previous Studies

Much of the water-quality data collected in the study area were for salinity studies. As a result, trace-constituent data often were not collected; however, a few studies provide selenium concentrations in water, soil, plants, and biota in the Uncompahgre Project area and the Grand Valley. Selenium data were collected as early as 1934–36 in the Uncompahgre Project area and in the Grand Valley (Anderson and others, 1961). These data were for the Gunnison and Colorado Rivers in the Grand Junction area, for the Uncompahgre River, for a few drains in irrigated areas of the Uncompahgre Valley and Grand Valley, and for soil and salt-crust samples. Anderson and others (1961) reported a selenium concentration of

2,680 µg/L in a new (when the sample was collected in the 1930's) drain near Mack in the Grand Valley. The USGS has collected selenium and other trace-constituent data since 1975 for the Gunnison and Colorado Rivers. These selenium data are summarized later in this report in the "Selenium Concentrations and Loads in the Gunnison and Colorado Rivers" section. The U.S. Department of Energy (1986) collected trace-constituent data, including selenium, from some wells near a uranium mill-tailings pile in Grand Junction.

Because of a suspected problem concerning human consumption of fish that had high levels of selenium, the Colorado Division of Wildlife collected selenium data for fish from Sweitzer Lake near Delta in 1974 and 1977 (Colorado Division of Wildlife, written commun., 1987). A summary of the data is in Butler and others (1991). Because of results of the fish sampling, a sign was posted in 1977 at Sweitzer Lake that warned about high selenium concentrations in fish in the lake.

A reconnaissance investigation of the Gunnison and Uncompahgre Rivers and Sweitzer Lake (Butler and others, 1991) was done in 1988–89 to determine if irrigation drainage from the Uncompahgre Project was affecting water, fish, and wildlife resources. Butler and others (1991) reported high selenium concentrations in some water, bottom-sediment, and biota samples and that the Uncompahgre Project was a significant source of selenium, dissolved solids, and sulfate to the Uncompahgre River. The maximum selenium concentration in water samples was 320 µg/L from the Garnet Canal diversion into Sweitzer Lake. A bottom-sediment sample from Sweitzer Lake had 41 µg/g of selenium. Selenium concentrations in whole-body fish samples from Sweitzer Lake ranged from 15.2 to 50.0 µg/g dry weight. There also were large selenium concentrations in some of the bird samples collected from Sweitzer Lake and from the Escalante State Wildlife Area, which is along the Gunnison River downstream from Delta (fig. 1). However, the reconnaissance investigation did not document adverse effects of selenium on fish and birds.

Selenium concentrations in soil, water, vegetables, and field crops in irrigated areas of the Uncompahgre Project and the Grand Valley were reported in Follett and others (1990). Sampling was limited to a few sites in each area. Follett and others

(1990) reported low selenium concentrations in vegetables (broccoli and sweet corn) and in field crops (alfalfa and wheat).

Considerable dissolved-solids and major-constituent data were collected in the study area for salinity studies and other studies related to agriculture. A study of irrigation-return-flow water quality in the Grand Valley was done by Duke and others (1976). Salinity data collected for a salinity-control demonstration project in the Grand Valley were reported by Binder and others (1978). The BOR has done several investigations concerning salinity studies in the Uncompahgre Project (Bureau of Reclamation, 1984, 1987) and in the Grand Valley (Bureau of Reclamation, 1978, 1983, 1985). The report by the BOR (1983) described a detailed water budget for the Grand Valley. The USGS collected dissolved-solids and major-ion data for several streams and washes in the Grand Valley between 1973 and 1983 for the salinity investigations. Whittig and others (1983) did a salinity investigation in the West Salt Creek Basin, located west of irrigated areas in the Grand Valley.

An early survey of soils in the Uncompahgre Valley was done in 1910 by the U.S. Department of Agriculture (Nelson and Kolbe, 1912). A more recent soil survey of the Uncompahgre Project area was done by Cline and others (1967). A study of soil in saline areas of the Grand Valley was done by Fireman and others (1951). Spears and Kleven (1978) did a soil survey of Mesa County, which includes the Grand Valley. Lusby (1978) described results of a long-term study of grazing effects on sediment runoff in a nonirrigated area in the western end of the Grand Valley.

Meeks (1950) investigated geology and ground water in the irrigated areas of the Uncompahgre Valley. Another investigation of ground water in the Uncompahgre Valley was done by Craig (1971). A reconnaissance study of ground-water resources in the lower Gunnison River Basin was described by Brooks and Ackerman (1985). Lohman (1965) described the geology and hydrology of artesian aquifers in the Grand Valley. Uranium and selenium-indicator plants that were used for uranium prospecting in the Colorado Plateau are described by Cannon (1954).

The BOR did several water-resource and hydrogeologic investigations of the Uncompahgre Project and the Grand Valley as part of the salinity-control projects in each area. A report by the BOR

(1977) contains ground-water reconnaissance and well-inventory information for the Uncompahgre Project (Lower Gunnison Basin Unit). The report also has some water-quality data, including data for arsenic and boron concentrations in ground water. Information about land and water resources, the irrigation system, water quality, and hydrogeology for the Uncompahgre Project is in two BOR reports (1982, 1984). Hydrogeologic investigations related to irrigation in the Grand Valley were reported in three BOR reports (1978, 1986a, b). The report from 1978 describes a detailed hydrogeologic investigation of the Reed Wash Basin for the Stage One salinity project. Geologic logs and salt-loading information for the cobble aquifer in the Grand Valley are in a BOR report (1986a).

Studies have been done since the early 1980's concerning threatened and endangered fish species in the Upper Colorado River Basin, and part of that work was done in the Grand Valley area. Most of the studies in the Grand Valley area concerned the Colorado River squawfish and the razorback sucker. Behnke and Benson (1983) and Archer and others (1985) described population, habitat, and reservoir effects on endangered fish in the Upper Colorado River Basin. A study of bonytail chub was described in Kaeding and others (1986), and a study of Colorado squawfish and razorback suckers in a reach of the Colorado River in the Grand Valley was described by Osmundson and Kaeding (1989). Concentrations of trace constituents in Colorado squawfish were described by Krueger (1988). Concentrations of organochlorine pesticides and trace constituents in endangered fish were described in Kurey (1985a, b).

## Acknowledgments

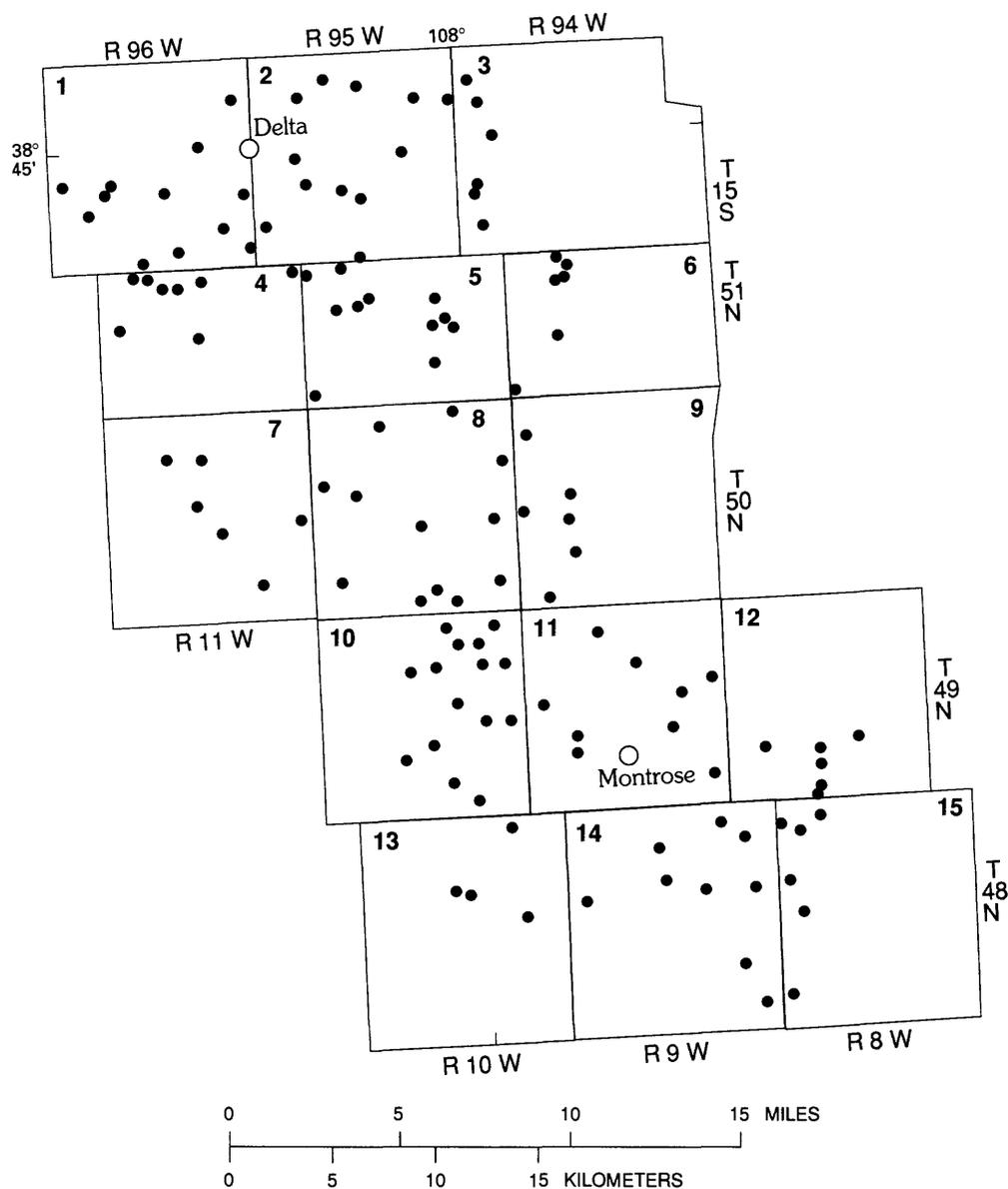
The authors thank the numerous property owners for allowing access to their property for collection of samples. We also thank Jack Cunningham and Kenneth Weston (BOR) for compilation of historical ground-water and aquifer-test data, Roger Fujii (USGS) for selenium-speciation analysis and for his insights concerning selenium geochemistry, David Wolny for his interpretation and valuable information on the local geology, and Jeffery Foster (USGS) for assistance with collection of surface-water and ground-water data. The authors also thank Larry Fukui of RUST Geotech, Inc.,

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## SOILS AND ALFALFA INVESTIGATIONS

An unbalanced, four-level, stratified random sampling design was used to define sources, distribution, and variability of selenium and other trace-constituent concentrations in the soils and associated alfalfa among and within geologic units in the Uncompahgre Project area. As part of the soil-sampling scheme, geologic units were mapped and described based on earlier geologic maps and soil-survey maps of the project area (Marshall, 1959; Williams, 1964; Cline and others, 1967; Tweto and others, 1976; Steven and Hail, 1989). Soils derived from five geologic units were sampled: Upper Cretaceous Dakota Sandstone (Kd); Upper Cretaceous Mancos Shale (Km); Quaternary deposits in ancient terraces and alluvial fans (Qt); Quaternary (Holocene) alluvium overlying Mancos Shale (Qm); and Quaternary (recent) flood-plain alluvium deposited by the Uncompahgre River and other streams (Qr). In the Uncompahgre Project area, most of the soils of unit Qm were derived from Mancos Shale. One site was sampled on Quaternary alluvium derived from Dakota Sandstone (Qd).

Fifteen townships were included in the study area, and the distribution of soil-sampling sites is shown in figure 6. All soil samples were collected in irrigated areas. Random sections were selected in each township until all geologic units in a township had been selected, in triplicate, for soil and alfalfa sampling (fig. 6). The sample distributions by geologic unit from the randomly selected sections are listed in table 1. Township 4 had four sites for the geologic unit Km; geologic unit Qd was sampled only in township 13 (table 1). If a preselected site was unacceptable in the field because of irrigation or absence of alfalfa, a new site was selected in an adjacent section as close as possible to the original site. To assess variability within a section, two samples about 100 m apart were collected in 14 randomly selected sections.



**Figure 6.** Distribution of soil-sampling sites within townships in irrigated areas of the Uncompahgre Project.

Soil cores of 1 m were removed using a 9-cm bucket auger, and the entire core was homogenized by mixing in a plastic container. A 1-kg portion of the 1-m core mixture was placed in a paper bag for transport to the laboratory. The top 20 cm of several alfalfa plants (*Medicago sativa* L.) at 10-percent bloom stage were sampled within a few meters of the auger bore, composited, placed in paper bags, and air dried. At several sites, alfalfa could not be obtained, and only the soil cores were taken.

### Sample Preparation and Analytical Methods

Soil samples were air dried in the laboratory at ambient room temperature (about 20°C), disaggregated using a mechanical mortar and pestle, and sieved to pass a 2-mm screen (10 mesh). A split of this material was ground to less than 100 mesh using a ceramic-plate grinder. The split was used for total analysis; the unground, 2-mm fraction was used for extractions. Field-dried alfalfa samples were washed

**Table 1.** Distribution of soil-sampling sites by geologic units in townships of the Uncompahgre Project area

[Numbers under geologic unit indicate the number of sites in each unit within each township; geologic units are defined as follows: Kd, Upper Cretaceous Dakota Sandstone; Km, Upper Cretaceous Mancos Shale; Qt, Quaternary terrace and alluvial-fan deposits; Qm, Quaternary (Holocene) alluvium overlying Mancos Shale; Qr, Quaternary (recent) flood-plain alluvium deposited by the Uncompahgre River and other streams; Qd, Quaternary alluvium derived from Dakota Sandstone; --, no samples]

Township number (fig. 6)	Township	Range (all west)	Geologic unit					
			Kd	Km	Qt	Qm	Qr	Qd
1	15 south	96	--	3	3	3	3	--
2	15 south	95	--	3	3	3	3	--
3	15 south	94	--	3	--	3	--	--
4	51 north	11	--	<sup>1</sup> 4	3	--	--	--
5	51 north	10	--	3	3	3	3	--
6	51 north	09	--	3	3	--	--	--
7	50 north	11	3	--	3	--	--	--
8	50 north	10	--	3	3	3	3	--
9	50 north	09	--	3	--	3	--	--
10	49 north	10	3	3	3	3	3	--
11	49 north	09	--	3	--	3	3	--
12	49 north	08	--	3	--	3	--	--
13	48 north	10	3	--	--	--	--	<sup>2</sup> 1
14	48 north	09	--	3	--	3	3	--
15	48 north	08	--	3	--	3	--	--

<sup>1</sup>Analytical data for all sites included for calculation of geometric means and ranges, but only first three sites used for analysis of variance (ANOVA).

<sup>2</sup>Analytical data included for calculation of geometric means and ranges, but not for ANOVA.

using tap water, rinsed several times in demineralized water, redried at ambient room temperature, and ground to pass a 2-mm screen in a Wiley mill. Each ground sample was mixed and split, and a part was ashed at 450°C in a muffle furnace for 24 hours.

Soils and plant ash were decomposed using a low-temperature mixed acid digestion (Crock and others, 1983). Solutions were analyzed simultaneously for 40 constituents using inductively coupled plasma atomic-emission spectroscopy (ICP-AES) (Crock and others, 1983). Soils and dried plant material for arsenic and selenium determinations were decomposed by mixed acids and hydrogen peroxide (Crock and others, 1994). Determinations were made by hydride-generation atomic absorption spectroscopy (HGAAS) (Crock and Lichte, 1982; Sanzolone and Chao, 1987).

Extractions on soils were done using deionized water (one part soil to five parts water, by weight) by agitation for 16 hours on a horizontal reciprocating shaker (Stewart and others, 1990). Solutions were clarified by centrifugation and filtration (0.45-µm

filter). Conductivity, pH, and anion concentrations were determined in solution by conductivity meter, standard combination pH electrode, and ion chromatograph (Wilson and others, 1987; Stewart and others, 1990). A part of each solution was predigested to oxidize organic matter, according to a modification developed by Presser and Barnes (1985), prior to arsenic and selenium determination by HGAAS.

### Selenium Concentrations in Soils and Alfalfa

The geometric means and ranges for total selenium in all soil samples from the Uncompahgre Project area and in soil samples from each geologic unit (Crock and others, 1994) are listed in table 2. Total-selenium concentrations in the 142 soil samples ranged from 0.1 to 8.6 µg/g (table 2). The geometric mean selenium concentration for all soil samples was 1.4 µg/g, compared to a geometric mean of 0.23 µg/g for Western soils (Shacklette and Boerngen, 1984).

Residual soils derived from Mancos Shale (Km) and alluvium overlying Mancos Shale (Qm) contained the highest geometric mean selenium concentrations of 2.2 and 2.9 µg/g (table 2). These values are 10 to 13 times the geometric mean for Western soils.

The geometric mean total-selenium concentrations in soils derived from the Quaternary terrace deposits (Qt), recent flood-plain alluvium (Qr), and Dakota Sandstone (Kd) were lower than the geometric mean concentrations in soils derived from Mancos Shale (Km), but exceeded the geometric mean for Western soils.

The geometric mean concentrations of water-extractable selenium for the soil samples, grouped by geologic unit, are listed in table 2. Concentrations ranged from 0.005 to 1.8 µg/g dry weight. As with the results of total-selenium analysis, the geometric mean concentration of water-extractable selenium was higher in alluvium overlying Mancos Shale (Qm) than in the residual soils derived from Mancos Shale (Km). The percent of total selenium that was water extractable was uniformly low for all geologic units and ranged from 1.5 to 2.7 percent.

Total-selenium concentrations in 128 alfalfa samples from the Uncompahgre Project area ranged from less than 0.03 to 9.5 µg/g dry weight (table 2).

Data for individual samples are listed in Crock and others (1994). The geometric mean selenium concentration of 0.33 µg/g (table 2) for all alfalfa samples exceeded the recommended minimum for cattle feed of 0.1 µg/g (Fisher and others, 1987). Only five alfalfa samples exceeded the recommended dietary tolerance limit of 4 µg/g (Byers, 1935). The alfalfa data from the Uncompahgre Project area indicates lower selenium concentrations compared to the Kendrick Reclamation Project area in Wyoming, where 15 percent of alfalfa samples from irrigated fields exceeded the tolerance limit (See and others, 1992). As with total and water-extractable selenium in soil, the highest geometric mean selenium concentrations in alfalfa were in plants growing on alluvium overlying Mancos Shale (Qm).

Selenium concentrations in alfalfa do not show the same trend as selenium concentrations in soil when the geometric means for the geologic units are compared. Residual soils derived from Mancos Shale (Km) and Quaternary terrace deposits (Qt) contained higher total-selenium concentrations in soil than did recent flood-plain alluvium (Qr), but selenium concentrations in alfalfa from units Km and Qt were significantly lower (significance level 0.05) than the concentrations in alfalfa from unit Qr.

**Table 2.** Geometric mean and observed range of total- and water-extractable selenium concentrations in soil and total-selenium concentrations in alfalfa for all samples from the Uncompahgre Project area, by geologic unit

[Selenium concentrations in soil and alfalfa, in micrograms per gram; geologic units are defined as follows: Kd, Upper Cretaceous Dakota Sandstone; Km, Upper Cretaceous Mancos Shale; Qt, Quaternary terrace and alluvial-fan deposits; Qm, Quaternary (Holocene) alluvium overlying Mancos Shale; Qr, Quaternary (recent) flood-plain alluvium deposited by the Uncompahgre River and other streams; <, less than; analytical duplicates not included; data for all samples includes one sample for geologic unit Qd, Quaternary alluvium overlying Dakota Sandstone]

Statistic	All samples	Kd	Km	Qt	Qm	Qr
<b>SOIL, TOTAL SELENIUM<sup>1</sup></b>						
Detection ratio	142:142	11:11	43:43	28:28	36:36	23:23
Geometric mean	1.4	.5	2.2	1.0	2.9	.6
Observed range	.1–8.6	.3–.6	.3–7.5	.3–3.4	.9–8.6	.1–2.9
<b>SOIL, WATER-EXTRACTABLE SELENIUM<sup>2</sup></b>						
Detection ratio	128:128	9:9	40:40	24:24	33:33	21:21
Geometric mean	.027	.009	.043	.013	.048	.018
Observed range	.005–1.8	.005–.019	.005–1.8	.005–.062	.008–.86	.005–1.0
<b>ALFALFA, TOTAL SELENIUM<sup>1</sup></b>						
Detection ratio	118:128	10:11	31:35	25:26	30:34	21:22
Geometric mean	.33	.12	.28	.25	.56	.48
Observed range	<.03–9.5	<.03–.69	<.03–1.6	<.03–1.8	<.03–6.3	<.03–9.5

<sup>1</sup>Data from Crock and others (1994). Site duplicates were considered independent samples.

<sup>2</sup>Data from Stewart and others (1993). Site duplicates were averaged to obtain one value for each site.

Selenium in alfalfa from unit Qr was not significantly different from selenium concentrations in alfalfa from alluvium overlying Mancos Shale (Qm), although the flood-plain alluvial soils contained only about 21 percent of total selenium and about 38 percent of the water-extractable selenium as did the soils on alluvium overlying Mancos Shale. In addition, the correlation of total selenium in alfalfa with water-extractable selenium in soils on unit Qr is 0.77, which is much higher than the same correlation for all samples of 0.47 (Stewart and others, 1993).

Results from analysis of variance (ANOVA) indicate that selenium distribution in the Uncompahgre Project is not uniform among geologic units or within geologic units. The percent of the variance for total and water-extractable selenium in soil and total selenium in alfalfa that are accounted for by each of the four levels in the ANOVA sampling

design (Stewart and others, 1993; Crock and others, 1994) are shown in figure 7. The ANOVA results in figure 7 show the variance among geologic units and the variance within geologic unit at the township, section, and within section scale. Fifty-seven percent of the variance in total selenium in soil was accounted for by geologic units. By contrast, only 30 percent of the total variance in water-extractable selenium in soil is accounted for by geologic units; differences among sections in the same geologic unit accounted for more of the total variance in water-extractable selenium than did differences among geologic units.

Ranges of selenium concentration were much greater in alfalfa from the alluvial units Qm (soils overlying Mancos Shale) and Qr (soils on recent flood-plain alluvium) than the ranges for the other geologic units—Kd (soils derived from Dakota Sandstone), Km (soils derived from Mancos Shale,

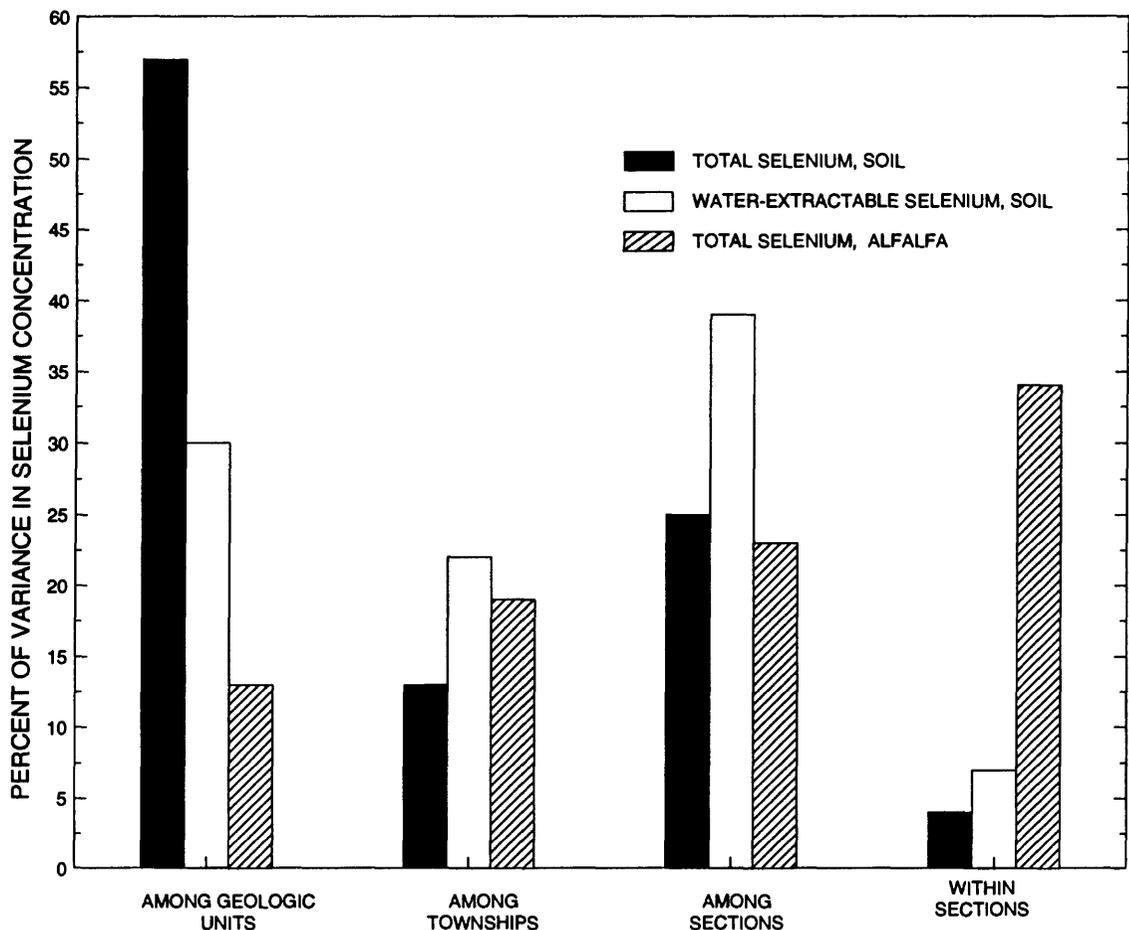


Figure 7. Percent of variance in selenium concentrations in soils and alfalfa for different levels in the sampling design.

and Qt (soils derived from terrace and alluvial-fan deposits) (table 2). Only 13 percent of the total variation in selenium concentration in alfalfa was attributed to differences among geologic units.

About one-third of the total variation resulted from concentration differences within sections, indicating high variability between samples collected in close proximity within the same geologic unit. Similar large variations in selenium concentrations in alfalfa collected in close proximity on the same parent geologic unit were reported for alfalfa in the Kendrick Reclamation Project area in Wyoming (See and others, 1992) and in native vegetation from seleniferous soils in South Dakota (Moxon and others, 1938; Olson and others, 1942).

The results indicate that selenium is mobilized from Mancos Shale and redistributed downslope in the Uncompahgre Project area by irrigation. The ANOVA results and the high correlations of selenium in alfalfa with water-extractable soil selenium, especially in alluvial soils, indicate that the forms of selenium have changed from immobile selenides incorporated in sulfide minerals and selenites sorbed to other iron minerals in the residual shale (Lakin, 1961; Elrashidi and others, 1989) to a higher proportion of the more mobile selenate in the alluvium (Geering and others, 1968; Balistrieri and Chao, 1987). This change in chemical species might occur because of increased exposure to ground water and of changing redox conditions in geographically lower elevations and could be expected to occur under the alkaline soil conditions that are present in the project area. Displacement of selenium downslope from a source area and an increase in content of dissolved species in contact with ground water was reported for the San Joaquin Valley in California (Tidball and others, 1989) and for the Kendrick Reclamation Project area in Wyoming (See and others, 1992). Because the Uncompahgre Project area generally is well drained, selenium does not accumulate to the levels that were reported in soils and alfalfa from the Kendrick Reclamation Project area (See and others, 1992), where irrigation drainage was evaporated in a closed basin.

Other trace constituents of environmental interest that had higher concentrations in soils of the Uncompahgre Project area than in soils in the Western United States were arsenic, molybdenum, uranium, and zinc. Concentrations of these trace constituents were highest in soils from alluvium overlying Mancos Shale (unit Qm), and the

geometric means for unit Qm are listed in table 3. Alfalfa from three of the five geologic units had mean copper to molybdenum ratios of less than 2:1. A minimum ratio of 2:1 in livestock feed is considered necessary to prevent symptoms of molybdenum-induced copper deficiency in cattle (Miltmore and Mason, 1971; Erdman and others, 1978).

**Table 3.** Geometric mean concentrations of arsenic, molybdenum, uranium, and zinc in soils from alluvium overlying Mancos Shale in the Uncompahgre Project area and in soils from the Western United States

[Concentrations, in micrograms per gram; data for Western United States soils from Shacklette and Boerngen (1984)]

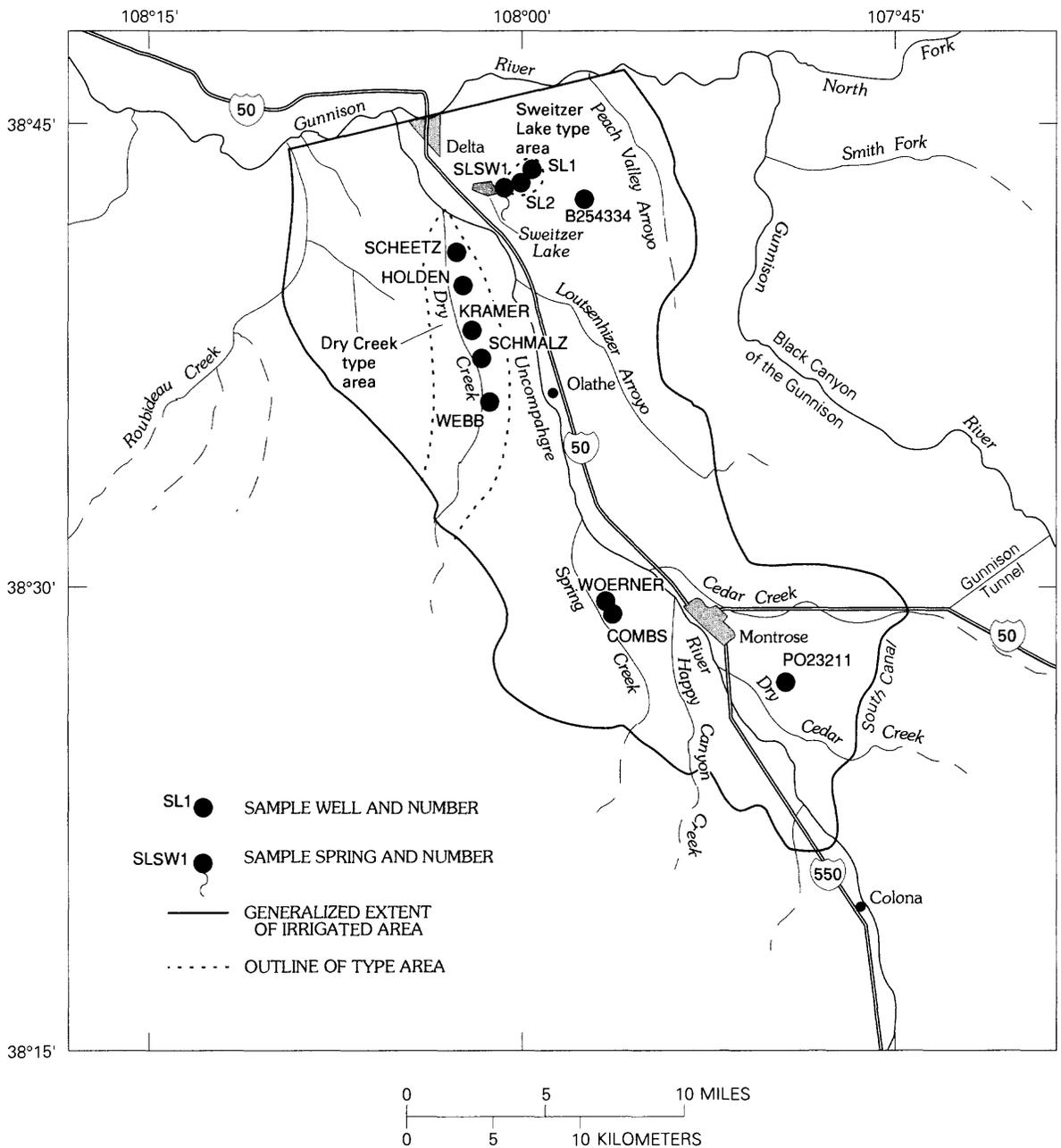
Area	Arsenic	Molybdenum	Uranium	Zinc
Uncompahgre Project— Alluvium from Mancos Shale (unit Qm)	9	5	5	110
Western United States	6	.9	3	55

## GROUND-WATER INVESTIGATIONS

The objectives of the ground-water investigations were to describe concentrations and distribution of selenium and other trace constituents in ground water in the Uncompahgre Project area and in the Grand Valley and to describe the hydrochemical processes affecting selenium release and mobilization in ground water in irrigated areas on Mancos Shale terrain. The approach was collection of geologic and ground-water-quality data from type areas that were representative of the hydrogeology of the whole area. Selection of type areas was based on the availability of historical ground-water data, existing wells, and geologic information. The type areas include:

1. Sweitzer Lake area in the eastern part of the Uncompahgre Project area—representing terrane on Mancos Shale residuum (fig. 8);
2. Dry Creek Basin in the western part of the Uncompahgre Project area—representing terrane on Quaternary terrace deposits (fig. 8); and,
3. Reed Wash Basin in the Grand Valley—representing terrane on Mancos Shale residuum and alluvium overlying Mancos Shale (fig. 9).

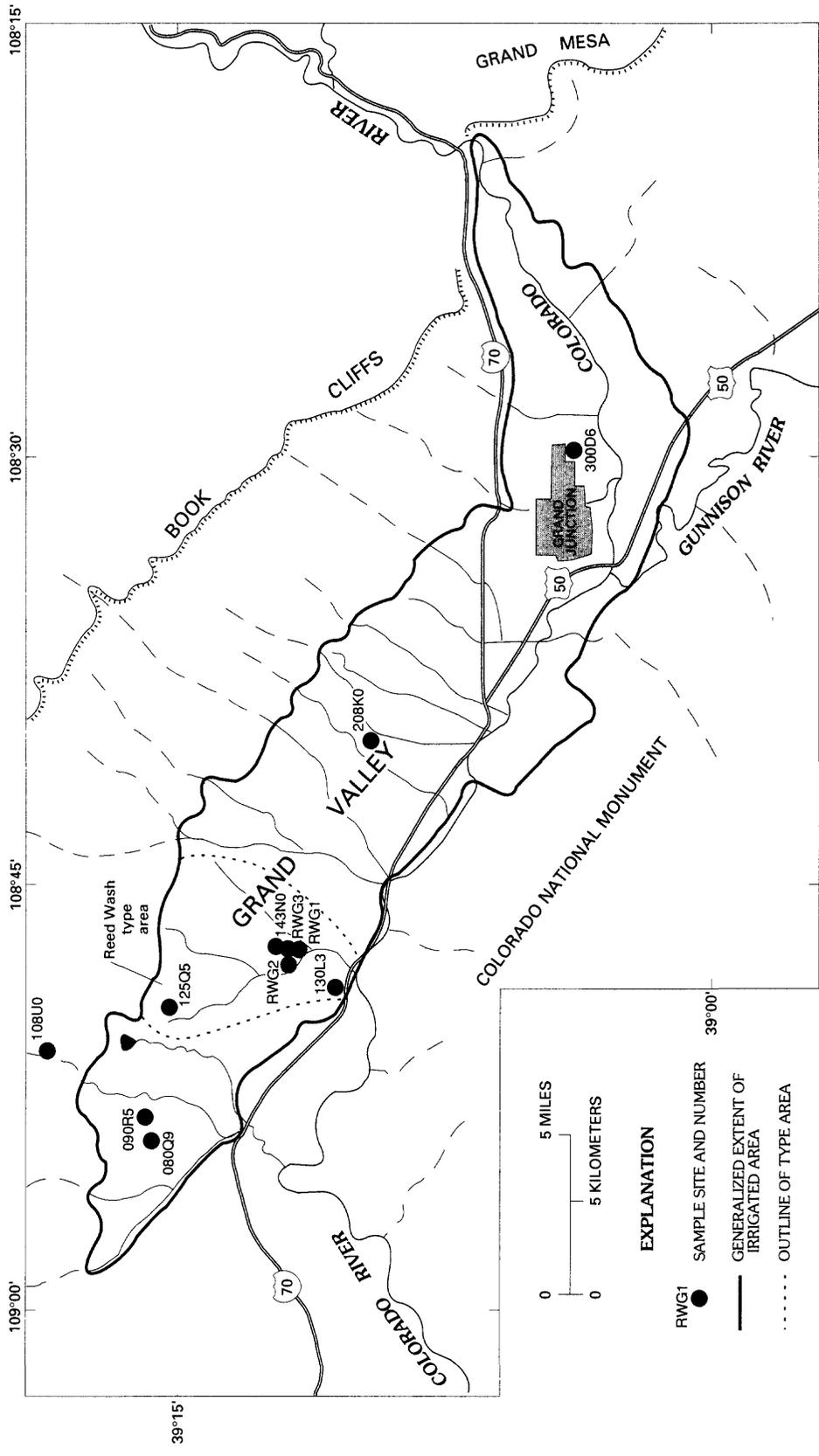
Hydrogeologic characteristics of the type areas are described in the "Ground-Water Hydrology" section.



**Figure 8.** Locations of type areas and locations of wells and springs in the Uncompahgre Project area where samples were collected for chemical analysis.

In the type areas, existing wells were inventoried and historical ground-water data were compiled, wells were installed where needed to supplement the existing wells, sediment-core samples were collected from boreholes, geologic information was compiled, and a data logger was installed in one well. In addition to the type-area investigations, wells were inventoried and ground-water samples were collected over a wide area to describe the areal distribution of selenium and other trace constituents. Deep wells

(privately owned) were inventoried and sampled to describe the boundary conditions for possible trace-constituent migration into the study area from deep aquifers. Where available, wells were inventoried and sampled outside the irrigated areas to describe natural or nonirrigated conditions. Samples of Mancos Shale bedrock were collected from cores archived at the USGS Core Research Center in Denver, Colo. Historical ground-water data, aquifer-test results, and digital-map data were compiled by the BOR.



**Figure 9.** Location of type area and wells in the Grand Valley where samples were collected for chemical analysis.

## Sample Collection and Analytical Methods

Many of the shallow wells used for the ground-water investigation were installed by the BOR as part of the salinity-control program in the Uncompahgre Project area and in the Grand Valley (Bureau of Reclamation, 1986a, b). Five shallow monitoring wells were installed by the USGS for this study using the hollow-stem auger method—three wells were installed in alluvium (Reed Wash type area) and two wells were installed in shale residuum (Sweitzer Lake type area). Aquifer-sediment samples were collected at 5-ft intervals using a split-spoon sampler. Sediment-core samples for trace-element analysis were air dried, and samples for selenium-speciation analysis were frozen. After installation of 2-in. polyvinyl chloride (PVC) casing with 5-ft screens, the wells were developed by purging about 30 well volumes of water from the wells. Depths of wells in the study area (BOR, USGS, and private) ranged from 8 to 1,000 ft below land surface.

Borehole samples were collected during installation of the shallow wells, topical samples were collected (outcrop of ash layers), and Mancos Shale bedrock-core samples were obtained from cores archived at the USGS Core Research Center in Denver, Colo. Selected sediment-core, bedrock-core, and topical samples were analyzed for (1) major and trace constituents by ICP-AES (Crock and others, 1983); (2) selenium and arsenic by continuous-flow HGAAS (Crock and Lichte, 1982; Sanzolone and Chao, 1987); (3) uranium and thorium by delayed neutron-activation counting (McKown and Mallard, 1987); and (4) total organic carbon by combustion-infrared detection (Jackson and others, 1987). Sequential extractions were performed on selected sediment-core samples (Fio and Fujii, 1990), and selenium speciation of the extraction fluids was performed by column chromatography and HGAAS (Makita and Fujii, 1992). X-ray diffraction (XRD) analyses were performed on bedrock, shale residuum, alluvium, and ground-water-filter residuum samples by L.M. Fukui (Senior Petrologist, Chem-RUST Geotech, Grand Junction, Colo.). Bedrock, shale residuum, alluvium, and ground-water-filter residuum samples were analyzed by scanning electron microscopy (SEM).

Water samples from wells and one spring were analyzed for (1) major ions, (2) selected trace constituents (including uranium), (3) nitrogen species,

(4) dissolved organic carbon, (5) stable isotopes of oxygen and hydrogen, (6) nitrogen isotopes of dissolved nitrate, (7) sulfur isotopes of dissolved sulfate, and (8) selenium species. Three to six well volumes of water were purged from the wells prior to sample collection, using a centrifugal pump. Samples were collected using a rinsed Teflon bailer and were carefully decanted into clean 1-L polyethylene bottles, using a bottom-emptying device on the bailer to prevent sample agitation and loss of volatile components (Barcelona and others, 1984). Dissolved-oxygen measurements for ground water were performed within the borehole by lowering the oxygen probe (Yellow Springs Instruments, Inc., dissolved-oxygen probe) on a cable and moving the probe vertically about 1 ft/s in the middle of the screened interval; the dissolved-oxygen meter was calibrated according to atmospheric pressure and the ambient ground-water temperature, and the meter was set to zero using a solution devoid of oxygen. Sample filtration and preservation, field-alkalinity titration, and measurement of water properties (pH, Eh, and specific conductance) were performed in a field vehicle. Oxidation-reduction potential (Eh, or redox potential) was measured using a platinum electrode, which was checked against ZoBell's solution at the ambient ground-water temperature. Water samples were filtered through a 0.45- $\mu\text{m}$  filter for alkalinity titrations, dissolved major-ion, nitrogen species, and trace-constituent analyses. Samples were filtered through a 0.20- $\mu\text{m}$  filter for sulfur-isotope and selenium-speciation analyses. Samples collected for dissolved-organic-carbon analyses were filtered through a 0.45- $\mu\text{m}$  silver filter. Samples collected for uranium and oxygen- and hydrogen-isotope analyses were unfiltered. Water samples collected for cation analyses were acidified using nitric acid to pH < 2; samples collected for nitrogen species analysis were preserved using liquid mercuric chloride; samples collected for mercury analyses were preserved using potassium dichromate; and samples collected for oxygen and hydrogen stable isotopes were preserved using mercuric chloride tablets. Water-sample filters were saved and dried for SEM and XRD analyses to describe the particulate phases that might affect ground-water quality.

A data logger was installed in one well in the Grand Valley for continuous recording of the water level and specific conductance of the ground

water. Two wells were sampled monthly—one in Mancos Shale residuum and one in alluvium overlying Mancos Shale—to describe the seasonal effects of irrigation on trace-element concentrations in ground water.

Historical ground-water-quality and ground-water-level data were compiled by the BOR to describe the long-term effects of irrigation on ground water in the study area. Hydraulic data from historical aquifer tests performed by the BOR also were compiled by the BOR.

## Ground-Water Hydrology

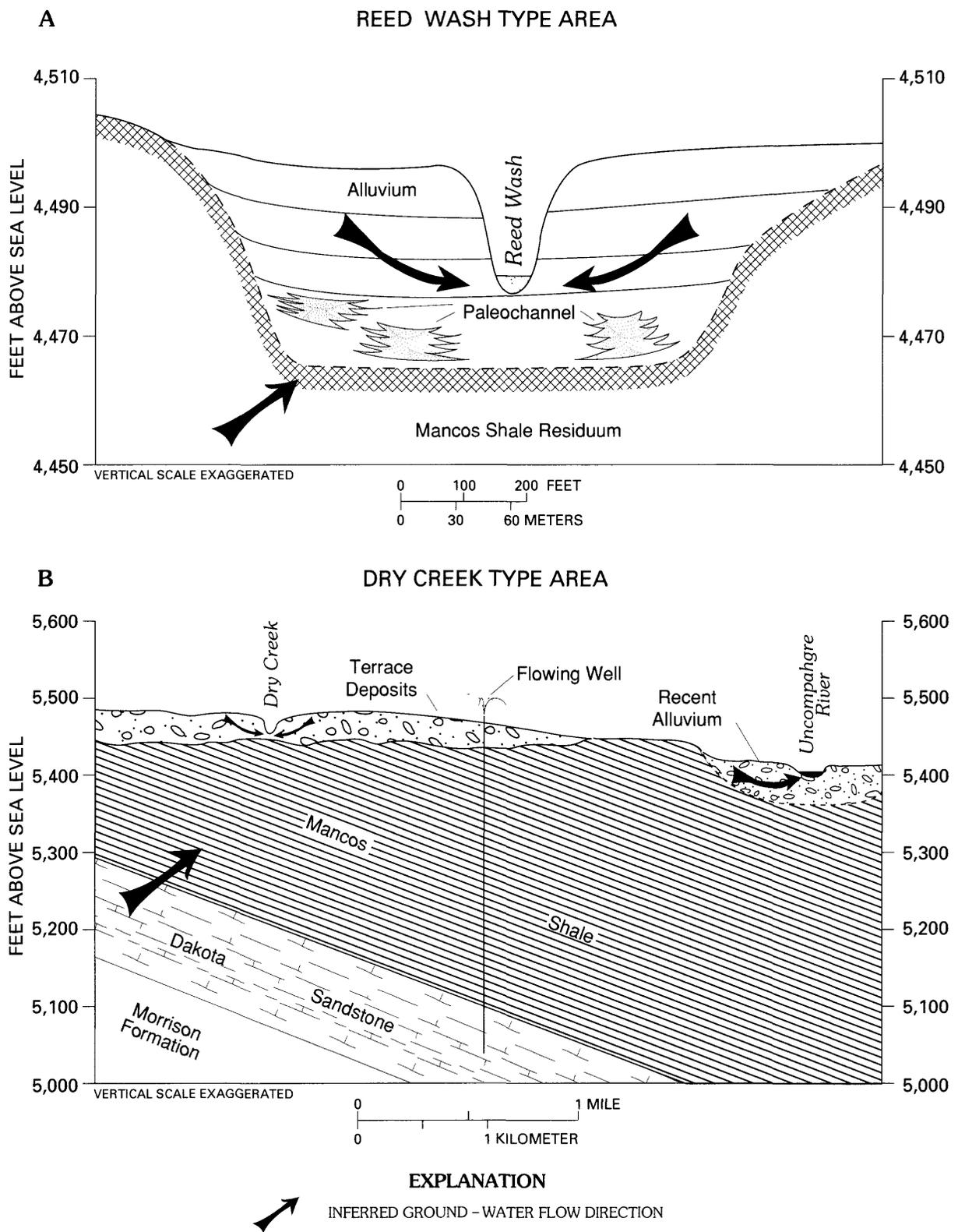
Ground water in the study area affected by irrigation occurs in shallow systems consisting of (1) Mancos Shale residuum, (2) alluvium overlying Mancos Shale, (3) the cobble aquifer in eastern

Grand Valley, and (4) terrace deposits in the western Uncompahgre Project area. The hydrogeologic settings, general lithologic descriptions, and general hydrogeologic characteristics of these ground-water-flow systems are described in table 4. Although the shallow systems might not have contained appreciable quantities of water in their natural (preirrigation) state, irrigation now provides substantial quantities of water for the existence of a water-table system in the shallow unconsolidated materials. The shallow ground-water systems generally discharge to local drains, streams, and rivers (fig. 10). Hydrogeologic characteristics differ greatly over short distances in the shallow system (table 4) because of the differences in composition of alluvium (which include paleochannels consisting of gravels and cobbles, fig. 10) and the differences in weathering and fracturing of the Mancos Shale.

**Table 4.** Hydrogeologic settings of the ground-water-flow systems affected by irrigation in the Uncompahgre Project area and in the Grand Valley

[Fm, Formation; ft, feet; n, number of data points; <, less than; ft/d, feet per day; hydraulic-conductivity data were provided by the Bureau of Reclamation; DC, Dry Creek type area; RW, Reed Wash type area; SL, Sweitzer Lake type area; --, hydrogeologic setting not studied as a type area]

Hydrogeologic setting	Type area	Source rock(s)	General lithologic description and hydrogeologic characteristics
Alluvium on Mancos Shale	RW	Mancos Shale, Mesaverde Fm (Grand Valley); Mancos Shale, Dakota Fm, San Juan Tuff, and gneisses of the Black Canyon of the Gunnison and Cimmaron Ridge areas (Uncompahgre Valley)	Clay, silt, sand, and gravel deposits of Holocene age. Grand Valley: Erosional detritus of clay, sand, and silt; mixture of Mesaverde Fm (indicated by <i>Inoceramus</i> and <i>Pychnodantes</i> fossils) and shale-derived clays (smectite and illite) that might be derived from mudflows. Thickness ranges from 5 to 40 ft. Eastern part of Uncompahgre Valley: Erosional detritus from Precambrian gneisses, Oligocene tuffs, and the Dakota Fm of Cretaceous age. Thickness ranges from 5 to 25 ft. Hydraulic conductivities range from 8 to 140 ft/d and average 74 ft/d (n=3).
Cobble aquifer (Grand Valley)	--	Grand Mesa basalts, Mesaverde Fm, Green River Fm, Wasatch Fm, Mancos Shale	Valley-fill deposits in an ancient valley of the Colorado River. Well-sorted pebbles, cobbles, and boulders in sandy matrix; alluvium and eolian sand might locally cover gravels. Late Holocene to Pleistocene age. Thickness ranges from 10 to 65 ft. Hydraulic conductivities range from 38 to 510 ft/d and average 190 ft/d (n=26).
Terrace deposits (western part of the Uncompahgre Valley)	DC	Glacial outwash and alluvium from the San Juan Mountains and the Uncompahgre Plateau	Poorly sorted materials ranging from fine rock flour through sand, gravel, cobbles, and boulders (Meeks, 1950). Glacial outwash and alluvium of Pleistocene age locally covered by recent alluvium. Thicknesses range from 5 to 60 ft. Hydraulic conductivity from one hydraulic test was 650 ft/d.
Mancos Shale residuum	SL	Mancos Shale	Clayey, silty residuum consisting of smectite, illite, and kaolinite clays. Abundant secondary gypsum occurs in shale partings and fractures; pyrite concretions altered to limonite; ash layers weathered to kaolinite and quartz containing some jarosite. Thickness ranges from <1 to 100 ft. Hydraulic conductivities range from 4.5 to 300 ft/d and average 88 ft/d (n=17).



**Figure 10.** Schematic showing hydrogeologic setting and ground-water flow in (A) Reed Wash type area and (B) Dry Creek type area.

Deep artesian ground-water-flow systems occur in the Uncompahgre Project area (fig. 10) and in the Grand Valley. Upward ground-water flow from these artesian systems into the shallow systems is not certain, except through wells that penetrate the deep aquifers. Detailed descriptions of the deep ground-water-flow systems are reported in Meeks (1950), Lohman (1965), and Craig (1971).

Recharge to the shallow ground-water-flow system occurs through the seasonal application of irrigation water, from snowmelt during spring, and from infrequent thunderstorms during summer. Water-level fluctuations in well 143N0 (located in the Grand Valley, fig. 9) and the fluctuations of specific conductance of ground water are shown in figure 11. Both respective traces of transducer and specific-conductance data show the effects of irrigation on ground-water recharge. Water-level altitude in well 143N0 increased during the irrigation season (April–September 1992) (fig. 11), and the water-level altitude slowly declined during the winter of 1992–93. The increase indicates storage of ground water in the shallow aquifers of the irrigated area surrounding well 143N0. Specific conductance of ground water

in well 143N0 decreased during late summer and early fall (August–October 1992) (fig. 11) following the irrigation season, indicating a delayed dilution of the ground-water-quality constituents in response to irrigation recharge. Irrigation recharge occurs through leakage of unlined canals and irrigation ditches and through flood-irrigation practices in the study area. Calculations of recharge are difficult because techniques frequently used for estimating recharge (such as hydrograph separation) might not accurately represent ground-water recharge in the irrigated area where streams fluctuate greatly. However, a spring in the Sweitzer Lake type area seemed to constantly discharge about 0.25 gal/min. Assuming that the discharge from the spring is constant throughout the year, a rough estimate of recharge in the 160-acre irrigated basin is about 0.03 in/yr. Snowmelt from mesas and mountains adjacent to the Uncompahgre Project area and the Grand Valley increases stream-flows during early spring and recharges the natural ground-water system near intermittent streams; however, a determination of natural recharge to the ground-water system from intermittent streams was not made.

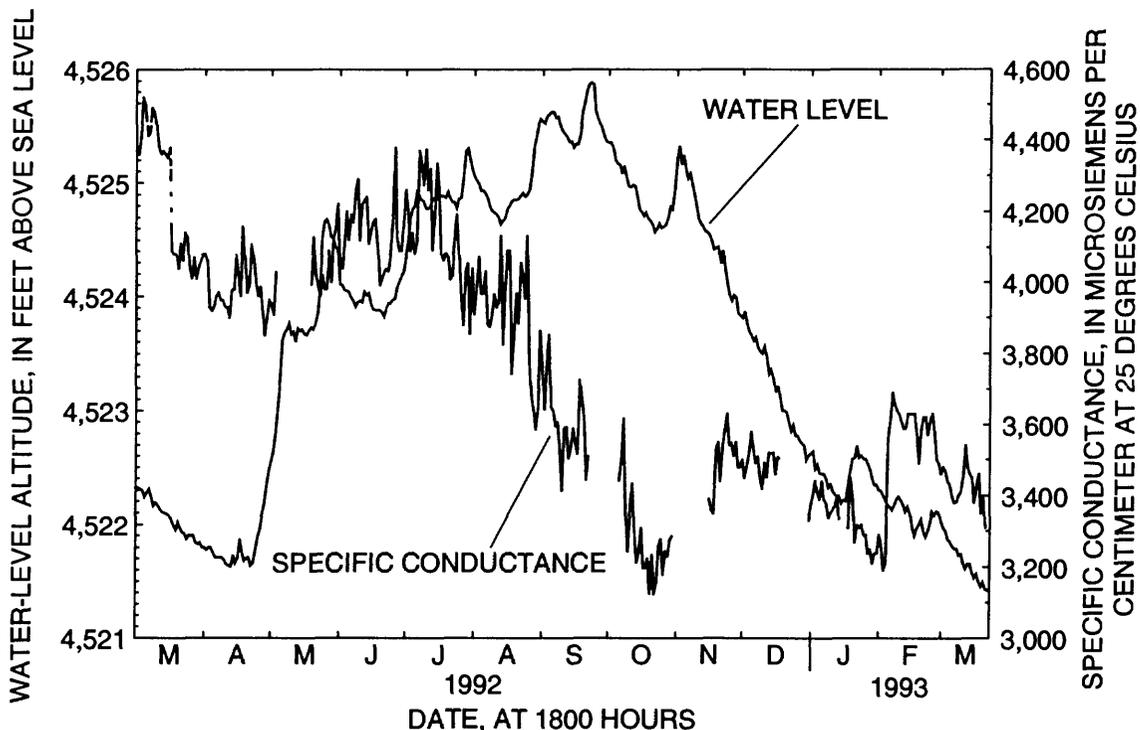


Figure 11. Water-level altitude and specific conductance of water in well 143N0, Grand Valley, March 1992–March 1993.

## Historical Ground-Water Quality

As part of the salinity-control program, ground-water-quality data were collected by BOR for about 75 shallow monitoring wells installed in the Uncompahgre Project area and about 270 shallow monitoring wells installed in the Grand Valley. Major-ion data were collected annually, quarterly, and sometimes monthly during 1974–84. The BOR wells were essential for the collection of trace-element data published as part of this report.

In general, the historical ground-water-quality data (Jack Cunningham, Bureau of Reclamation, written commun., 1992) indicate high calcium, sodium, sulfate, and dissolved-solids concentrations in ground water (sources of the salinity problems). The historical ground-water-quality data indicate that high dissolved-solids concentrations are ubiquitous in areas underlain by Mancos Shale. The historical data also indicate a relation between water level in wells (reflecting the seasonal application of irrigation water) and dissolved-solids concentrations in ground water (fig. 12). When water levels rise because of irrigation, dissolved-solids concentrations in ground water decrease; when water levels fall because of cessation of irrigation in winter, dissolved-solids concentrations in ground water increase (fig. 12). This cyclic flushing of the ground-water system has transported many soluble constituents from shallow aquifers to the streams and rivers, which could result in an eventual decrease in dissolved-solids concentrations and an eventual decline in the salinity problem; however, this effect is not evident in the 12 years of data presented for well 125Q5 (fig. 12). Ground-water-quality data are not available for the beginning of irrigation (in the 1880's in the Grand Valley); therefore, the amount of decrease in dissolved-solids concentrations in ground water since the beginning of irrigation is unknown.

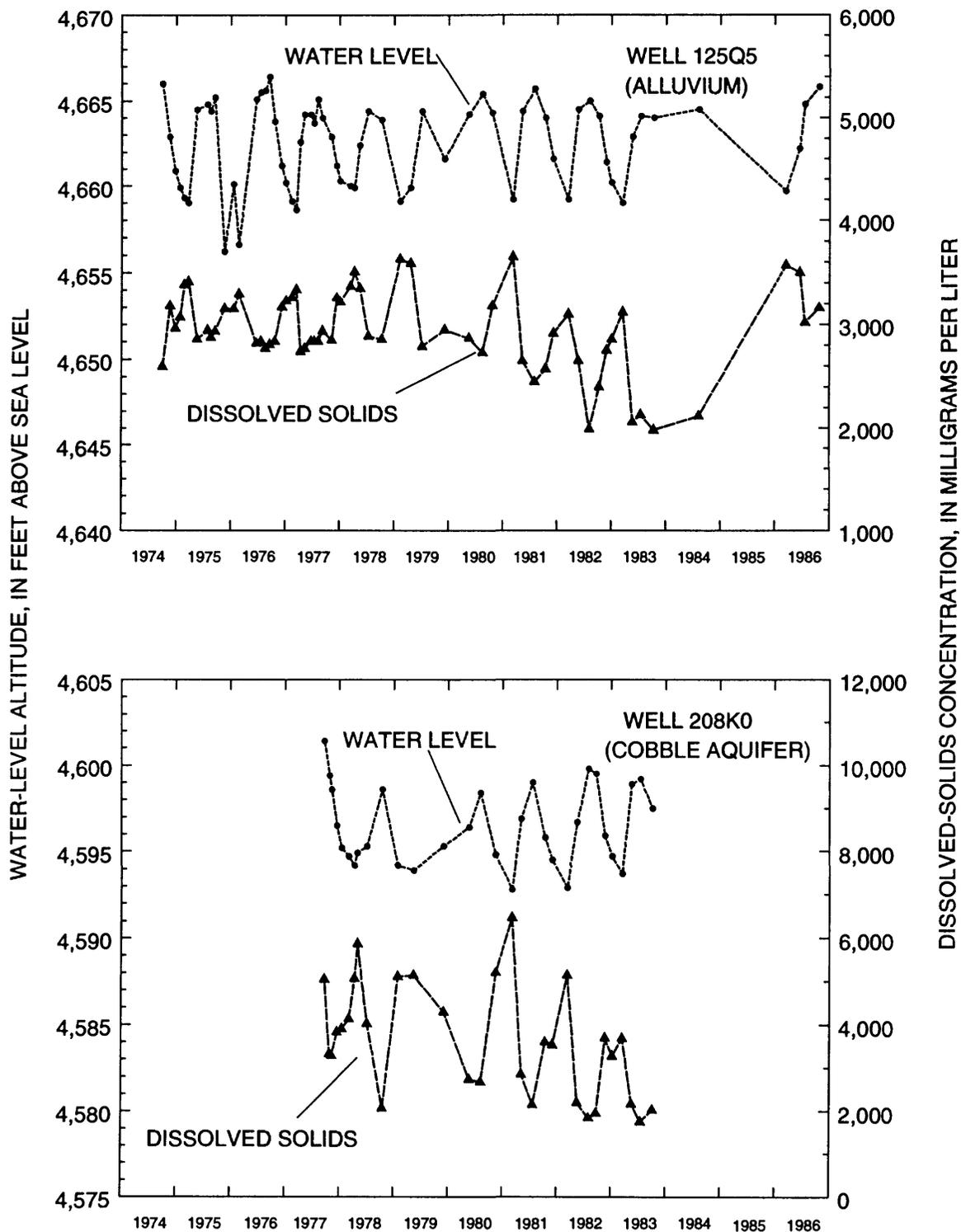
## Major-Ion Chemistry

Factors affecting concentrations of major ions in ground water of the Uncompahgre Project area and of the Grand Valley include: (1) The source of irrigation water; (2) dissolution, oxidation, and mobilization of major constituents in Mancos Shale, alluvium overlying Mancos Shale, and terrace deposits; (3) oxidation-reduction state of the ground water;

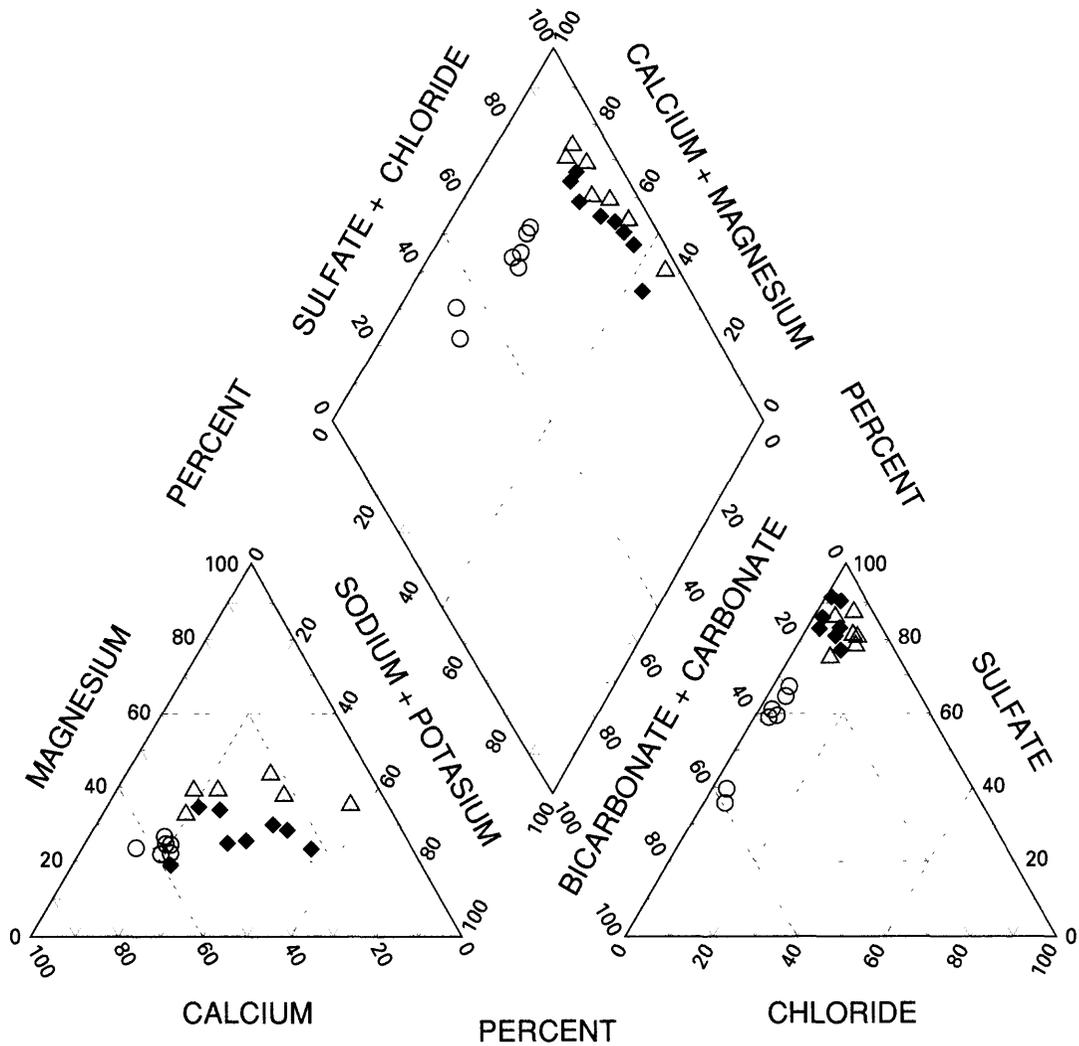
and (4) evaporative concentration of ground water. Because of the widespread presence of the Mancos Shale, the general quality of ground water in the study area is poor because of the calcium, sodium, and magnesium salts weathered from Mancos Shale. However, one area in the southwestern part of the Uncompahgre Project area has relatively good quality ground water because of the absence of Mancos Shale detritus in the terrace deposits. Few wells are used for drinking-water supply, and only those wells located on terrace deposits in the western part of the Uncompahgre Project area are useful for lawn irrigation. A characteristic of the poor ground-water quality is the presence of salt crust (or efflorescent minerals) evident in ground-water-discharge zones.

The quality of the source of irrigation water differs between the two parts of the study area. Dissolved-chloride concentrations are much higher in the Colorado River, which receives sodium chloride water from hot springs, than in the Uncompahgre and Gunnison Rivers. The mean chloride concentration in ground water of the Uncompahgre Project area is 24 mg/L (13 wells) and in the Grand Valley is 262 mg/L (10 wells). The difference in mean chloride concentrations is caused by the different source water for irrigation.

Observations of the general characteristics of ground-water quality in the study area can be described using a water-analysis diagram (fig. 13). This diagram, sometimes referred to as a trilinear diagram or a Piper diagram, shows the relations among concentrations of cations and anions. The values are expressed as percentages of the total milliequivalents per liter of cations (lower left triangle) or of anions (lower right triangle) and are not shown as actual concentrations. The central quadrilateral graph shows the combined cationic and anionic chemical quality of the water by a third point, which is at the intersection of the rays projected from the points on the cation and anion plots. Ground water in Mancos Shale residuum and in alluvium overlying Mancos Shale predominantly is a calcium magnesium sodium sulfate water type, and water from some of the wells predominantly is a sodium sulfate water type. Water from Mancos Shale residuum tends to fall into a group different from water from the alluvium because of the difference in percentages of sodium (the mean sodium concentration in Mancos Shale residuum is 630 mg/L, and the mean in alluvium overlying Mancos Shale is 350 mg/L).

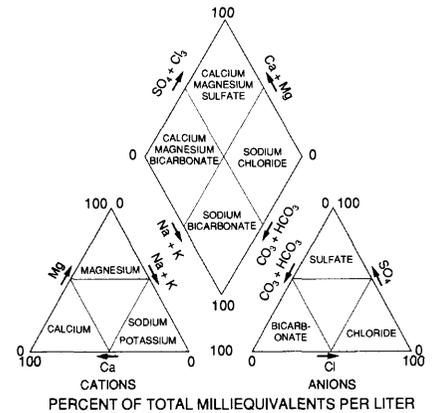


**Figure 12.** Historical water-level altitudes and dissolved-solids concentrations in water from wells 125Q5 and 208K0 located in the Grand Valley (Jack Cunningham, Bureau of Reclamation, written commun., 1992).



### EXPLANATION

- ◆ WATER FROM WELL IN MANCOS SHALE RESIDIUM  
MEAN DISSOLVED-SOLIDS CONCENTRATION = 5,270 MILLIGRAMS PER LITER  
MEAN pH = 6.93
- △ WATER FROM WELL IN ALLUVIUM OVERLYING MANCOS SHALE  
MEAN DISSOLVED-SOLIDS CONCENTRATION = 4,730 MILLIGRAMS PER LITER  
MEAN pH = 6.94
- WATER FROM WELL IN TERRACE DEPOSITS, WESTERN PART OF THE UNCOMPAGHRE PROJECT AREA  
MEAN DISSOLVED-SOLIDS CONCENTRATION = 810 MILLIGRAMS PER LITER  
MEAN pH = 7.15



**Figure 13.** Trilinear diagram showing percentages of major ions in water from selected wells during the irrigation season in the Uncompahgre Project area and in the Grand Valley.

Water from wells in terrace deposits in the western Uncompahgre Project area was distinctly different, being predominantly a calcium sulfate tending toward a calcium bicarbonate water type. The mean dissolved-solids concentrations additionally describe differences in water quality between the different hydrogeologic settings. Water in Mancos Shale residuum and in alluvium overlying Mancos Shale had a mean dissolved-solids concentration of 5,270 mg/L and 4,730 mg/L, respectively. Water in terrace deposits on the western part of the Uncompahgre Project area had a mean dissolved-solids concentration of 810 mg/L.

The thermodynamic equilibrium speciation of major dissolved constituents in ground water of the study area was determined using the geochemical speciation program WATEQ4F (Ball and Nordstrom, 1991). Saturation indices are listed for different mineral compounds that were in the aqueous phase (table 5); saturation indices greater than zero indicated oversaturation (and possible precipitation of that mineral), and values less than zero indicated undersaturation (where that mineral could continue to dissolve). Ground water in Mancos Shale residuum and alluvium overlying Mancos Shale is near saturation or oversaturated with calcite, aragonite, dolomite, gypsum, ferrihydrite, and quartz. Ground water in terrace deposits is near saturation or oversaturated only with calcite, ferrihydrite, and quartz. Mineral species in ground water of the study area identified by the model are similar to the evaporite mineral species identified by Whittig and others (1982) in salt efflorescence samples collected from the Grand Valley (table 6).

Evapotranspiration can affect ground-water quality by concentrating major ions and trace constituents—called evaporative concentration. Effects of evapotranspiration on ground-water recharge could be great in the Uncompahgre Project area and in the Grand Valley because annual precipitation averages about 8 to 10 in/yr, and estimates of pan evaporation range from 40 to 50 in/yr. However, the effects of evaporative concentration in the Uncompahgre Project area and in the Grand Valley are not great, based on data for oxygen and hydrogen stable-isotope values (fig. 14). When  $\delta^{18}\text{O}$  [or the O-18/O-16 stable-isotope ratio referenced to the Vienna Standard Mean Ocean Water (VSMOW)] and  $\delta^2\text{H}$  (or the H-2/H-1 stable-isotope ratio referenced to the VSMOW) from surface and ground water are plotted on one graph for the Uncompahgre Project area and the Grand Valley, the data plot near and parallel to

the meteoric water line (Gat, 1981) and do not indicate an evaporation trend. When plotted separately by area, a slight evaporation trend is indicated by the data; however, outliers from one well in the Grand Valley seem to skew the results (fig. 14). The meteoric water line is described by  $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$  (Gat, 1981). The evaporation line for the Uncompahgre Project area can be defined by  $\delta^2\text{H} = 6.7 \delta^{18}\text{O} - 12.4$  ( $r^2 = 0.89$ ); the evaporation line for the Grand Valley can be defined by  $\delta^2\text{H} = 4.2 \delta^{18}\text{O} - 53.9$  ( $r^2 = 0.71$ ). The differences in the groupings of data points for the two areas might be related to precipitation used for irrigation water falling and being stored at different altitudes of the Rocky Mountains and being affected by reservoir evaporation, particularly in the Gunnison River Basin (data for the Uncompahgre Project area). Effects of evaporative concentration on ground water are evident in water from a few wells inside and in water from a well located outside the irrigated area; however, in general, evaporative concentration is not a major factor in ground-water quality in the irrigated areas. The effects of evaporation might not be great in the study area because flood-irrigation practices keep the system well flushed, and the relatively steep terrain provides rapid drainage of the shallow ground-water system compared to other irrigation-drainage study areas, such as the broad sedimentary basin of the San Joaquin Valley, Calif. (Deverel and others, 1984; Dubrovsky and others, 1990).

## Review of Selenium Geochemistry

Selenium is known to have volcanic, magmatic, and hydrothermal sources (Trelease and Beath, 1949; Coleman and Delevaux, 1957; Sindeeva, 1964; Howard, 1977) and is present in relation to hydrothermal and roll-type uranium deposits (Sindeeva, 1964; Fishman and others, 1985; Fishman and Reynolds, 1986). Selenium enrichment of geologic materials occurred during the Cretaceous age and was related to volcanic emanations of element-rich gases and ashes. Volcanic detritus was ultimately deposited in the Cretaceous sea that covered much of the interior of North America. The organic-rich reducing environment of the Cretaceous sea bottom was capable of precipitating sulfide minerals, such as pyrite ( $\text{FeS}_2$ ) and chalcopyrite ( $\text{CuFeS}_2$ ). Because selenium is isomorphous with sulfur, selenium substituted for sulfur in the crystalline structure of sulfide minerals in the Cretaceous shales.

**Table 5. Results of thermodynamic speciation calculations for water from wells in the Uncompahgre Project area and from the Grand Valley**

[--, no data; speciation calculations performed using WATEQ4F (Ball and Nordstrom, 1991); spg. spring]

Site name or number (figs. 8 and 9)	Sampling date	Log P <sub>CO2</sub>	Saturation indices												
			Calcite	Aragonite	Dolomite	Gypsum	Anhydrite	Epsomite	Mirabilite	Siderite	Ferrhydrite	Jarosite	Rhodochlorite	Quartz	
<b>MANCOS SHALE RESIDUUM</b>															
SL1	09-11-91	-1.62	0.01	-0.14	0.0	-0.05	-0.30	-2.3	-3.4	--	--	--	--	-0.83	0.42
	03-02-92	-1.60	-0.03	-0.19	-0.04	-0.25	-2.3	-3.3	-3.7	--	--	--	--	-1.0	.46
SL2	09-11-91	-1.47	.02	-0.13	.04	-0.29	-2.4	-3.7	-3.7	--	--	--	--	-0.69	.47
	03-02-92	-1.63	-0.02	-0.17	-0.25	.01	-2.4	-2.3	-3.3	-0.40	1.8	1.5	-1.5	-0.65	.52
SLSW1 (spg)	03-05-92	-2.44	.66	.50	1.2	-0.2	-2.6	-2.1	-2.1	-2.3	3.7	2.1	2.1	.10	.78
108U0 <sup>1</sup>	10-04-91	-2.15	1.1	.96	2.8	-0.28	-0.53	-2.1	-2.2	-0.55	-3.3	-1.8	-1.8	-0.09	.45
<b>TERRACE DEPOSITS</b>															
Schmalz	07-02-91	-1.66	-0.10	-0.25	-0.66	-0.76	-1.0	-3.5	-6.2	-3.8	1.7	-2.6	-2.6	-2.4	--
	03-23-92	-1.69	.0	-0.14	-0.44	-0.84	-1.1	-3.6	-6.2	-4.2	2.3	-1.2	-1.2	-1.8	.80
<b>ALLUVIUM OVERLYING MANCOS SHALE</b>															
RWG1	08-28-91	-1.55	.02	-0.13	.56	.05	-0.19	-1.7	-2.1	--	--	--	--	-0.92	.44
	02-20-92	-1.52	.07	-0.07	.62	.04	-0.21	-1.7	-2.3	--	--	--	--	-0.92	.48
RWG2	08-28-91	-1.48	.09	-0.06	.36	.0	-0.25	-2.1	-3.3	--	--	--	--	-0.78	.50
	02-20-92	-1.33	-0.13	-0.28	-0.16	-0.01	-0.28	-2.2	-3.6	--	--	--	--	--	.51
RWG3	08-28-91	-1.38	-0.06	-0.22	-0.14	-0.02	-0.27	-2.3	-4.3	-2.8	1.5	-0.67	-0.67	-0.29	.39
	02-18-92	-1.29	-0.15	-0.31	-0.37	-0.02	-0.26	-2.3	-4.3	--	--	--	--	-0.44	.46

<sup>1</sup>Well located outside of the irrigated area.

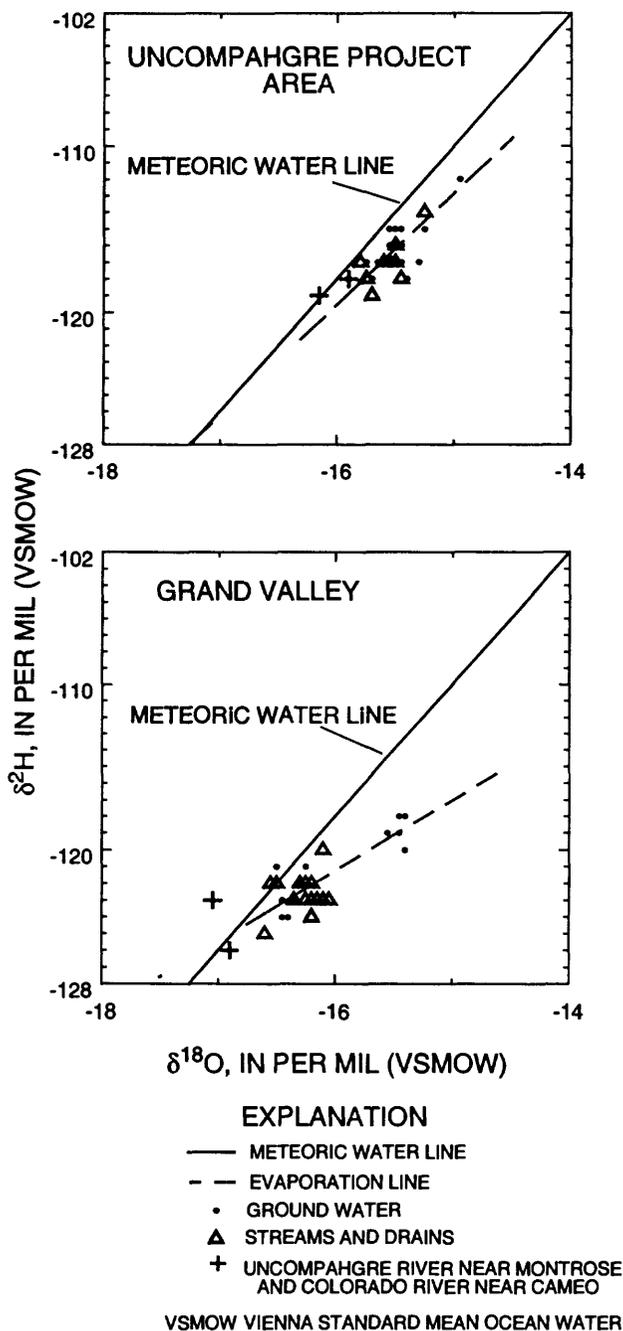
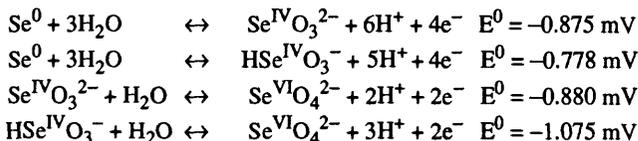
Selenium, therefore, might be directly related to volcanic-ash layers in Cretaceous shales. In contrast, Sindeeva (1964, p. 290–291) indicated that selenium was present in sizable amounts in recent sea-bottom sediments and could be precipitated directly from river water entering the oceans, but these recent selenium concentrations in ocean sediment also could be attributed to the burning of fossil fuels (particularly coal), which puts trace concentrations of selenium into the atmosphere, lakes, rivers, and oceans.

**Table 6.** Evaporite mineral species and salt efflorescence associated with the Mancos Shale and shale residuum in the Grand Valley (from Whittig and others, 1982)

[X, mineral species identified; --, mineral species not identified]

Evaporite species	Occurring in Mancos Shale	Occurring in efflorescence
Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )	X	X
Epsomite ( $\text{MgSO}_4 \cdot 10\text{H}_2\text{O}$ )	--	X
Hexahydrite ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ )	--	X
Pentahydrite ( $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ )	--	X
Starkeyite ( $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ )	--	X
Kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ )	--	X
Mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ )	--	X
Thenardite ( $\text{Na}_2\text{SO}_4$ )	--	X
Loewite [ $\text{Na}_4\text{Mg}_2(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$ ]	--	X
Bloedite [ $\text{Na}_2\text{Mg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ ]	--	X

Selenium is present as a trace constituent in pyrite in the Mancos Shale within the study area; concentrations range from 0.003 to 1.6 percent (Coleman and Delevaux, 1957). When the Mancos Shale is exposed to weathering, selenium weathers (or is oxidized) from pyrite (where the selenium has a valence state of  $-2$ ) to further transformations in valence state ( $-2 \rightarrow 0 \rightarrow +4 \rightarrow +6$ ) that become increasingly more soluble with increasing valence: elemental selenium ( $\text{Se}^0$ , selenium valence of 0), selenite ( $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ , selenium valence of +4), biselenite ( $\text{HSe}^{\text{IV}}\text{O}_3^-$ , selenium valence of +4), and selenate ( $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ , selenium valence of +6). The oxidation of selenium compounds can be represented by the following half reactions:



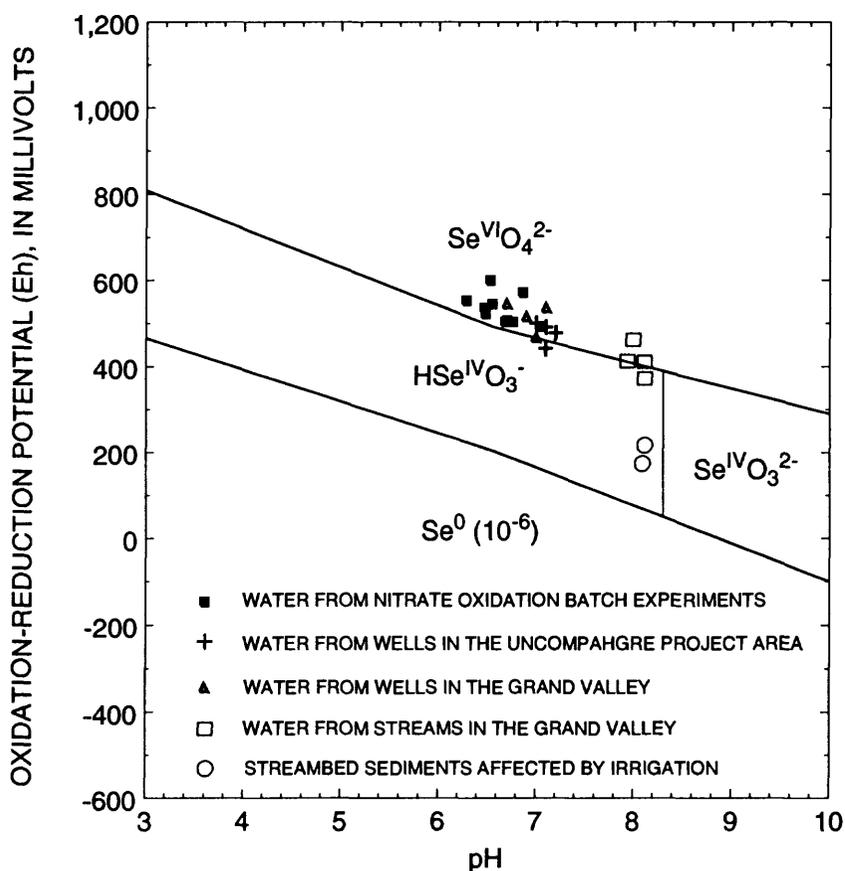
**Figure 14.** Oxygen and hydrogen stable isotope values in water from selected wells, streams, and rivers in the Uncompahgre Project area and in the Grand Valley.

The species that are present in solution after oxidation of reduced selenium species primarily are a function of the pH and the oxidation-reduction potential (Eh-pH) of the geochemical environment (fig. 15). Selenite ( $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ ) and biselenite ( $\text{HSe}^{\text{IV}}\text{O}_3^-$ ) readily adsorb to aquifer sediments or coprecipitate with ferric oxyhydroxide complexes,

and selenate ( $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ ) is very soluble and is easily transported in an oxidized hydrologic system (Howard, 1977; Electric Power Research Institute, 1980; Balistrieri and Chao, 1987; Bar-Yosef and Meek, 1987). Selenate can adsorb to aquifer sediments, but selenate forms an outer-layer complex (more easily desorbed) with iron oxides, whereas selenite forms an inner-layer complex (less easily desorbed) with iron oxides (Hayes and others, 1987). These adsorption processes are completely reversible (Electric Power Research Institute, 1980; Balistrieri and Chao, 1987), indicating that selenium could be desorbed from clay and mineral surfaces and put back into solution.

Previous studies have been published about the distribution of selenium in the San Joaquin Valley, California. Sources of dissolved selenium in ground and surface water in the San Joaquin Valley were hypothesized to be sulfides in shale (the Moreno Formation of Cretaceous age) of the Coast Range of

California (Presser and others, 1990) and sediments of the west-central San Joaquin Valley derived from Coast Range rocks (Deverel and others, 1984; Gilliom, 1989; Izbicki, 1989). Studies by Deverel and Millard (1988) and by Fujii and Deverel (1989) concluded that high concentrations of selenium in ground and surface water were a result of evaporative concentration of ground water, which was indicated by isotopic enrichment of oxygen and hydrogen stable isotopes and by correlation of elevated selenium concentrations with ground-water salinity. The hydrogeochemical processes involved in the immobilization of selenium from the aqueous phase has been the focus of several studies (Dubrovsky and others, 1990; Masscheleyn and others, 1991; Sposito and others, 1991; White and others, 1991). The well-accepted conclusions of these studies are that dissolved selenium primarily occurs in the selenate form and is transported to deeper zones (10 to 50 ft) of reducing geochemical environments where selenium



**Figure 15.** Stability-field diagram for selenium species in natural waters and data points calculated from selenium-speciation data collected for this study. Thermodynamic data are from Garrels and Christ (1965) and from P.F. Bell and D.R. Parker (University of California, Riverside, written commun., 1991).

is reduced to the less mobile selenite and elemental selenium species. Hypotheses for mobilization and transport of selenium by oxidation-reduction and adsorption/desorption processes were described, and the platinum-electrode potential was observed to be an important parameter for recognizing geochemical conditions suitable for the reduction of selenium.

Selenium can be absorbed from some soils by food and forage plants in sufficient amounts to make them highly poisonous to animals. Several native range plants of the Western United States require selenium and can uptake selenium in concentrations as high as 15,000 parts per million (Trelease and Beath, 1949, p. 85); however, the concentrations of selenium in the plants vary according to seasonal growth and development (Beath and others, 1937). Several of these native plants (for example, *Astragalus bisulcatus*, *Stanleya bipinnata*, *Xylorhiza parryi*, and *Oonopsis condensata*) are called primary indicators for the presence of highly seleniferous soils. Other native plants tolerate selenium and are called secondary indicators. The presence of selenium-indicator plants is significant enough to allow the mapping of selenium-bearing geological formations from the recognition of these plants. The uptake of selenium by farm crops differs by species, soil pH, soil texture, and soil organic matter; however, certain grains and hay grown on seleniferous soils can uptake selenium in concentrations high enough to be deleterious to animal health. Selenium accumulation in farm crops generally ranges from greatest to least in root and bulb crops, field crops, leafy vegetables, seed vegetables, vegetable fruits, and tree fruits (Mikkelsen and others, 1989, p. 74).

According to Trelase and Beath (1949), native seleniferous vegetation is widely distributed in Colorado. Most of the seleniferous plants have been collected on formations of Cretaceous age. The Dakota, Mesaverde, and McDermott Formations (sandstones) have plants with the lowest selenium concentrations. The Mancos Shale, Greenhorn, and Benton Formations bear plants with medium concentrations of selenium, and the Pierre Shale and Niobrara Formation produce highly seleniferous vegetation. Seleniferous plants are capable of converting inorganic selenium (probably as  $\text{Se}^0$ ,  $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ , or  $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ ) into organic selenium (such as selenomethionine, selenocysteine, and selenocystine), transforming the selenium into a much more toxic form (Thompson-Eagle and Frankenberger, 1992).

Microbiological processes might be important for transformation of selenium species. Bacteria and fungi can volatilize  $\text{Se}^0$ ,  $\text{SeO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ , and organoselenides into mobile methylated derivatives, such as dimethylselenide and dimethyl diselenide (Frankenberger and Karlson, 1992; Thompson-Eagle and Frankenberger, 1992). Selenium reduction and volatilization have been studied as possible mitigative measures to ameliorate selenium-contaminated agricultural drainwater. Oxidized forms of selenium (such as mobile aqueous  $\text{SeO}_4^{2-}$ ) can be reduced to less mobile forms ( $\text{Se}^0$  and  $\text{SeO}_3^{2-}$ ) by anaerobic bacteria (Oremland, Hollibaugh, and others, 1989; Oremland and others, 1990; Steinberg and Oremland, 1990). Reduced selenium species can be oxidized by autotrophic bacteria (Lipman and Waksman, 1922; Sarathchandra and Watkinson, 1981); however, little work has been performed to investigate the mechanisms involved in selenium oxidation (Sarathchandra and Watkinson, 1981; Thompson-Eagle and Frankenberger, 1992).

In summary, at least four processes—oxidation-reduction, adsorption/desorption, vegetative uptake and transformation, and microbial mediation—could affect selenium speciation and concentrations in natural water and in the environment. Reduction originally played a role in precipitation of sulfide minerals (incorporating trace concentrations of selenium) possibly related to volcanic-ash-layer deposits in Cretaceous geological formations. Uplift and emergence exposed the shale to natural weathering that oxidized the sulfides and released selenium into the environment. Irrigation is speeding up the weathering process in which selenium is mobilized in the hydrologic environment.

## Sources of Selenium and Other Trace Constituents

Core samples of Mancos Shale, Mancos Shale residuum, and alluvium were collected from the study area and were analyzed to determine the concentrations of selenium and other trace constituents in the solid-phase samples (table 7). Selenium is isomorphous with sulfur and substitutes in the crystalline structure of sulfide minerals (Coleman and Delevaux, 1957); therefore, core samples were collected to describe the relation of sulfide mineralization (and the source of selenium) to depositional environment in the Mancos Shale. Disseminated sulfides in the Mancos

Shale core range in size from 0.01 to 0.05 mm viewed under 20X microscope. The disseminated sulfides almost always are associated with darker layers (organic-rich lenses) in shale bedrock. Sulfide euhedrons (0.1 to 0.5 mm) occur immediately adjacent to the bottom side of ash layers that were examined in core. XRD and SEM analyses of sulfide-mineral euhedrons adjacent to ash layers indicate that the sulfides in this part of the Mancos Shale are pyrite (table 7).

The selenium concentration in a Mancos Shale bedrock sample (representing disseminated pyrite) was 0.8 µg/g, selenium concentration in one ash-layer sample was less than the reporting limit (<0.1 µg/g), and selenium concentration in one pyrite sample adjacent to the bottom side of an ash layer was 19 µg/g (table 8). Coleman and

Delevaux (1957) tabulated selenium concentrations from sulfides in the Mancos Shale ranging from 0.002 to 1.6 percent (2 to 1,600 µg/g).

Analyses of trace-element concentrations in shale residuum and weathered ash indicate that more selenium and uranium were contained in the weathered ash sample than in shale residuum and bedrock samples. XRD analyses of weathered ash indicate that the dominant clay minerals are kaolinite and smectite (table 7). Bar-Yosef and Meek (1987) and Balistrieri and Chao (1987) indicated that selenium is readily adsorbed by kaolinite and smectite. Kaolinite is present in shale residuum and alluvium (table 7), and smectite is present in weathered ash. These clay minerals adsorb trace constituents and could be sources for the leaching of selenium and other trace constituents.

**Table 7.** Semiquantitative clay and bulk mineralogy of Mancos Shale bedrock core, shale residuum, alluvium, and ground-water-filter residuum (L.M. Fukui, Chem-Nuclear Geotech, written commun., 1992)

[III/Smec, illite/smectite; nd, not detected; tr, less than 7 percent of intensity of dominant phase; min, 7 to 30 percent of intensity of dominant phase; mod, 30 to 70 percent of intensity of dominant phase; dom, predominant mineral in X-ray pattern; sdom, 70 to 99 percent of intensity of dominant phase; cdom, predominant minerals have same relative intensities; P, plagioclase; K, potassium; ft BLS, feet below land surface]

Sample description	Illite	III/Smec	Kaolinite	Smectite	Chlorite
Mancos Shale bedrock	nd	tr	min	min	tr?
Sulfide euhedron from core	nd	nd	nd	nd	nd
Ash layer from core	nd	min	min	mod	min?
Weathered ash layer	nd	nd	dom	sdom	nd
Residuum, SL1, 5 ft BLS	cdom	min	cdom	min	tr
Residuum, SL1, 15.5 ft BLS	cdom	tr	cdom	min	tr
Alluvium, RWG1, 6 ft BLS	cdom	mod	cdom	tr	tr
Alluvium, RWG1, 24.5 ft BLS	cdom	mod	cdom	tr	tr

Sample description	Quartz	Feldspar		Calcite	Dolomite	Gypsum	Pyrite
		P	K				
Mancos Shale bedrock	dom	tr	nd	min	nd	nd	nd
Sulfide euhedron from core	nd	nd	nd	nd	nd	nd	dom
Ash layer from core	dom	nd	nd	tr?	nd	nd	nd
Weathered ash layer	mod	nd	nd	nd	tr	nd	nd
Residuum, SL1, 5 ft BLS	sdom	tr	tr	min	min	dom	nd
Residuum, SL1, 15.5 ft BLS	dom	tr	tr	min-mod	min	nd	nd
Alluvium, RWG1, 6 ft BLS	dom	min	tr	min	min	nd	nd
Alluvium, RWG1, 24.5 ft BLS	dom	tr	nd	mod	min-mod	tr	nd
Alluvium, RWG1, 27.5 ft BLS	sdom	tr	tr	dom	min	nd	tr
Ground-water-filter residuum <sup>1</sup>	dom	min-tr	nd	min-tr	min-tr	nd	tr

<sup>1</sup>Well 108U0, which is completed in shale residuum and located outside the irrigated area.

**Table 8.** Element and organic-carbon concentrations in soil and rock samples from the Uncompahgre Project area and from the Grand Valley

[Se, selenium; U, uranium; V, vanadium; Fe, iron;  $\mu\text{g/g}$ , micrograms per gram, which is equivalent to parts per million; BLS, below land surface; ft BLS, feet below land surface; --, no data]

Sample description	Se ( $\mu\text{g/g}$ )	U ( $\mu\text{g/g}$ )	V ( $\mu\text{g/g}$ )	Fe (percent)	Organic carbon (percent)
<b>MANCOS SHALE BEDROCK</b>					
Mancos Shale, bedrock sample from core, 2,317 ft BLS	0.8	7.4	50	1.7	1.36
Ash layer, bedrock sample from core, 2,271 ft BLS	<.1	13.9	4	1.8	.12
Pyrite and shale, bedrock sample adjacent to ash layer, 2,297 ft BLS	1.6	11.2	13	2	1.55
Pyrite euhedron, isolated from bedrock core, adjacent to ash layer	19	--	--	--	--
<b>MANCOS SHALE RESIDUUM</b>					
Weathered ash, outcrop of ash layer, upper Mancos Shale	3.9	8.38	40	2.3	.39
Shale residuum, sediment-core sample from well SL2, 2 ft BLS	1.1	4.77	130	2.1	.44
Shale residuum, sediment-core sample from well SL2, 7 ft BLS	.8	4.63	160	2.4	.56
Shale residuum, sediment-core sample from well SL2, 9 ft BLS	.8	4.16	160	2.5	.51
Gypsum, from bedding-plane parting, well SL1	<1	--	--	--	--
<b>ALLUVIUM OVERLYING MANCOS SHALE</b>					
Alluvium, sediment-core sample from well RWG1, 6 ft BLS	3.6	4.55	150	2.2	.38
Alluvium, sediment-core sample from well RWG1, 8 ft BLS	2.8	4.48	140	2.1	.32
Alluvium, sediment-core sample from well RWG1, 27 ft BLS	1.7	3.79	100	2	.32

Selenium concentrations in alluvium samples were more than 4 times greater than in shale bedrock (table 8), indicating a concentrating effect from adsorption of selenium onto clay minerals and possibly reduction of selenium to a less mobile form. The concentrations of selenium, uranium, and vanadium indicate an upward gradient, possibly indicating transport toward the ground surface by capillary action and a concentrating effect from evaporation.

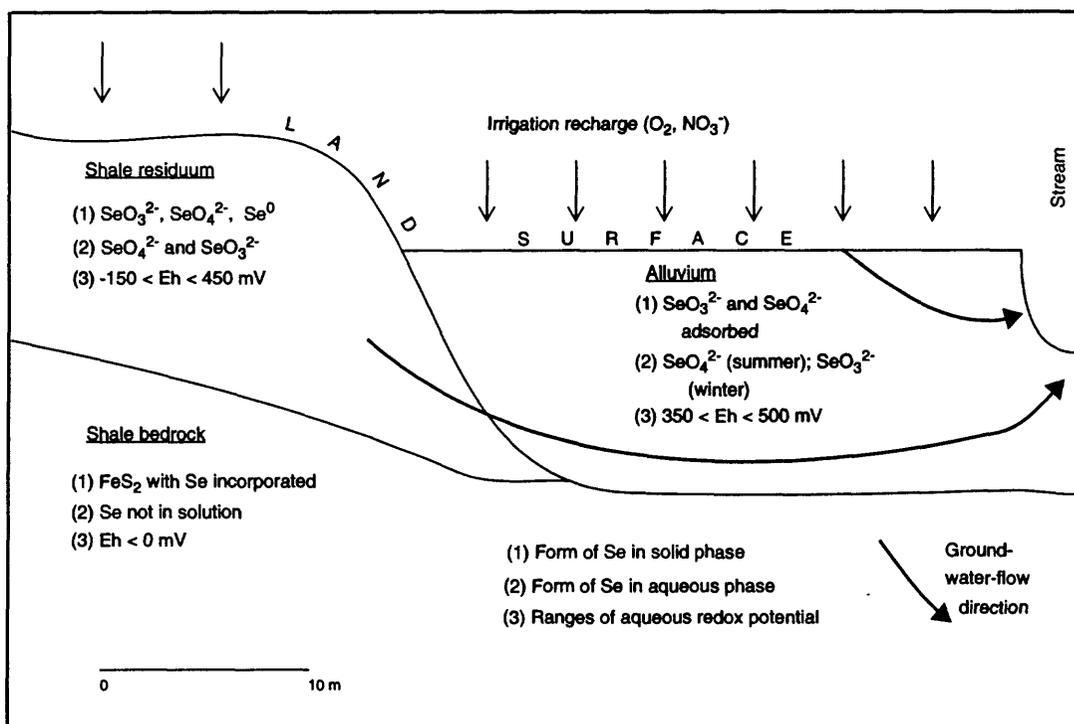
## Occurrence of Selenium in Ground Water

### Distribution

The conceptual model for the occurrence, mobilization, and redistribution of solid-phase and dissolved selenium in the Mancos Shale, shale residuum, and alluvium includes: (1) Oxidation of pyrite containing trace concentrations of selenium; (2) mobilization of selenium by ground water under oxidizing conditions; (3) immobilization and redistribution of selenium by biogeochemical reduction,

coprecipitation, or adsorption, or all three; or (4) transport of oxidized selenium to streams and drains. Aqueous selenium complexes could migrate from oxidized zones into zones of geochemically reducing environments where dissolved selenium would be converted to less mobile species (or redistributed) by biogeochemical reduction, adsorption, or coprecipitation. Adsorbed selenium could be mobilized by desorption or oxidation, or both. A conceptualized model of the occurrence of selenium in Mancos Shale, shale residuum, and alluvium in the irrigated areas of the Uncompahgre Project area and the Grand Valley is shown in figure 16.

In the Uncompahgre Project area and in the Grand Valley, distribution and concentrations of dissolved selenium differ according to geochemical environment and hydrogeologic setting (table 9). In general, the highest concentrations of dissolved selenium—as high as 1,300  $\mu\text{g/L}$ —were in water from wells completed in alluvium overlying the Mancos Shale and where nitrate concentrations were high. The lowest concentrations of dissolved selenium were in water from wells completed in terrace deposits on the western side



**Figure 16.** Conceptual model of the occurrence of selenium (Se) in Mancos Shale, shale residuum, alluvium, and ground water in the Uncompahgre Project area and in the Grand Valley.

of the Uncompahgre Valley (the terrace deposits are of glacial origin and do not contain detritus from weathered Mancos Shale), in water from wells completed in Mancos Shale residuum, and where iron concentrations were high.

The distribution of selenium and other elements (such as nitrogen, iron, and manganese) are affected by the oxidation potential of the geochemical environment. Where table 9 lists the general classifications of the geochemical environments pertinent to selenium occurrence and distribution, table 10 lists ground-water data for common indicators of the oxidation-reduction characteristics of the subsurface geochemical environment. Where geochemical conditions are anoxic, dissolved iron, manganese, and ammonia concentrations are relatively high, and dissolved oxygen, nitrate, and selenium concentrations are low (table 10). In contrast, where geochemical conditions are oxic, dissolved iron, manganese, and ammonia concentrations are relatively low, and dissolved oxygen, nitrate, and selenium concentrations are high (table 10). Many factors can affect these conditions, such as rainfall, snowmelt, irrigation, and bacteria that can mediate chemical reactions.

**Table 9.** Geochemical environments of the ground-water-flow systems, hydrogeologic settings, and ranges of dissolved-selenium concentrations in Mancos Shale residuum and alluvium in the irrigated Uncompahgre Project area and in the Grand Valley

[Oxic/anoxic environment, ground water with dissolved-oxygen concentrations ranging from 0.5 to 2 mg/L (milligrams per liter); anoxic,  $\leq 0.5 \text{ mg/L}$ ;  $\mu\text{g/L}$ , micrograms per liter; Mn, manganese; Fe, iron;  $\text{NO}_3^-$ , nitrate]

Geochemical environment	Hydrogeologic setting	Ranges of dissolved-selenium concentrations in ground water
Oxic/anoxic	Alluvium on Mancos Shale	Moderate—43 to 80 $\mu\text{g/L}$
Oxic/anoxic Mn rich	Alluvium, shale residuum	Low to high— $<1$ to 170 $\mu\text{g/L}$
Oxic/anoxic Fe rich	Mancos Shale residuum	Low— $<1$ to 35 $\mu\text{g/L}$
Anoxic Mn rich	Mancos Shale residuum	Low to moderate— $<1$ to 65 $\mu\text{g/L}$
Anoxic Fe rich	Mancos Shale residuum	Very low— $<1 \mu\text{g/L}$
Anoxic $\text{NO}_3^-$ rich	Alluvium on Mancos Shale	Moderate to high—25 to 1,300 $\mu\text{g/L}$

**Table 10.** Concentrations of dissolved redox-active constituents, water properties, and hydrogeologic setting of water from wells in alluvium and shale residuum in the Uncompahgre Project area and in the Grand Valley

[mV, millivolts; mg/L, milligrams per liter; µg/L, micrograms per liter; NO<sub>3</sub><sup>-</sup>, dissolved nitrate as N; NH<sub>4</sub><sup>+</sup>, dissolved ammonia as N; Se, dissolved selenium as Se; Mn, dissolved manganese as Mn; Fe, dissolved iron as Fe; <, less than]

Site number (figs. 8 and 9)	Hydrogeologic setting	Sampling date	Platinum-electrode potential (mV)	pH	Dissolved oxygen (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NH <sub>4</sub> <sup>+</sup> (mg/L)	Se (µg/L)	Mn (µg/L)	Fe (µg/L)
SL1	Shale residuum	09-11-91	360	7.04	0.50	3.10	0.07	50	180	<10
		12-05-91	460	6.96	.30	3.50	.02	60	200	<10
		01-10-92	472	6.83	.30	3.70	.02	34	170	<10
SL2	Shale residuum	09-11-91	370	6.94	1.60	1.80	.08	18	260	<10
		03-02-92	247	7.02	.50	.96	.04	4	330	1,200
130L3	Shale residuum	09-03-91	335	6.97	.80	4.10	1.40	5	550	80
		02-19-92	310	6.57	.80	3.81	1.10	3	540	260
RWG1	Alluvium	08-28-91	434	7.12	.60	210	.07	1,100	140	<10
		12-10-91	460	7.10	.00	190	.04	1,300	120	20
		01-13-92	430	7.10	.00	180	.02	1,100	100	10
		02-20-92	447	7.09	.03	190	.03	990	130	<10
RWG2	Alluvium	08-28-91	405	6.96	.60	1.20	.10	43	190	<10
		02-20-92	414	6.84	.10	1.00	.01	1	<130	<10
B254334	Shale residuum/alluvium	06-19-91	500	6.89	.20	9.82	.09	45	70	<10
		03-04-92	390	6.86	.10	3.25	.01	25	30	10
108U0	Shale residuum (outside irrigation area)	10-04-91	-120	8.01	.03	.005	2.80	<1	80	40
		03-20-92	150	7.73	.00	<.05	2.50	<1	40	320

The oxidation-reduction potential (or redox potential, expressed in millivolts) can be approximated in the field by a platinum electrode. Platinum-electrode potential is an important indicator of geochemical conditions—low platinum-electrode potential (generally less than about 400 mV) indicates a geochemically reducing environment and high platinum-electrode potential (generally greater than about 400 mV) indicates an oxidizing geochemical environment. In the Uncompahgre Project area and in the Grand Valley, dissolved selenium occurs in lower concentrations where the platinum-electrode potential is lower and the hydrogeologic system is more reducing, such as in the Mancos Shale residuum (fig. 17). These conditions indicate that selenium is more mobile in oxygenated environments (onsite platinum-electrode potential greater than about 300 mV), and selenium is immobilized in reducing environments (onsite platinum-electrode potential less than about 300 mV). In the reduction sequence of aqueous complexes called the redox ladder (Berner, 1981), reduction of selenate follows oxygen and nitrate, which then are followed by the reduction of manganese, iron, and sulfate.

### Seasonal Effects

Dissolved selenium concentrations in ground water of the study area generally tend to increase during summer (irrigation season) when irrigation water is applied. Selenium concentrations generally decrease in winter (nonirrigation season) when irrigation water is turned off and reducing geochemical conditions remove selenium from the aqueous phase (fig. 18). Of the 16 wells sampled seasonally, selenium concentrations were lower in winter than in summer in water from 9 of 16 wells. Primarily, water from wells in shale residuum showed these seasonal effects; water from wells in alluvium might not indicate such seasonal effects because oxidizing conditions could be maintained in the alluvial aquifer.

During the nonirrigation season, dissolved selenium can be reduced to less mobile species where geochemical conditions are favorable for selenium reduction. Selenium-speciation data for dissolved selenium in selected ground-water samples collected during the nonirrigation

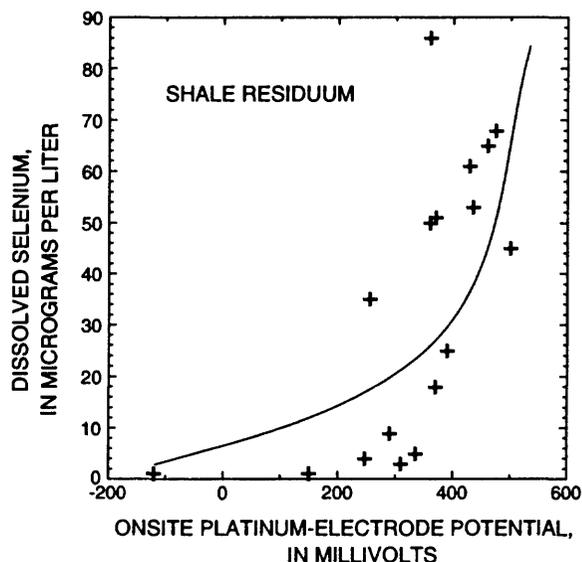


Figure 17. Platinum-electrode potential and concentrations of dissolved selenium in water from wells in Mancos Shale residuum. (Hand-fitted correlation shown.)

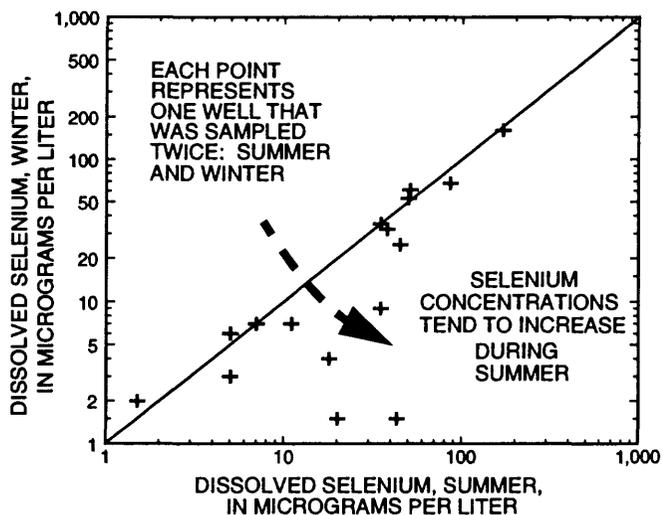


Figure 18. Dissolved selenium in water from wells in shale residuum and alluvium during the irrigation season (summer) and nonirrigation season (winter).

season are listed in table 11. The percent of  $\text{Se}^{\text{IV}}\text{O}_3^{2-}$  (selenite) in two samples was 28.3 and 50.5 percent of the total dissolved-selenium concentration in the samples, indicating that reducing conditions could have been converting  $\text{Se}^{\text{VI}}\text{O}_4^{2-}$  (selenate) to  $\text{Se}^{\text{IV}}\text{O}_3^{2-}$  and tending to remove dissolved selenium from the aqueous phase.

**Table 11.** Speciation of dissolved selenium in selected ground-water samples from the Uncompahgre Project area and from the Grand Valley (analyses courtesy of Roger Fujii and A.T. Chalmers, U.S. Geological Survey, written commun., 1992)

[ $\mu\text{g/L}$ , micrograms per liter;  $\text{mg/L}$ , milligrams per liter; Se, selenium;  $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ , selenate;  $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ , selenite]

Site number (figs. 8 and 9)	Hydrogeologic setting	Sampling date	Dissolved Se ( $\mu\text{g/L}$ )	$\text{Se}^{\text{VI}}\text{O}_4^{2-}$ ( $\mu\text{g/L}$ )	$\text{Se}^{\text{IV}}\text{O}_3^{2-}$ ( $\mu\text{g/L}$ )	Percent $\text{Se}^{\text{IV}}\text{O}_3^{2-}$
RWG1	Alluvium in Mancos Shale setting, Grand Valley, $\text{NO}_3^- = 200 \text{ mg/L}$	03-19-92	1,056.2	1,055.4	0.8	0.08
RWG2	Alluvium overlying Mancos Shale, Grand Valley	03-19-92	1.9	1.4	.5	28.3
SL1	Mancos Shale residuum, Uncompahgre Valley	03-23-92	50.1	49	1.1	2.3
Schmalz	Terrace deposits, Uncompahgre Valley	03-23-92	6.9	3.4	3.5	50.5

## Mobilization and Transport of Selenium

Selenium in the Uncompahgre Project area and in the Grand Valley can be mobilized by oxidation of reduced selenium species, by desorption of selenate and selenite salts from aquifer sediments, and by dissolution of selenium. Dissolved selenium can be immobilized by natural reducing conditions. During summer, selenium could be mobilized and transported more readily by irrigation water; during winter, the water table lowers and geochemical conditions become more reducing by the action of naturally occurring microorganisms, which tend to remove selenium from solution in the ground-water system. Selenium mobilization in the study area is affected by salinity, desorption or ion exchange, and oxidation-reduction processes, depending on the hydrogeologic system that controls the geochemical environment, similar to hypotheses presented by See and others (1992).

Selenium can be mobilized by oxidation of reduced selenium species. Oxidation of selenium occurs by the chemical actions of dissolved-oxygen and nitrate in ground water. Nitrate can act as an oxidant to mobilize selenium (Wright, 1994; Wright and McMahon, 1994; Wright, 1995), and nitrate can inhibit selenium reduction (Oremland and others, 1989). More discussion on this topic is provided in the "Selenium Oxidation." section.

Dissolved selenium can be mobilized by desorption of selenate and selenite salts that are adsorbed to aquifer sediments. Sequential extractions were

performed on aquifer-sediment samples to estimate the water-extractable selenium (selenate salts) and the surface-adsorbed selenium (selenite salts) (Roger Fujii and A.T. Chalmers, U.S. Geological Survey, written commun., 1992). An estimate of the water-extractable selenium was obtained by using a 0.25M KCl (potassium chloride) extraction solution that indicates the potentially water-soluble selenium in the sediment sample (Fujii and others, 1988). An estimate of the surface-adsorbed selenium was obtained by using a 0.1M  $\text{K}_2\text{HPO}_4$  (potassium phosphate) extraction solution adjusted to pH 8 with KOH (potassium hydroxide) (Fujii and others, 1988). Selenium-speciation analyses were performed on the extractions (Makita and Fujii, 1992). Speciation of sequential extractions from two alluvial-aquifer-sediment samples indicates that the extractions estimating the water-soluble phases consisted mostly of selenate ( $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ ), and the extractions estimating the surface-adsorbed phases consisted mostly of selenite ( $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ ) (table 12). Selenate forms a weakly bonded, outer-sphere complex; selenite adsorbs much more strongly than selenate and forms a stronger bonded, inner-sphere complex (Electric Power Research Institute, 1980; Balistrieri and Chao, 1987; Hayes and others, 1987).

Kaolinite and smectite (dominant clay minerals in Mancos Shale residuum, weathered ash layers, and alluvium) are reported to readily adsorb selenium and affect selenium concentrations in soil solutions (Electric Power Research Institute, 1980; Bar-Yosef and Meek, 1987); and dissolved selenium can coprecipitate with ferric hydroxide (Electric Power

**Table 12.** Speciation of extractable selenium in alluvial-aquifer-sediment samples from the Grand Valley (analyses courtesy of Roger Fujii and A.T. Chalmers, U.S. Geological Survey, written commun., 1992)

[Total KCl extractable Se is the potentially water-soluble selenium in sediment sample; total  $K_2HPO_4$  extractable Se is an estimate of the surface-adsorbed selenium;  $\mu\text{g/g}$ , micrograms per gram; ft BLS, feet below land surface]

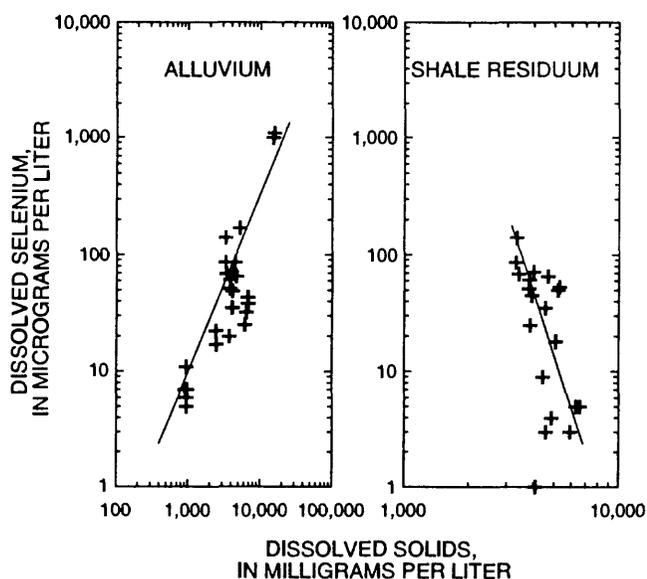
Site number (fig. 9)	Hydrogeologic setting	Sampling date	Total KCl extractable Se ( $\mu\text{g/g}$ )	Percent $\text{Se}^{IV}\text{O}_3^{2-}$ in sample	Total $K_2HPO_4$ extractable Se ( $\mu\text{g/g}$ )	Percent $\text{Se}^{IV}\text{O}_3^{2-}$ in sample
RWG1	Alluvium on Mancos Shale, Grand Valley, 13 ft BLS	08-25-91	0.16	1.5	0.12	96
RWG1	Alluvium on Mancos Shale, Grand Valley, 24 ft BLS	08-25-91	.020	4	.084	76

Research Institute, 1980), adsorb to goethite (Hayes and others, 1987), or precipitate as iron selenite after fluid migration to reducing zones (Elrashidi and others, 1987). These adsorption processes are completely reversible (Balistrieri and Chao, 1987), indicating that desorption could mobilize selenium. In addition, high salinity concentrations could change the electrical nature of the outer layer of clay minerals (the salinity effect), whereby the hydroxyl ion could displace selenium oxyanions from outer-layer adsorption sites (Balistrieri and Chao, 1987), thereby mobilizing selenium.

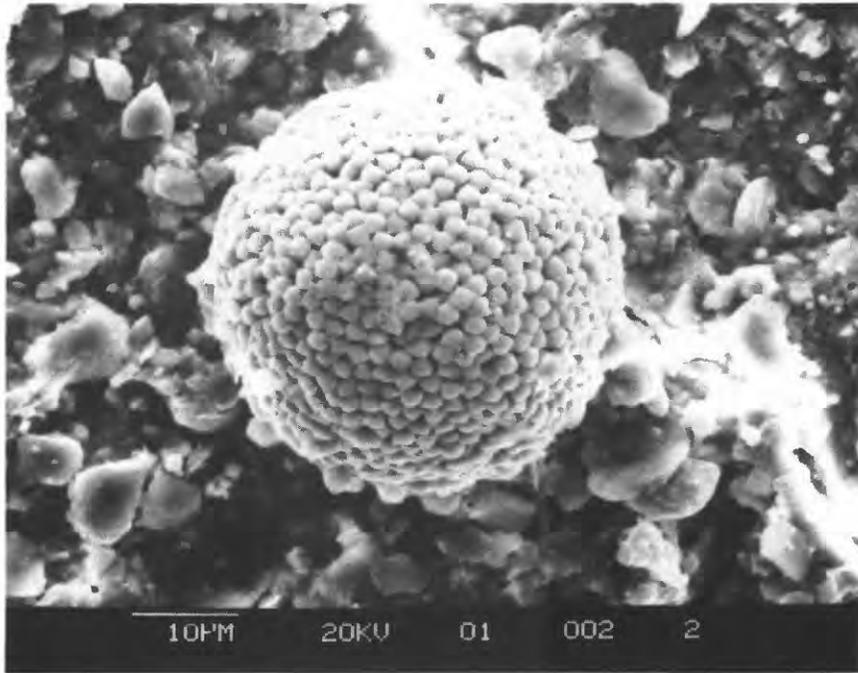
Selenium can be mobilized by dissolution. Dissolved selenium in ground water of the Uncompahgre Project area and of the Grand Valley is positively correlated with dissolved-solids concentrations in water from wells completed in alluvium, but dissolved selenium is negatively correlated with dissolved-solids concentrations in water from wells completed in shale residuum (fig. 19). The negative correlation for shale residuum could be related to dissolved-solids concentrations that increase during the nonirrigation season (a concentrating effect), and biogeochemical reduction of dissolved selenium occurs concurrently with the concentrating effect (Wright and Butler, 1993). Consequently, dissolved selenium is more mobile in alluvium than in shale residuum, which also is reflected by selenium concentrations in shale residuum.

Selenium can be immobilized by natural reducing conditions. Framboidal pyrite (fig. 20) was collected on filter paper from filtered ground water from a well (100 ft deep in Mancos Shale residuum) located outside the irrigated area in the

Grand Valley. The geochemical conditions were sufficiently reducing ( $Eh = -120$  mV) to precipitate pyrite from available dissolved iron and abundant sulfate in the ground water; likewise, selenium would be reduced and immobilized and possibly incorporated into the crystalline structure of the pyrite. Similar reducing conditions might occur during winter within the irrigated areas that could immobilize dissolved selenium. If not for irrigation, geochemical conditions within the study area could be reducing; however, irrigation infiltration provides oxidizing conditions suitable for mobilization and transport of selenium.



**Figure 19.** Correlation of dissolved solids and dissolved selenium in water from wells in alluvium ( $r = +0.85$ ) and shale residuum ( $r = -0.55$ ) (from Wright and Butler, 1993).



**Figure 20.** Scanning-electron photomicrograph of framboidal pyrite collected on 0.45-micrometer water-filter paper from a well located outside the irrigated Grand Valley area, October 1991. Platinum-electrode potential was  $-120$  millivolts, and  $\delta^{34}\text{S}$  was  $+6.4$  per mil. Scale bar in lower left indicates 10 micrometers.

## Selenium Oxidation

Reduced selenium complexes occurring in the Mancos Shale residuum and alluvium might be mobilized by oxidants, such as dissolved oxygen and nitrate, in ground water. In ground-water systems that can become depleted of oxygen, such as organic-rich systems in the Mancos Shale and Mancos Shale residuum,  $\text{NO}_3^-$  might act as an oxidant for mobilization of selenium.  $\text{NO}_3^-$  concentrations in ground-water samples range from  $< 0.05$  to  $210$  mg/L as N in the study area (table 5). Thermodynamic relations for selenium oxidation indicate that elemental selenium could be oxidized to selenite ( $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ ) and selenate ( $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ ) by nitrate and nitrite, and theoretical energies for some of the reactions almost equal the energy available for oxidation of selenium by oxygen (table 13). Several investigators have indicated that  $\text{NO}_3^-$  inhibits the reduction of  $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ . Oremland and others (1989), in anaerobic culture experiments, indicated that the inhibition of  $\text{Se}^{\text{VI}}\text{O}_4^{2-}$  reduction by  $\text{NO}_3^-$  was caused by either action of  $\text{NO}_3^-$  as a competitive electron acceptor or that  $\text{NO}_3^-$  is able

to reoxidize reduced, precipitated selenium from sediment. Weres and others (1989) postulated that  $\text{NO}_3^-$  poised the pE value too high for significant  $\text{Se}^{\text{VI}}\text{O}_4^{2-}$  reduction. Because selenium reduction was the focus of these investigations, the oxidation of selenium by  $\text{NO}_3^-$  was not elaborated upon further. Korom (1992), in a review of denitrification processes, presented a reaction for oxidation of  $\text{FeS}_2$  by  $\text{NO}_3^-$ , which yields  $\text{N}_2$  and  $\text{SO}_4^{2-}$  and also indicates that the process might be mediated by bacteria.

Laboratory-batch experiments were performed for this study to test the hypothesis that selenium could be oxidized by nitrate. Samples of Mancos Shale residuum were placed in different concentrations of nitrate. All preparations were made in an argon-filled glovebox to prevent the introduction of atmospheric oxygen into the samples. Preliminary results indicate that selenium can be oxidized by nitrate under laboratory conditions of elevated temperature ( $25^\circ\text{C}$ ) and nitrate concentrations of 5, 50, 100, and 1,000 mg/L (Wright and McMahon, 1994; Wright, 1995); however, extrapolation of these rates to field

conditions have not been done. The oxidation rate depends on the nitrate concentration. Additional research is needed to document if these reactions actually are occurring and if the reaction rate is high enough to be of significance in ground water associated with irrigation in the study area.

**Table 13.** Energies of reaction for oxidation of selenium by oxygen and nitrate

[0, IV, and VI indicate the oxidation state of the selenium;  $\Delta G_R^0$ , Gibbs free energy term; kJ/mol, kilojoules per mole; thermodynamic data are from Garrels and Christ (1965)]

Selenium reactant	Oxidant	Selenium product	Theoretical energy for reaction ( $\Delta G_R^0$ , kJ/mol)
Se <sup>0</sup>	O <sub>2</sub>	Se <sup>IV</sup> O <sub>3</sub> <sup>2-</sup>	-724
	NO <sub>3</sub> <sup>-</sup>	Se <sup>IV</sup> O <sub>3</sub> <sup>2-</sup>	-525
HSe <sup>IV</sup> O <sub>3</sub> <sup>-</sup>	O <sub>2</sub>	Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup>	-264
	NO <sub>3</sub> <sup>-</sup>	Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup>	+46
	NO <sub>2</sub> <sup>-</sup>	Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup>	-464
Se <sup>IV</sup> O <sub>3</sub> <sup>2-</sup>	O <sub>2</sub>	Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup>	-270
	NO <sub>3</sub> <sup>-</sup>	Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup>	+8.7
FeHSe <sup>IV</sup> O <sub>3</sub> <sup>2+</sup>	O <sub>2</sub>	Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup>	-300
	NO <sub>3</sub> <sup>-</sup>	HSe <sup>IV</sup> O <sub>3</sub> <sup>-</sup>	-27
	NO <sub>3</sub> <sup>-</sup>	Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup>	+94

## Indicators of Microbial Activity

Selenium is sensitive to oxidation-reduction processes in a ground-water system. Many of these processes are mediated by microbes (bacteria), and a carbon source (such as kerogen in Mancos Shale and Mancos Shale residuum) is necessary for bacterial metabolism. This microbial activity leaves imprints in geochemical characteristics of the water. Sulfur isotopes of dissolved sulfate ( $\delta^{34}\text{SO}_4$ ) can be such an indicator of microbial activity.

The sulfur-34/sulfur-32 isotope ( $\delta^{34}\text{S}$ ) values of pyrite in the Mancos Shale range from -34 to +22 per mil CDT (Canyon Diablo troilite) (G. Breit, U.S. Geological Survey, oral commun., 1992). The  $\delta^{34}\text{SO}_4$  values for ground water in the study area range from -26 to +6.4 per mil CDT; however, in the irrigated areas,  $\delta^{34}\text{SO}_4$  ranges from -26.4

to -8.9 per mil CDT (table 14). When  $\delta^{34}\text{SO}_4$  in summer (irrigation-season samples) to winter (nonirrigation-season samples) are compared, some of the wells show a depletion in  $\delta^{34}\text{SO}_4$ , and some of the wells show an enrichment in  $\delta^{34}\text{SO}_4$ . Wells in Mancos Shale residuum all showed a depletion in  $\delta^{34}\text{SO}_4$  values.

The effects of irrigation water and the presence of anthropogenic nitrate could keep ground water in Mancos Shale residuum in a transitional redox state. The winter dissolved-SO<sub>4</sub><sup>2-</sup> pool could partly be reduced to intermediate oxidation states (such as sulfite or thiosulfate) with no isotope effect (Kemp and Thode, 1968) and then reoxidized by oxidizing bacteria that could impart a fractionation showing a depletion in  $\delta^{34}\text{SO}_4$  (Fry and others, 1988). These dynamic changes in  $\delta^{34}\text{SO}_4$  indicate an active microbial system that could affect selenium mobility.

## Relation of Selenium to Other Constituents

Dissolved selenium in ground water in the Uncompahgre Project area and in the Grand Valley primarily is determined by the oxidizing conditions present in the ground water. Oxidizing conditions suitable for selenium mobilization are indicated by the relation of dissolved selenium to other dissolved constituents (fig. 21). Presser and others (1990) reported that selenium precipitates with magnesium-based evaporite complexes (such as thenardite) and does not precipitate with calcium-based evaporite complexes (such as gypsum), indicating that selenium prefers to complex with magnesium-based compounds in solution, which might be related to the solubilities of the different calcium- and magnesium-based evaporites and the saturation states of the evaporite complexes that weather from marine shales. A positive correlation between dissolved magnesium and dissolved selenium is shown in figure 21; however, this trend does not conclusively prove any geochemical significance regarding selenium mobilization in the presence of dissolved magnesium.

**Table 14.** Sulfur-isotope data for water from selected wells in shale residuum and alluvium

[Sampling date is significant for irrigation season—April through October;  $\delta^{34}\text{SO}_4$  values, in per mil referenced to the CDT (Canyon Diablo troilite) standard; --, no previous data for comparison]

Site number (figs. 8 and 9)	Sampling date	$\delta^{34}\text{SO}_4$ (per mil)	Comments
<b>MANCOS SHALE RESIDUUM</b>			
130L3	September 1991	-14.8	--
130L3	February 1992	-16.0	Depleted 1.2 per mil from September 1991
125Q5	September 1991	-8.9	--
125Q5	February 1992	-19.7	Depleted 10.8 per mil from September 1991
SL1	September 1991	-20.9	--
SL1	February 1992	-22.0	Depleted 1.1 per mil from September 1991
B254334	June 1991	-26.4	--
108U0 <sup>1</sup>	October 1991	+6.4	Framboidal pyrite on water-filter paper
<b>ALLUVIUM OVERLYING MANCOS SHALE</b>			
RWG1	August 1991	-21.0	--
RWG1	February 1992	-20.8	Enriched 0.2 per mil from August 1991
RWG2	August 1991	-20.3	--
RWG2	February 1992	-20.6	Depleted 0.3 per mil from August 1991
RWG3	August 1991	-19.6	--
RWG3	February 1992	-18.5	Enriched 1.1 per mil from August 1991
143N0	February 1992	-17.0	--

<sup>1</sup>Well located outside the irrigated area.

Selenium is positively correlated with nitrate (fig. 21). When conditions in the ground water are reduced to the point where ammonia is the dominant nitrogen species, selenium is reduced out of the dissolved phase; hence, selenium and ammonia are negatively correlated (fig. 21). Iron goes into solution when oxidation-reduction conditions reach a point where ferrous iron ( $\text{Fe}^{2+}$ , the more soluble iron species) becomes the dominant iron species; oxidized selenium species become immobilized in such reducing conditions (fig. 21). The negative correlations of these oxidation-reduction-sensitive species with dissolved selenium in ground water indicates a high level of bacterial activity in the Mancos Shale that is capable of reducing selenium out of the dissolved phase. If not for irrigation, oxidation-reduction conditions in the Mancos Shale would be sufficiently reducing to prevent the mobilization and transport of dissolved selenium.

The trace elements uranium and vanadium react similarly to oxidation-reduction conditions as does selenium. Selenium and uranium and selenium and vanadium, therefore, are positively correlated in water from wells in the Uncompahgre Project area and in the Grand Valley (fig. 21). Selenium and sulfate are positively correlated in water from wells in the Uncompahgre Project area and in the Grand Valley. Selenium is isomorphous with sulfur and substitutes in the crystalline structure of sulfide minerals; therefore, when pyrite in the Mancos Shale is oxidized by infiltrating irrigation water (putting sulfate into solution), selenium also is oxidized and brought into solution. Selenium precipitates with magnesium sulfate evaporite complexes; therefore, when evaporite complexes are dissolved by infiltrating irrigation water, selenium is put into solution.

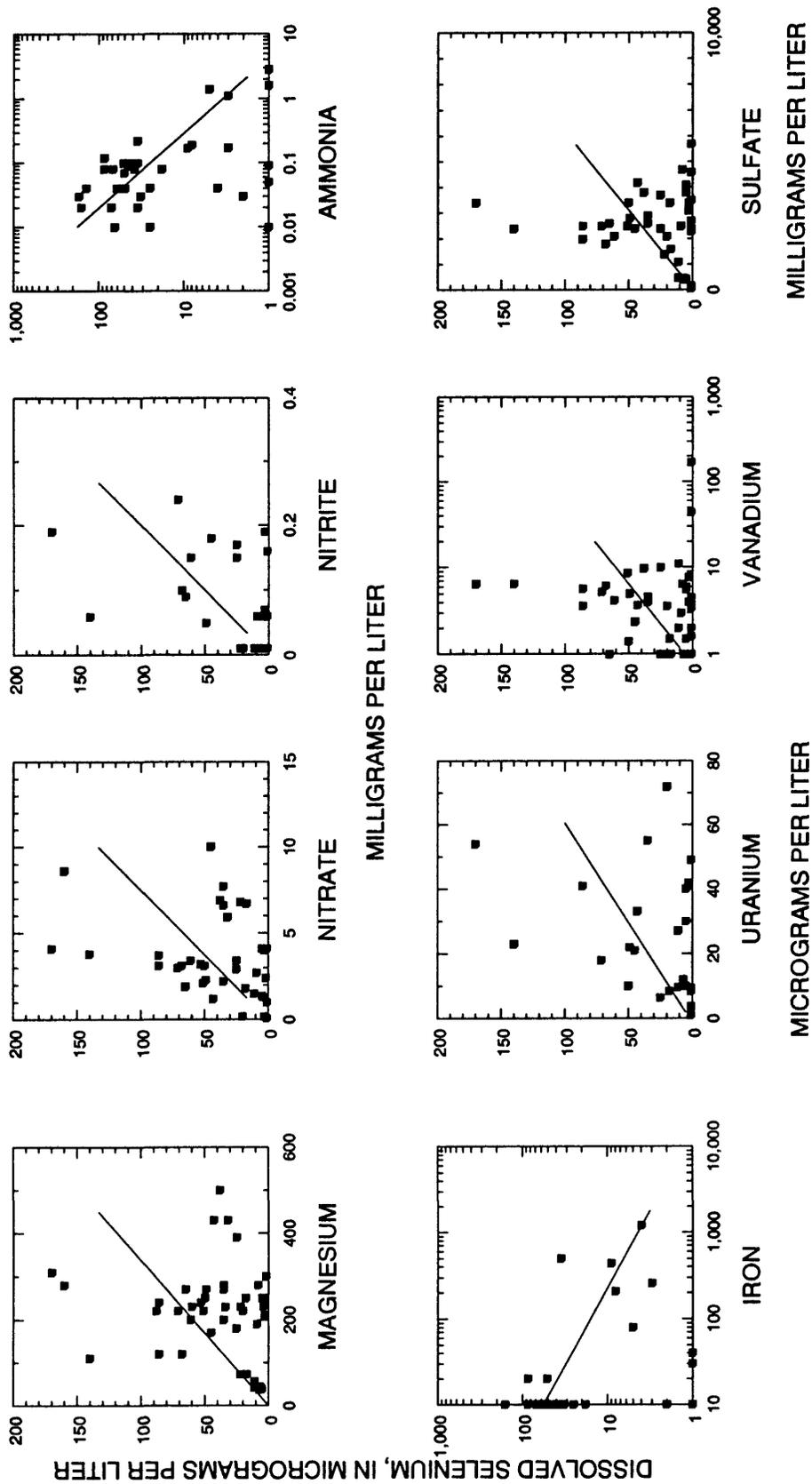


Figure 21. Correlations of dissolved selenium with various dissolved constituents in water from wells in the Uncompahgre Project area and in the Grand Valley.

## **SURFACE-WATER INVESTIGATIONS**

Selenium data for surface-water sites were used to determine areal and seasonal variations of selenium concentrations and loads in the irrigated areas. Selenium loads were used to delineate drainage basins that were major source areas of selenium discharging into the Gunnison and Colorado Rivers. Dissolved-solids and major-ion data were collected to describe general water quality and to determine if there were relations between concentrations of selenium and dissolved solids and major constituents in the study area. Data also were collected for other trace constituents and pesticides that could be potentially harmful to biota.

Sample collection in 1991 was essentially an expanded reconnaissance of the Uncompahgre Project area and a first-time reconnaissance of the Grand Valley to collect selenium and other trace-constituent data for streams, washes, and ditches draining irrigated areas. Selenium and other trace-constituent data for surface water in the study area were scarce, except from a few sites on the Gunnison and Colorado Rivers and from Sweitzer Lake. Also, there was a lack of information about selenium in irrigated areas outside the Uncompahgre Project in the lower Gunnison River Basin where irrigation drainage could be a source of selenium. During July 1991, samples were collected at 4 sites each on the Gunnison and Uncompahgre Rivers, at 17 sites on major streams or canals draining the Uncompahgre Project, and at 5 sites on tributaries of the Gunnison River that drain irrigated areas adjacent to or upstream from the Uncompahgre Project. For a reconnaissance of the Grand Valley, 20 sites were sampled in March and in late August–early September in 1991. Major tributary streams and washes of the Colorado River and selected smaller drainages were sampled to provide a general geographical distribution of sites in the Grand Valley. Samples for analysis of various insecticides were collected in the Grand Valley at 11 of the reconnaissance sites and at 2 sites on the Colorado River in the summer of 1991. Water samples also were collected in June 1991 from three ponds in or adjacent to the Uncompahgre Project and from one pond in the Grand Valley.

In 1992, samples were analyzed for fewer constituents, and sampling focused on the irrigated areas in the Uncompahgre Project and in the Grand Valley. Data were collected for synoptic surveys during the winter of 1992 to describe the distribution

of selenium and other constituent concentrations and loads in all major drainage basins and in selected drainage ditches in the irrigated areas. The synoptic data also were used to determine water-quality differences between and within basins. Samples for synoptic surveys for individual drainage basins were collected in 2 days, although sampling for all the surveys was done over about 7 weeks from late January to mid-March. In February 1992, stream-discharge data and water-quality samples were collected at 16 sites on the Uncompahgre River, including sites at all diversions for winter water, and at major inflows to estimate selenium and other constituent loading to the river during low and stable stream discharge. Monthly samples were collected at four tributary sites and from the Uncompahgre River in water year 1992 to describe seasonal variations in constituent concentrations and loads. Selenium-speciation data were obtained for five streams in the Grand Valley in March 1992 for use in a risk assessment of selenate and selenite to endangered fish. Water samples were collected from two ponds in the Uncompahgre Project area and two ponds in the Grand Valley in June 1992.

### **Sample Collection and Analytical Methods**

Onsite measurements at surface-water sites included stream discharge, specific conductance, pH, water temperature, and dissolved oxygen. Water-quality measurements were made using methods similar to methods described by Knapton (1985). Stream discharge for sites at streamflow-gaging stations was determined from the stage record and the stage-discharge rating table. Otherwise, stream discharge was measured using methods described by Rantz and others (1982).

Water samples were collected using depth-integrating samplers and equal-width methods (Ward and Harr, 1990) when possible. At sites where the water depth was too shallow, samples were collected from the centroid of flow or at several verticals in a cross section using 1-L plastic or glass bottles. Samples for selected organophosphate and carbamate insecticide analyses were collected directly in bottles supplied by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo.

Samples collected for analyses of dissolved-inorganic constituents and uranium were filtered in the field through a 0.45- $\mu\text{m}$  cellulose filter using a plastic filter unit. Samples for analyses of inorganic constituents, uranium, and insecticides were processed and preserved for shipment to the NWQL according to standard procedures of the USGS. Samples for selenium-speciation analyses were acidified with hydrochloric acid and chilled with ice.

Quality-assurance sampling at surface-water sites included collection of three deionized water blanks that were filtered and processed as regular water samples, five sequential duplicate samples, and five split samples. Selenium was not detected in the blanks (less than 1  $\mu\text{g/L}$ ). For the duplicate and split samples in which selenium concentrations exceeded 10  $\mu\text{g/L}$ , the difference between concentrations in the original sample and in the quality-assurance sample ranged from 3 to 12 percent. Except for uranium, the differences in other trace-constituent concentrations between duplicate or split samples generally were less than 10 percent.

The analyses of water samples for major constituents, nitrogen and phosphorus species, and trace constituents (except uranium) were done at the NWQL. Analytical methods described by Fishman and Friedman (1989) and laboratory quality-assurance methods described by Jones (1987) were used. Uranium was analyzed by a laboratory contracted by NWQL using a method described by Thatcher and others (1977). Insecticides in water were analyzed using methods described by Wershaw and others (1987). Stable isotopes of hydrogen and oxygen were analyzed using methods described by Epstein and Mayeda (1953) and Kendall and Coplen (1985). Selenium-speciation analyses of water samples were done by HGAAS (Fio and Fujii, 1990). The selenium-speciation analyses were done by the USGS in Sacramento, Calif. (R.F. Fujii, U.S. Geological Survey, written commun., 1992).

## **Selenium Concentrations and Loads in the Gunnison and Colorado Rivers**

Selenium data have been collected since August 1975 at USGS streamflow-gaging stations on the Gunnison River at Whitewater (site GUN6)

and on the Colorado River near the Colorado-Utah State line (site COL8) (fig. 1) for the USGS's National Stream Quality Accounting Network. Selenium data for the Gunnison River downstream from the Gunnison Tunnel (site GUN1), at Delta (site GUN4), and upstream from Escalante Creek (site GUN5) (fig. 1) were collected for the reconnaissance investigation of the Gunnison and Uncompahgre River Basins (Butler and others, 1991). Most of the selenium data for site GUN4 during water years 1991–92 were collected for another water-quality program of the USGS. Selenium data also were collected for the detailed study at selected gaging stations on the Gunnison and Colorado Rivers during 1991–92 to supplement ongoing data-collection activities.

### **Selenium Concentrations**

Selenium concentrations for sites on the Gunnison and Colorado Rivers and for Plateau Creek (fig. 1) are summarized in table 15. Median selenium concentrations in the Gunnison and Colorado Rivers upstream from irrigated areas were less than 1  $\mu\text{g/L}$  (table 15). That concentration also is representative of the selenium concentration in most of the irrigation-supply water for both areas, except for the Redlands area (fig. 3) in the Grand Valley, which is irrigated with water diverted from the Gunnison River downstream from site GUN6 (fig. 1). Selenium concentrations increase in the Gunnison and Colorado Rivers downstream from irrigated areas. The median concentrations at the two outflow sites for each river (sites GUN6 and COL8) are greater than at the sites upstream from the irrigated areas (table 15). Selenium concentrations in about 64 percent of the samples from site GUN6 and almost 50 percent of the samples from site COL8 exceeded the chronic aquatic-life criterion of 5  $\mu\text{g/L}$  established by the U.S. Environmental Protection Agency (1987). The chronic criterion is a recommended guideline for protection of aquatic life from long-term exposure to selenium that could result in reproduction problems or mortality in fish and wildlife through food-chain bioaccumulation. The selenium concentrations in the lower Gunnison River and in the Colorado River in the Grand Valley area might be of concern in the recovery of endangered fish in the study area. Presently (1996),

the FWS and BOR are studying locations along the Gunnison River downstream from Delta and along the Colorado River in the Grand Valley as possible recovery sites for endangered fish.

Analysis of the seasonal distribution of selenium concentrations (1975–92) at sites GUN6 and COL8 indicated maximum selenium concentrations occurred during August through October, which is the last one-half of the irrigation season. The selenium concentrations were slightly higher during the late irrigation season than during winter, although stream discharge was not necessarily lower in late summer than during winter at the two sites, particularly for the Colorado River. Minimum selenium concentrations occurred during May and June, coincident with the peak snowmelt runoff.

Time-series plots of selenium concentrations for the Gunnison River at Whitewater (site GUN6) and Colorado River near the Colorado-Utah State line (site COL8) are shown in figure 22. A smooth curve was fitted through the data points for each site using a LOWESS (LOcally WEighted Scatterplot Smoothing) procedure, which uses residual weighting functions to decrease the effect of outliers (Schertz and others, 1991). Generally, the smoothed curves indicate decreasing concentrations to about 1980, a minimum in the mid-1980's, followed by a slight

increase, and then relatively no change since about 1987. The low concentrations in the 1980's can be accounted for by dilution caused by high stream discharge in the Colorado River Basin from 1983 to 1986.

A computer program called ESTREND (ESTimate TREND) (Schertz and others, 1991) was used to test the selenium data for monotonic time trends. The program uses a nonparametric test, the seasonal Kendall test, to examine water-quality data for monotonic trends. The seasonal Kendall test decreases the effect that seasonal differences in constituent concentrations could have on trend detection by comparing data from the same seasons of the year. For trend tests on selenium data, the year was divided into the nonirrigation season (November through March) and the irrigation season (April through October); the irrigation season was further divided into the runoff season (April through June) and the post-runoff season (July through October). The variability in stream discharge could mask or overwhelm trends in selenium concentrations. The ESTREND program computes trend statistics on the actual concentrations and on the flow- (stream discharge) adjusted concentrations. Trend tests on flow-adjusted concentrations increase the chance of detecting a trend in concentrations that was the result of some effect other than a change in stream discharge.

**Table 15.** Summary of selenium concentrations in the Gunnison and Colorado Rivers and Plateau Creek and the number of samples exceeding aquatic-life criteria of the U.S. Environmental Protection Agency

[Concentrations in micrograms per liter; chronic aquatic-life criterion is 5 micrograms per liter, and the acute criterion is 20 micrograms per liter (U.S. Environmental Protection Agency, 1987); <, less than; a single value is listed for the range for one sample; --, no value]

Site number (fig. 1)	Site name	Period of record	Number of samples	Median	Range	Number of samples exceeding criteria	
						Chronic	Acute
GUN1	Gunnison River downstream from the Gunnison Tunnel	1987–91	5	<1	<1–<1	0	0
GUN3	Gunnison River at Austin	1991	1	--	1	0	0
GUN4	Gunnison River at Delta	1987–92	13	4	<1–13	2	0
GUN5	Gunnison River upstream from Escalante Creek	1987–91	5	5	4–10	2	0
GUN6	Gunnison River at Whitewater	1975–92	73	7	<1–25	47	1
COL2	Colorado River near Cameo	1980–92	<sup>1</sup> 22	1	<1–2	0	0
COL5	Colorado River upstream from Gunnison River	1991	1	--	2	0	0
COL8	Colorado River near the Colorado-Utah State line	1975–92	75	5	<1–30	37	1
PLT	Plateau Creek near mouth	1991–92	7	<1	<1–2	0	0

<sup>1</sup>Includes one sample collected in January 1992 at Palisade because of ice conditions at site COL2.

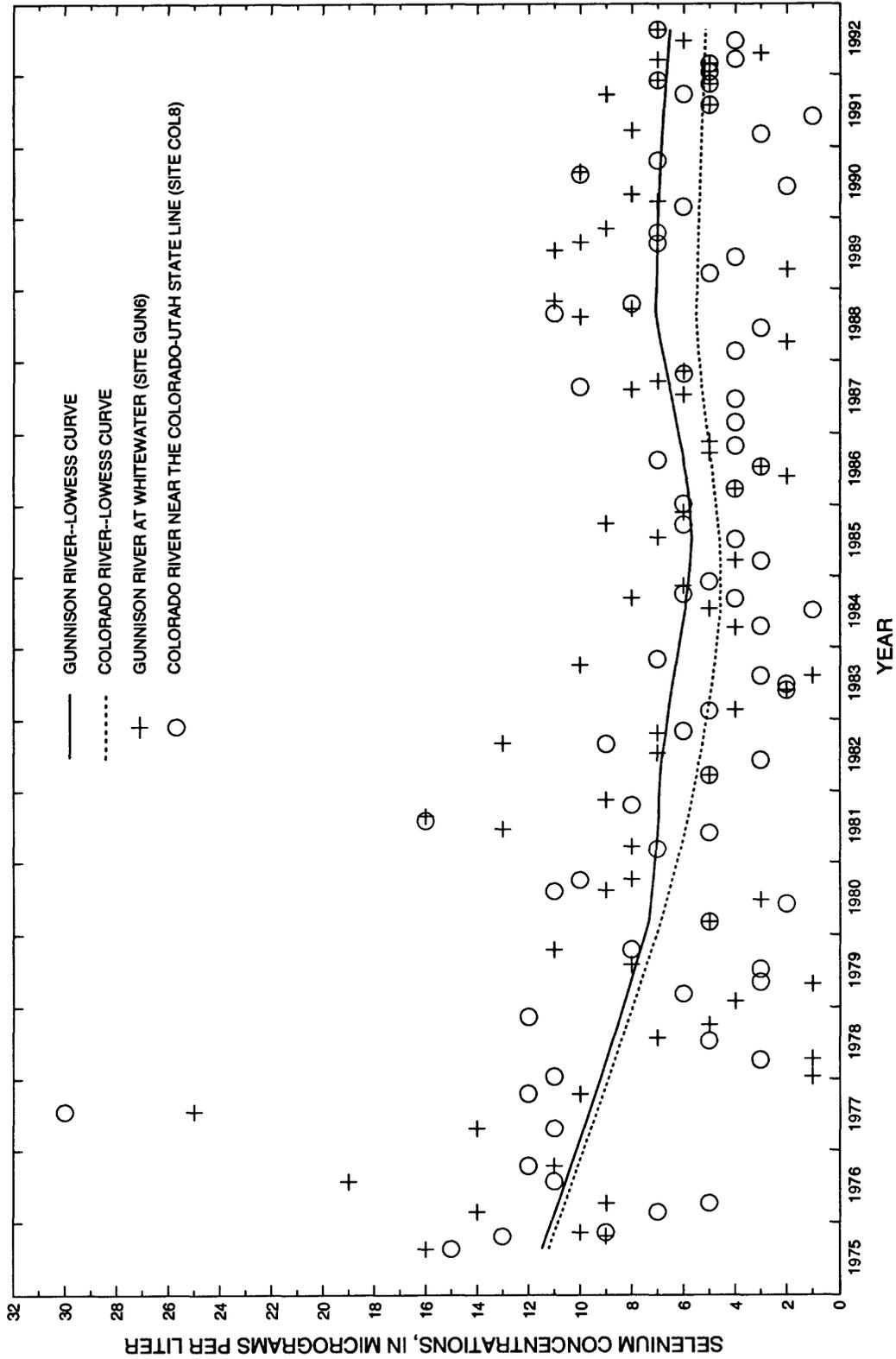


Figure 22. Dissolved-selenium concentrations and the LOWESS smoothed curves of selenium concentrations for the Gunnison River at Whitewater (site GUN6) and the Colorado River near the Colorado-Utah State line (site COL8), 1975-92.

The ESTREND program was used to analyze the selenium data for 1975–92 for the Gunnison River (site GUN6) and Colorado River (site COL8) for monotonic time trends. A trend was considered significant if the significance level ( $p$ ) of the statistical test was 0.05 or less. For the Gunnison River, neither the trend in selenium concentrations of  $-0.13$  ( $\mu\text{g/L}/\text{yr}$ ) was significant ( $p = 0.28$ ) nor was the trend in flow-adjusted concentrations of  $-0.18$  ( $\mu\text{g/L}/\text{yr}$ ) significant ( $p = 0.065$ ). For comparative purposes, sulfate concentrations for 1975–92 also were analyzed for trends. Sulfate concentrations could be affected by irrigation drainage in the study area. For 1975–92, the concentration and flow-adjusted concentration trends for sulfate were not significant for the Gunnison River, which is the same result as for the selenium data.

For the Colorado River, the trend in selenium concentrations of  $-0.20$  ( $\mu\text{g/L}/\text{yr}$ ) ( $p = 0.003$ ) and the trend in flow-adjusted concentrations of  $-0.15$  ( $\mu\text{g/L}/\text{yr}$ ) ( $p = 0.005$ ) were significant for 1975–92. Conversely, neither the concentration nor the flow-adjusted concentration trends for sulfate in the Colorado River for 1975–92 were significant. Because of the decrease in selenium concentrations in the Colorado River during the 1970's (fig. 22), trend analysis was done on the Colorado River selenium data for 1978–92, 1979–92, and 1980–92. For these three periods, the selenium-concentration trends were not significant, but the flow-adjusted concentration trends were still significant [ $-0.14$  to  $-0.16$  ( $\mu\text{g/L}/\text{yr}$ ) with  $p$  values of 0.002 to 0.006]. The trend results seem to indicate a decreasing trend in flow-adjusted selenium concentrations for the Colorado River downstream from the Grand Valley.

### Selenium Loads

Selenium loads in the Gunnison River, Uncompahgre River, and tributaries of the Gunnison River were used to estimate the proportion of selenium load in the Gunnison River at Whitewater (site GUN6, the outflow site for the Gunnison River Basin) that is discharged from the Uncompahgre Project. To obtain such an estimate, the selenium loads in the Gunnison River at Delta (site GUN4), the Uncompahgre River at Delta (site UC16), and the

Gunnison River at Whitewater (fig. 23) were estimated. Estimates of selenium loading from the Uncompahgre Project into the Gunnison River between Peach Valley Arroyo and site GUN4 and between the Uncompahgre River and Roubideau Creek (fig. 23) also were made. Selenium-load estimates were considered approximate because of the limited quantity of selenium-load data for the Gunnison River and for tributaries.

Results of the sampling in July 1991 indicate that the selenium load in the Gunnison River increased from 5.6 to 23.1 lb/d between sites GUN3 and GUN4 (fig. 23). About 53 percent of the load in the Gunnison River at site GUN4 in July 1991 was accounted for in Peach Valley Arroyo (site PVA1), an unnamed drainage near Read (site RD1), and the Bonafide Ditch (site BFD) (fig. 23). Most of the selenium load from the three drainages was at sites RD1 and BFD. For three sets of samples collected at sites RD1, BFD, and GUN4 in 1992, the selenium loads at sites RD1 and BFD accounted for 29 to 45 percent of the selenium load at site GUN4. Unmeasured selenium loading into the Gunnison River between Peach Valley Arroyo and site GUN4 is from other ditches and drainages that discharge relatively small selenium loads from irrigated areas of the Uncompahgre Project and selenium loads from nonproject irrigated areas north of the river. Selenium data were collected for the detailed study in 1993 for tributaries of the Gunnison River that drain the Uncompahgre Project (unpublished data, U.S. Geological Survey). For three sets of samples collected in the summer of 1993, about 53 percent of the selenium load at site GUN4 was accounted for by discharge from the Uncompahgre Project upstream from site GUN4. Based on selenium data collected during 1991–93, 50 percent of the selenium load at site GUN4 was assumed to be from the Uncompahgre Project.

Selenium loads for sites GUN4 and GUN6 and for site UC16 were estimated from daily selenium loads. Daily selenium loads were computed using predicted selenium concentrations from regression relations of selenium concentration to stream discharge and from the daily mean stream discharge for water years 1991–92. Regression relations had coefficient of determinations ranging from 0.52 to 0.82 (all significance levels were less than 0.05).

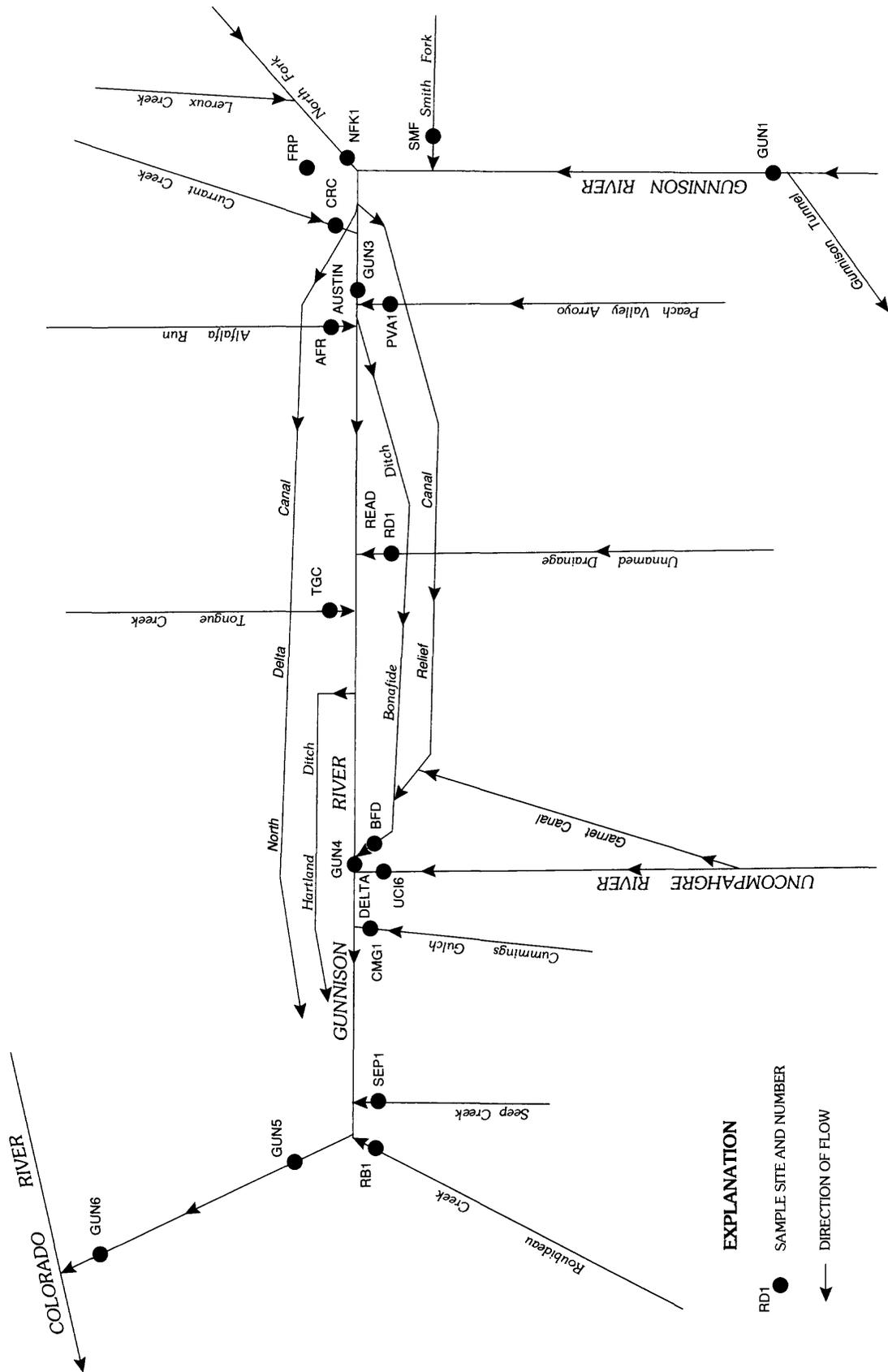


Figure 23. Schematic diagram showing the lower Gunnison River Basin and relative locations of selected surface-water-sampling sites.

Fifty percent of the difference in selenium load between sites GUN4 and GUN6, minus the load for site UC16, was assumed to be selenium loading from the Uncompahgre Project into the Gunnison River between the Uncompahgre River and Roubideau Creek (fig. 23). That estimate is derived from selenium data collected in 1991–92 (Butler and others, 1994) and from data collected in 1993 (unpublished data, U.S. Geological Survey). Selenium loads for the Uncompahgre River (discussed in the “Selenium Loads” section) indicate that about 95 percent of the selenium load in the river at site UC16 was from the Uncompahgre Project. The fraction of the selenium load at site GUN6 attributable to the Uncompahgre Project was computed using: [(0.5 times the selenium load at site GUN4) plus (0.95 times the selenium load at site UC16) plus (0.5 times the difference in selenium load between sites GUN6 minus GUN4 and UC16)] divided by the selenium load at site GUN6. Using the periodic selenium and daily stream-discharge data for water years 1991–92, the Uncompahgre Project accounted for about 68 percent of the selenium load in the Gunnison River at Whitewater (site GUN6). That estimate is considered a general approximation because of the limited selenium-loading data for streams, washes, and ditches that discharge into the Gunnison River between sites GUN3 and Roubideau Creek.

Selenium loads in the Gunnison River at Whitewater (site GUN6) and in the Colorado River near the Colorado-Utah State line (site COL8) in water years 1991–92 for samples collected within 2 days of each other are shown in figure 24. Site COL8 is the outflow site for the entire study area and is downstream from all irrigation drainage from the Gunnison River Basin and from the Grand Valley. The residual selenium load shown in figure 24 is equal to the selenium load of the Colorado River at site COL8 minus the load for the Gunnison River at site GUN6. The residual load represents the selenium load in the Colorado River upstream from the Grand Valley plus the selenium load from the Grand Valley. The selenium load in the Colorado River upstream from the Grand Valley is essentially equal to the selenium load in the Colorado River at site COL2 (fig. 1), plus the small load from Plateau Creek (site PLT). Because unaged surface- and ground-water dissolved-solids loads from natural sources into the Grand Valley are negligible (Bureau of Reclamation, 1983), selenium loads from natural sources in the Grand Valley also

are assumed to be negligible. Therefore, selenium loading from the Grand Valley was assumed to be from irrigation-induced sources.

A regression of selenium concentration to stream discharge using data for 1991–92 was determined for the Colorado River at site COL8 and then used to estimate daily mean selenium loads for that site. The stream discharge for the Colorado River upstream from the Grand Valley was equal to the combined stream discharge of the Colorado River at site COL2 and Plateau Creek at site PLT (fig. 1). About 75 percent of the selenium concentrations were reported as less than 1 µg/L in samples collected in 1991–92 at sites COL2 and PLT. An arbitrary mean selenium concentration of 0.7 µg/L was used to compute the daily mean selenium loads in the Colorado River upstream from the Grand Valley. The selenium-load estimates for water years 1991–92 indicate that the Colorado River upstream from the Grand Valley accounted for about 10 percent of the selenium load at site COL8, the Gunnison River (site GUN6) accounted for about 45 percent of the load, and the Grand Valley accounted for the remaining 45 percent of the selenium load in the Colorado River.

These selenium-load estimates for the Gunnison and Colorado Rivers are considered approximations, but might be useful for comparing relative contributions of the Uncompahgre Project and the Grand Valley with the selenium load in the Colorado River. About two-thirds of the selenium load in the Gunnison River at site GUN6 was attributed to the Uncompahgre Project; therefore, the Uncompahgre Project accounts for about 30 percent of the selenium load in the Colorado River at site COL8. The Grand Valley accounts for about 45 percent of the selenium load in the Colorado River at site COL8. Although the uncertainty associated with these estimates was not determined, the selenium-loading estimates indicate that the Uncompahgre Project and the Grand Valley are major sources of selenium to the Colorado River.

Longer term selenium loads in the Gunnison River and from the Grand Valley were estimated by using the selenium data collected during water years 1976–92 for sites GUN6 and COL8 (fig. 22). The same methods used for estimating selenium loads for the Colorado River upstream from the Grand Valley and for sites GUN6 and COL8 for water years 1991–92 were used to estimate selenium

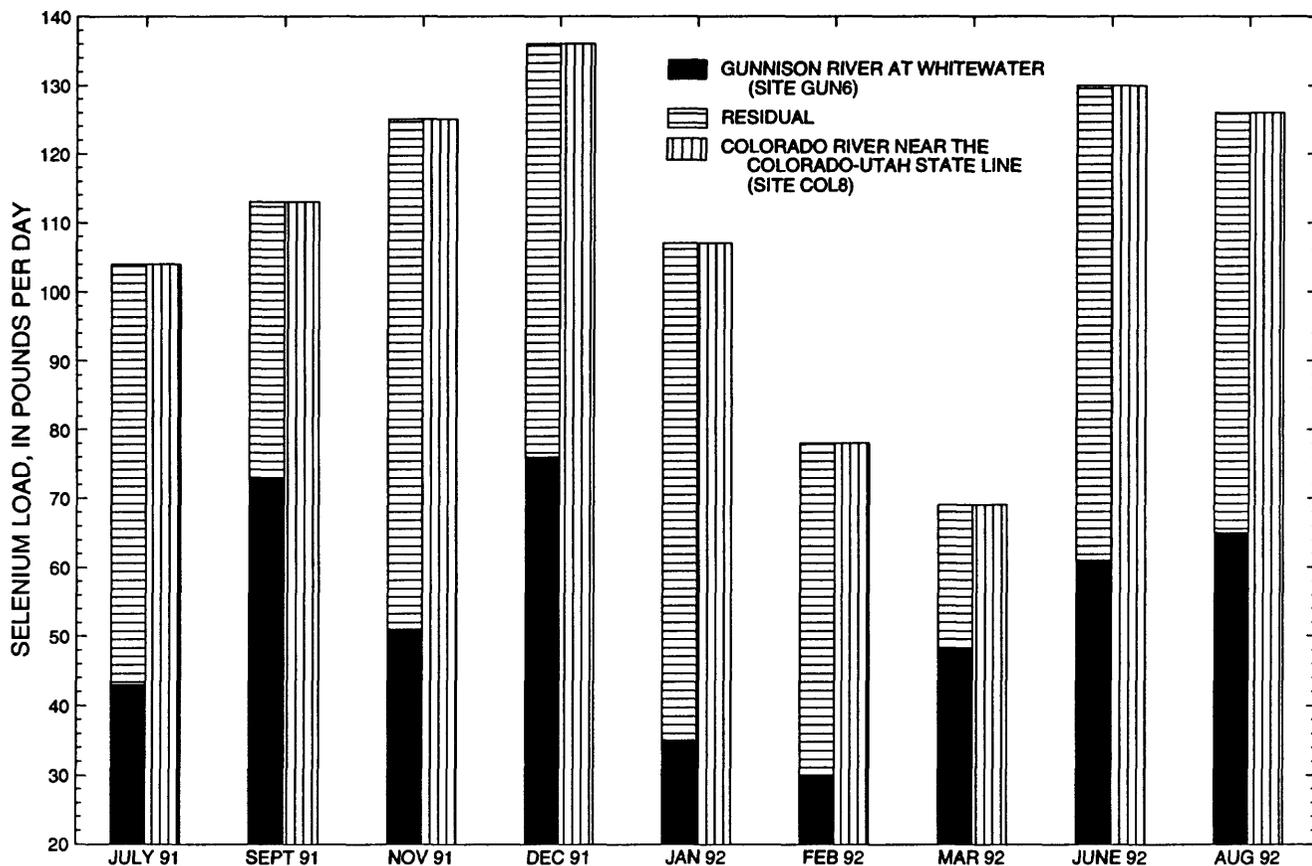


Figure 24. Selenium loads in the Gunnison River at Whitewater (site GUN6) and the Colorado River near the Colorado-Utah State line (site COL8), July 1991–August 1992, and the residual loads. (Only samples collected at both sites in the same week are shown. Residual is the selenium load at site COL8 minus the selenium load at site GUN6.)

loads for water years 1976–92. The selenium load in the Colorado River upstream from the Grand Valley accounted for about 9 percent, the Gunnison River about 43 percent, and the selenium load from the Grand Valley about 48 percent of the selenium load in the Colorado River at site COL8. The results for the Gunnison River and Grand Valley selenium loads for water years 1976–92 are comparable to the estimates for water years 1991–92.

### Distribution, Magnitude, and Variation of Selenium Concentrations

Distribution, magnitude, and variation of selenium concentrations are described for irrigated areas in the Uncompahgre Project and in the Grand Valley and in areas adjacent to the Uncompahgre Project. Selenium concentrations are compared to aquatic-life criteria established by the U.S. Environmental Protection Agency (1987).

Irrigation drainage is considered the groundwater component of water in streams, washes, canals, and ditches within the irrigated areas. Surface-return flow is defined as the irrigation water from field runoff and the excess water in the canals and laterals that was discharged into streams and washes during the irrigation season. Winter water is water that was diverted from streams into canals and laterals during the nonirrigation season (November–March) for livestock water supplies. Unused winter water also was discharged into the streams and washes and essentially is equivalent to surface-return flow.

### Uncompahgre Project Area

#### Tributaries, Canals, and Ditches

All water samples collected during the nonirrigation season from the east side of the Uncompahgre Project exceeded the chronic aquatic-life criterion of 5 µg/L and all but one sample exceeded the acute

criterion of 20 µg/L (table 16). Sampling sites are shown in schematic diagrams for the Uncompahgre Project in figures 25 and 26. The schematic diagrams show major streams, washes, canals, and miscellaneous ditches. Eight of the 11 irrigation-season samples from the eastern side that exceeded the acute criterion were monthly samples collected from Loutsenhizer Arroyo at site LZA1 (fig. 26). Selenium concentrations in about one-half the nonirrigation-season water samples from the western side exceeded 5-µg/L chronic criterion, but only three concentrations exceeded the 20 µg/L acute criterion. Although surface-return flow diluted selenium concentrations during the irrigation season, almost all selenium concentrations in irrigation-season samples from the eastern side exceeded the chronic aquatic-life criterion (table 16). The three samples from the eastern side that had selenium concentrations that did not exceed the chronic aquatic-life criterion were collected from Gretts, Markley, and Brozina Ponds (sites GTP, MKP, and BZP in fig. 26). The source water for these ponds is irrigation-supply water, surface-return flow, and irrigation drainage. Chemical and biological processes might remove some selenium from water in the ponds and immobilize the selenium in bottom sediment (Lemly and Smith, 1987).

Selenium concentrations were much higher in surface water on the eastern side of the Uncompahgre Project (east of the Uncompahgre River) than on the western side (table 16). The larger selenium concentrations on the eastern side of the Uncompahgre Project primarily are the result of geologic differences between the eastern and

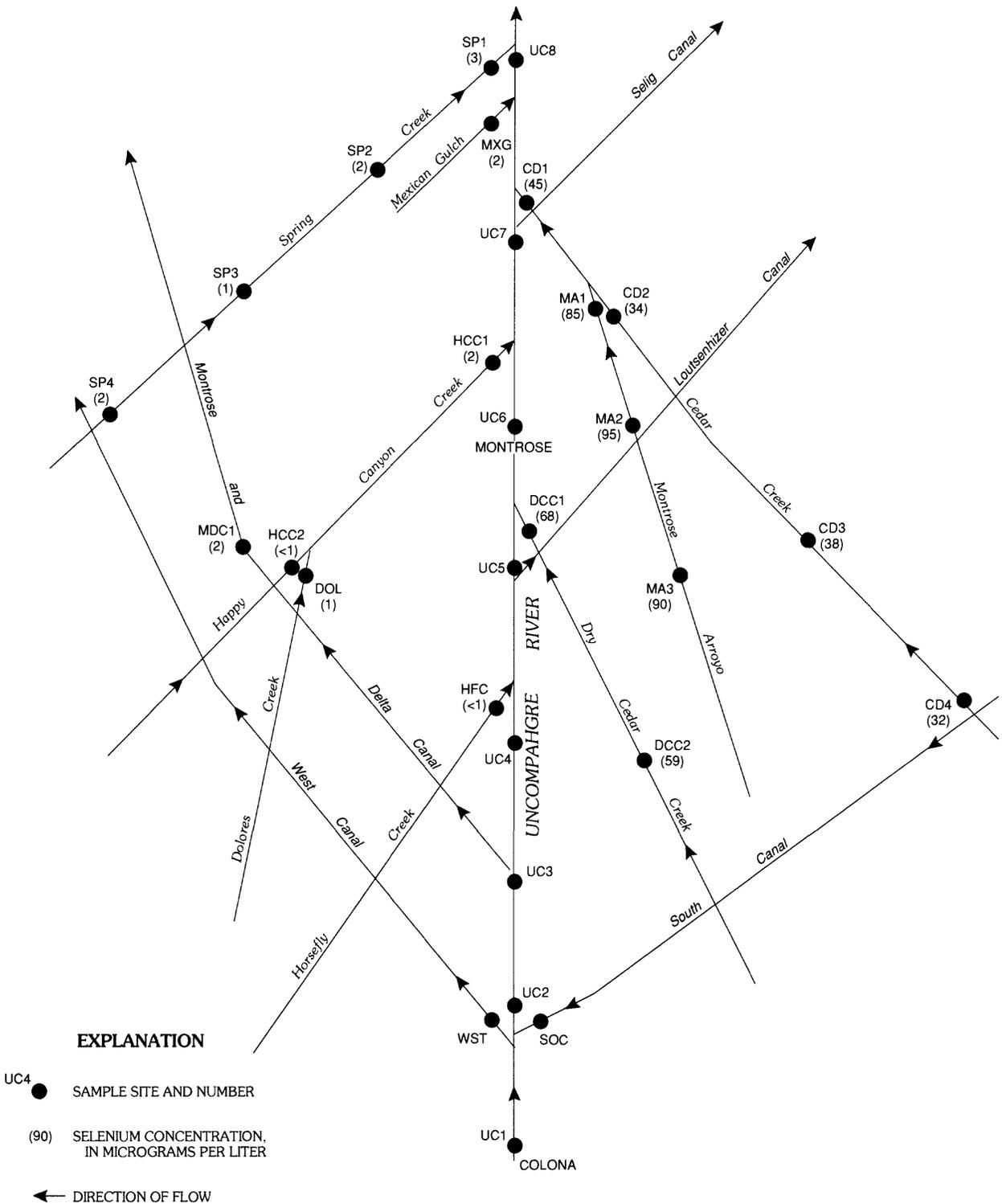
western sides (fig. 4). About 85 percent of the irrigated land on the eastern side is on soils primarily derived from Mancos Shale (adobe soils), but only about 4 percent of the irrigated land on the western side is on adobe soils (Bureau of Reclamation, 1982). Most of the irrigated land on the western side is on soils derived from terrace deposits and the Dakota Sandstone that probably contain none or small amounts of shale detritus. Geometric mean concentrations of total and water-extractable selenium were about 2 to 5 times greater for soils derived from the Mancos Shale than for soils derived from the Dakota Sandstone or terrace deposits (table 2).

An analysis of the distribution of selenium concentrations in the Uncompahgre Project during the nonirrigation season was done by examination of the data collected for the synoptic surveys in 1992. Selenium concentrations in samples collected for the synoptic surveys were much higher on the eastern side of the project than on the western side (table 17). Selenium concentrations in each sample collected during synoptic surveys are shown on the schematic diagrams in figures 25 and 26. Major drainage basins, selected ditches, and canals that had winter water were sampled during synoptic surveys. Excluding winter-water samples (coded WW in table 17), median selenium concentrations for synoptic-survey samples collected in the major drainage basins and geographical areas on the eastern side of the Uncompahgre Project ranged from 59 to 170 µg/L, compared to 1 to 16 µg/L for the western side of the project.

**Table 16.** Summary of selenium concentrations in irrigated areas of the Uncompahgre Project in 1991–92 and the number of samples that exceeded aquatic-life criteria of the U.S. Environmental Protection Agency

[Concentrations in micrograms per liter; west and east irrigated areas separated by the Uncompahgre River; irrigation-season samples were collected in July and October 1991 and April through August 1992; nonirrigation-season samples were collected from November 1991 through March 1992; chronic aquatic-life criterion is 5 micrograms per liter, and the acute criterion is 20 micrograms per liter (U.S. Environmental Protection Agency, 1987); <, less than]

Area	Season	Number of samples	Median	Range	Number of samples exceeding criteria	
					Chronic	Acute
West	Irrigation	14	1.5	<1–9	4	0
West	Nonirrigation	37	5	<1–55	18	3
East	Irrigation	36	11	2–56	33	11
East	Nonirrigation	36	105	19–260	36	35



**Figure 25.** Schematic diagram showing the southern part of the Uncompahgre Project, relative locations of surface-water-sampling sites, and selenium concentrations in samples collected during synoptic surveys, January–March, 1992.



**Table 17.** Summary of selenium concentrations in samples collected during the synoptic surveys of the Uncompahgre Project, January through March 1992

[Concentrations in micrograms per liter; (WW), winter-water samples; <, less than]

Drainage basin or canal	Number of sites	Sites included (figs. 25 and 26)	Median	Range
<b>AREAS WEST OF THE UNCOMPAHGRE RIVER</b>				
West Canal/Montrose and Delta Canal (WW)	4	WST, UC3, MDC1, MDC2	2.5	2-3
Ironstone Canal (WW)	3	UC9, IRC1, IRC2	11.5	8-16
Horsefly and Happy Canyon Creek Basins	4	HFC, HCC1, HCC2, DOL	1	<1-2
Spring Creek Basin and Mexican Gulch	5	SP1-SP4, MXG	2	1-3
Dry Creek Basin	7	DRY1-DRY5, CC1, CC2	7	<1-10
Miscellaneous ditches	5	UNBL, CAL, ASH, UND1, UND2	9.5	6-55
Cummings Gulch and Seep Creek Basins	5	CMG1, CMG2, BXG, SEP1, SEP2	16	10-23
Roubideau Creek Basin	5	RB1-RB3, BMC, WSC	4	<1-5
<b>AREAS EAST OF THE UNCOMPAHGRE RIVER</b>				
Selig Canal (WW)	3	UC7, SGC1, SGC2	9	5-12
Dry Cedar and Cedar Creek Basins	9	DCC1, DCC2, CD1-CD4, MA1-MA3	59	32-95
Loutsenhizer Arroyo Basin	8	LZA1-LZA5, WLZ1-WLZ3	170	100-230
Peach Valley Arroyo and unnamed drainage	5	PVA1, PVA2, RD1-RD3	88	19-200
Garnet Canal and Bonafide Ditch	7	GAR1-GAR4, UNGR, RFD, BFD	160	23-260

Perhaps one reason for lower selenium concentrations on the western side of the Uncompahgre Project during the nonirrigation season was dilution of subsurface-irrigation drainage by winter water. Winter water was discharged into all of the major tributaries on the western side of the Uncompahgre Project during collection of samples for the synoptic surveys in early 1992. The sole source of winter water in canals was water diverted from the Uncompahgre River. During the synoptic sampling in 1992, winter water was diverted only into the Selig Canal on the eastern side and into all three canals that serve the western side of the project (figs. 25 and 26). Analysis of the selenium concentrations in streams and in winter water (table 17) and of selenium concentrations in ground-water samples from the Dry and Spring Creek Basins does not indicate that dilution by winter water is the only cause of lower selenium concentrations on the western side during the nonirrigation season. The similarity of selenium concentrations between winter water and major streams on the western side (figs. 25 and 26; table 17) indicates that either most of the water in the streams consisted of winter water or that selenium concentrations in irrigation drainage that discharged into western-side streams and ditches were not markedly different than

concentrations in winter water. For example, a comparison of selenium concentrations in Dry Creek with concentrations in winter water in the Ironstone Canal and in the Montrose and Delta Canal was made using figures 25 and 26. The samples at sites IRC1, MDC1, and MDC2 were collected during the same 2 days as the samples from Dry Creek. Water samples from Dry Creek represented mixtures of irrigation drainage, winter water, and small quantities of natural flow. The selenium concentrations in Dry Creek at sites DRY1, DRY2, and DRY3 ranged from 8 to 11 µg/L in February (fig. 26), and these sites are downstream from the Ironstone Canal and its laterals. At site DRY4, which could only receive winter water from the Montrose and Delta Canal, the selenium concentration was 3 µg/L. The relatively high selenium concentrations (for the western side) in the Cummings Gulch and Seep Creek Basins (table 17) could partly be the result of transport of winter water into those basins by laterals from the Ironstone Canal.

The water samples from sites ASH, UNBL, and SEP2 (fig. 26) were the only samples from the western side in which selenium concentrations (23 to 55 µg/L) were substantially greater than concentrations in winter water. Most of the water sampled at these

three sites was assumed to be irrigation drainage because of the small stream discharges (less than  $0.5 \text{ ft}^3/\text{s}$ ) and because dissolved-solids concentrations were much higher in these drainages than in winter water diverted from the Uncompahgre River. Those three sites are near or in areas where soils could contain detritus from the Mancos Shale. Although irrigation drainage from Mancos Shale areas on the western side can contain substantial selenium concentrations, areas on Mancos Shale represent only about 4 percent of the irrigated area west of the Uncompahgre River.

The highest selenium concentrations during the nonirrigation season on the eastern side of the Uncompahgre Project generally were in the Loutsenhizer Arroyo Basin, in an unnamed drainage near Read, and in the Garnet Canal area (fig. 26; table 17). The small amount of winter water in the Selig Canal ( $7.5 \text{ ft}^3/\text{s}$  in March 1992) probably did not have a major effect on selenium concentrations in streams on the eastern side of the project. The synoptic-survey data (figs. 25 and 26) indicate that selenium concentrations on the eastern side of the Uncompahgre Project had large variability among sites and within drainage basins during the nonirrigation season. For example, the maximum selenium concentration in surface-water samples collected in 1991–92 in the Uncompahgre Project area was  $260 \text{ }\mu\text{g/L}$  for site RFD, and a sample collected from a nearby natural drainage at site UNGR had  $200 \text{ }\mu\text{g/L}$  of selenium (fig. 26). By contrast, the synoptic-survey sample collected from the Garnet Canal at site GAR3 (fig. 26), about 2 mi southwest of site RFD, had only  $23 \text{ }\mu\text{g/L}$  of selenium. The synoptic-survey samples were collected within a 2-day period in March 1992 at sites RFD, UNGR, and GAR3, and the sole water source at those sites was subsurface-irrigation drainage. There also were major differences in selenium concentrations in the Cedar Creek and Loutsenhizer Arroyo Basins (figs. 25 and 26).

Water from the Garnet Canal is used to keep Sweitzer Lake full during the year. During the irrigation season, water from the Uncompahgre River and Loutsenhizer Arroyo is used to fill the Garnet Canal. Historically, there were periods of insufficient flow in the Uncompahgre River at the Garnet diversion to fill the canal during the irrigation season. Therefore, a diversion from Loutsenhizer Arroyo is used (at site LZAM in fig. 26) to divert some of the water in

the arroyo into the Garnet Canal to supplement the river diversion. During the nonirrigation season, the river diversion is closed, and a small quantity of water from Loutsenhizer Arroyo usually flows into the canal and is discharged into Sweitzer Lake. As a result, irrigation drainage having some of the highest selenium concentrations in the Uncompahgre Project area discharges into Sweitzer Lake.

Selenium concentrations seem to be further increased in the Garnet Canal upstream from Sweitzer Lake by the discharge of irrigation drainage that contains high selenium concentrations into the canal between site GAR1 and the diversion into Sweitzer Lake at site GAR2. The water sample collected in March 1992 at site GAR1 consisted solely of water diverted from Loutsenhizer Arroyo. The selenium concentration increased from  $160$  to  $240 \text{ }\mu\text{g/L}$  between sites GAR1 and GAR2 (fig. 26), and the discharge in the canal increased by about  $0.4 \text{ ft}^3/\text{s}$ . In March 1993, two drainage ditches located about 0.4 mi south of Sweitzer Lake at sites DR1 and DR2 (fig. 26) were sampled. Site DR1 is on a small ditch draining a seep area near the canal, and site DR2 is on a drainage ditch that extends to the east and southeast of the Garnet Canal. Both ditches discharge directly into the canal. On March 2, 1993, a sample from site DR2 had a selenium concentration of  $600 \text{ }\mu\text{g/L}$ . On March 24, a sample from site DR1 had a selenium concentration of  $73 \text{ }\mu\text{g/L}$ , and a sample from site DR2 had a concentration of  $520 \text{ }\mu\text{g/L}$ . The selenium concentrations for site DR2 were much higher than the maximum selenium concentration of  $260 \text{ }\mu\text{g/L}$  (at site RFD) for the surface-water samples collected in 1991–92 in the Uncompahgre Project area. Stream discharge at site DR1 was about  $0.01 \text{ ft}^3/\text{s}$  and at site DR2 about  $0.10 \text{ ft}^3/\text{s}$ . Visual observations of flow in the Garnet Canal seem to indicate that various reaches in the canal upstream and downstream from sites DR1 and DR2 were gaining or losing water. Apparently, discharge of irrigation drainage from the drainage ditch at site DR2 and from nonpoint seepage into the canal caused the higher selenium concentrations in the Garnet Canal at the Sweitzer Lake diversion (site GAR2) than in the canal at site GAR1.

Selenium concentrations in eastern-side drains were much lower during the irrigation season compared to the nonirrigation season (sites CD1, LZA1, and RD1 in fig. 27). Large quantities of surface irrigation-return flow dilute selenium concentrations in eastern-side drains during the irrigation

season. Stream discharges measured at the time of sampling were about 5 to 15 times greater during the irrigation season than during the nonirrigation season for the samples shown in figure 27. The ranges of instantaneous stream discharges measured in eastern-side streams were 15.4 to 215 ft<sup>3</sup>/s for Cedar Creek (11 measurements at site CD1), 13.3 to 109 ft<sup>3</sup>/s for Loutsenhizer Arroyo (13 measurements at site LZA1), and 4.9 to 76 ft<sup>3</sup>/s for the unnamed drainage near Read (6 measurements at site RD1). Despite the dilution effect by surface-return flows during the irrigation season, selenium concentrations in all water samples from Loutsenhizer Arroyo at site LZA1 exceeded the acute aquatic-life criterion of 20 µg/L (U.S. Environmental Protection Agency, 1987) (fig. 27).

Selenium concentrations had much less seasonal variation in western-side streams than in eastern-side streams, as indicated by the small range of concentrations (4 to 10 µg/L) in Dry Creek at site DRY1 (fig. 27). The range in stream discharge for 11 instantaneous stream-discharge measurements at site DRY1 (July 1991 to June 1992) was 51.9 to 200 ft<sup>3</sup>/s. Selenium concentrations were only slightly lower in the samples collected in July 1991 compared to samples collected in the winter of 1992 at the outflow sites on Horsefly Creek (site HFC), Happy Canyon Creek (site HCC1), Spring Creek (site SP1), Cummings Gulch (site CMG1), and Roubideau Creek (site RB1), although stream discharge averaged about five times greater for samples collected in July 1991 than for samples from the winter of 1992.

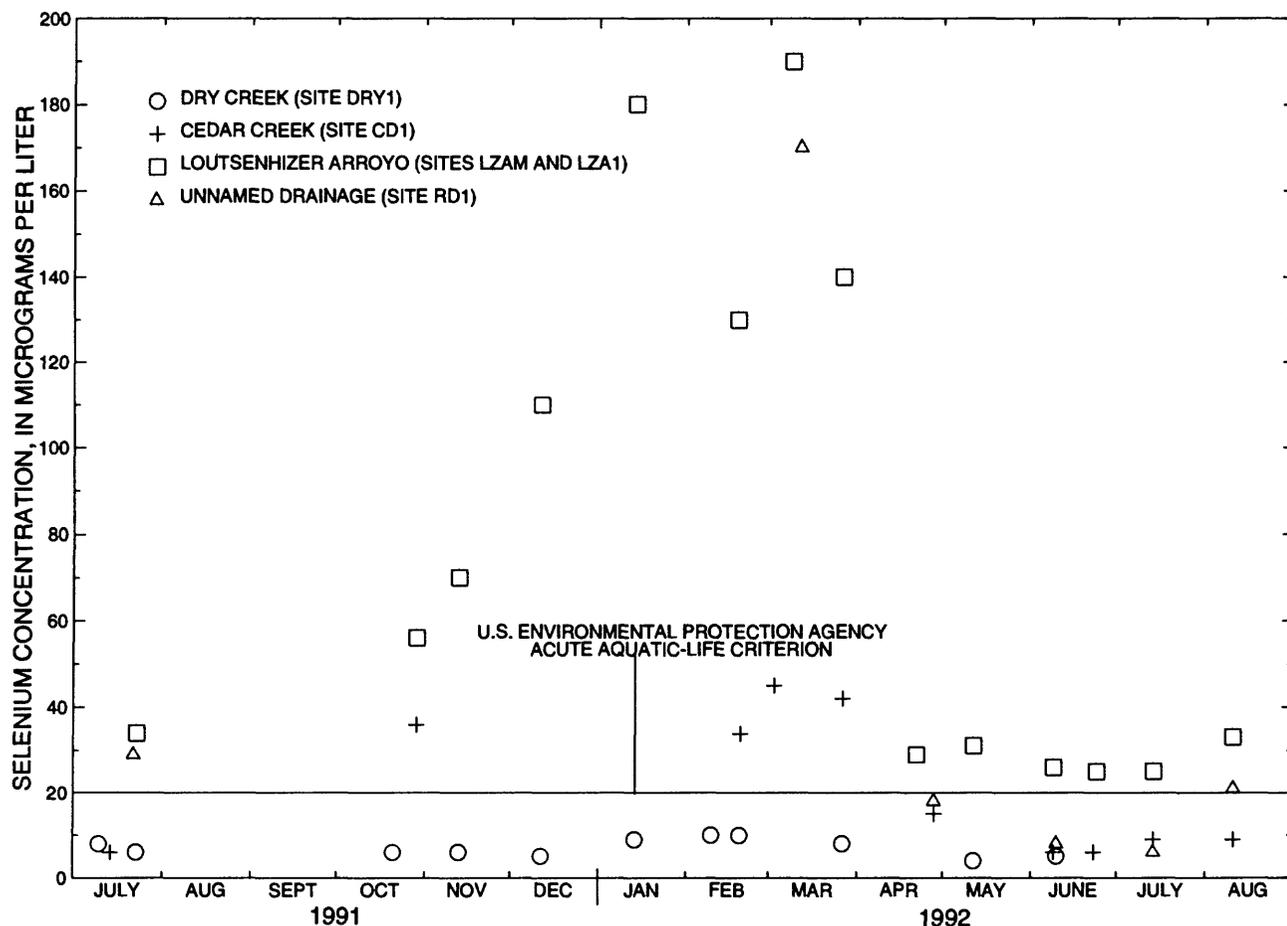


Figure 27. Selenium concentrations in samples from Dry Creek at site DRY1, Cedar Creek at site CD1, Loutsenhizer Arroyo at sites LZAM and LZA1, and an unnamed drainage at site RD1, July 1991–August 1992.

## Uncompahgre River

Samples were collected approximately monthly from May 1991 to August 1992 at the outflow site for the Uncompahgre River at Delta (site UC16 in fig. 26), and all selenium data collected at site UC16 since 1987 are shown in figure 28. The median selenium concentration in the Uncompahgre River at site UC16 was 15 µg/L. Concentrations generally were higher during the nonirrigation season (November through March) than during the irrigation season. Selenium concentrations throughout the Uncompahgre Project would have been diluted during the irrigation season because of the import of about 1,000 ft<sup>3</sup>/s of water from the Gunnison River that had less than 1 µg/L of selenium. Except for two samples, selenium concentrations in water samples collected at site UC16 exceeded the chronic criterion for aquatic life (5 µg/L), and seven of the concentrations exceeded the acute criterion of 20 µg/L (fig. 28). By comparison, the median selenium concentration for 14 samples collected during 1987–92 from the Uncompahgre River at Colona (site UC1 in fig. 25), which is upstream from irrigated areas of the Uncompahgre Project, was 1 µg/L, and the maximum concentration was 2 µg/L.

Results of a gain-loss study of the Uncompahgre River on February 19–20, 1992, indicated that selenium concentrations increased noticeably in only 3 of the 15 sampled reaches between sites UC1 and UC16 (fig. 29). Stream discharge was measured and water samples were collected at 16 sites on the Uncompahgre River (fig. 29). Relative locations are shown in figures 25 and 26. Winter-water diversions from the Uncompahgre River were measured and sampled at site WST (West Canal at Highway 550), site UC3 (Montrose and Delta Canal), site UC7 (Selig Canal), and site UC9 (Ironstone Canal). The three reaches of the river that had conspicuous increases in selenium concentrations coincided with inflow from Dry Cedar Creek (reach UC5–UC6), Cedar Creek (reach UC7–UC8), and Loutsenhizer Arroyo (reach UC12–UC13) (figs. 25, 26, and 29). Inflow from western-side streams either caused no change in selenium concentrations or diluted the concentrations in the Uncompahgre River. The large decrease in concentration between sites UC14 and UC15 was caused by Dry Creek, which almost doubled the stream discharge of the Uncompahgre River. Data collected for the gain-loss study indicated

that the largest selenium concentrations in the Uncompahgre River occurred in the reach between Loutsenhizer Arroyo and Dry Creek and not at the outflow site in Delta (site UC16).

## Adjacent Areas in the Lower Gunnison River Basin

Selenium data were collected once, in July 1991, in selected drainage basins in the lower Gunnison River Basin to document selenium concentrations in irrigated areas adjacent to the Uncompahgre Project. Samples were collected from five streams draining irrigated areas in the lower Gunnison River Basin: Smith Fork (site SMF), North Fork (site NFK1), Currant Creek (site CRC), Alfalfa Run (site AFR), and Tongue Creek (site TGC) (fig. 23). Since December 1990, the USGS has collected periodic selenium data at a gaging station on lower Leroux Creek (fig. 23), which drains irrigated areas in the lower North Fork Basin. Selenium was not detected in water samples from the Smith Fork nor in Alfalfa Run (fig. 23). Selenium was detected in samples from the North Fork (4 µg/L), Currant Creek (19 µg/L), and Tongue Creek (6 µg/L). The range of selenium concentrations in nine samples from Leroux Creek was 7 to 21 µg/L. Although many of the samples were collected in summer, the samples collected at the latter four sites were at relatively low stream discharge. Upstream diversions for irrigation depleted water in the lower North Fork, Leroux, Currant, and Tongue Creek Basins during summer.

## Grand Valley

There was a large range of selenium concentrations in irrigated areas of the Grand Valley (table 18). The samples summarized in table 18 include all samples collected from streams, washes, drainage ditches, and ponds located in irrigated areas of the Grand Valley, excluding the Colorado River. Sampling sites are shown on the schematic diagrams in figures 30 and 31. Selenium concentrations in samples collected during the nonirrigation season in the Grand Valley exceeded the chronic aquatic-life criterion of 5 µg/L (U.S. Environmental Protection Agency, 1987) in 73 of 76 samples, and selenium concentrations exceeded the acute criterion of 20 µg/L in about 82 percent of the samples (table 18).

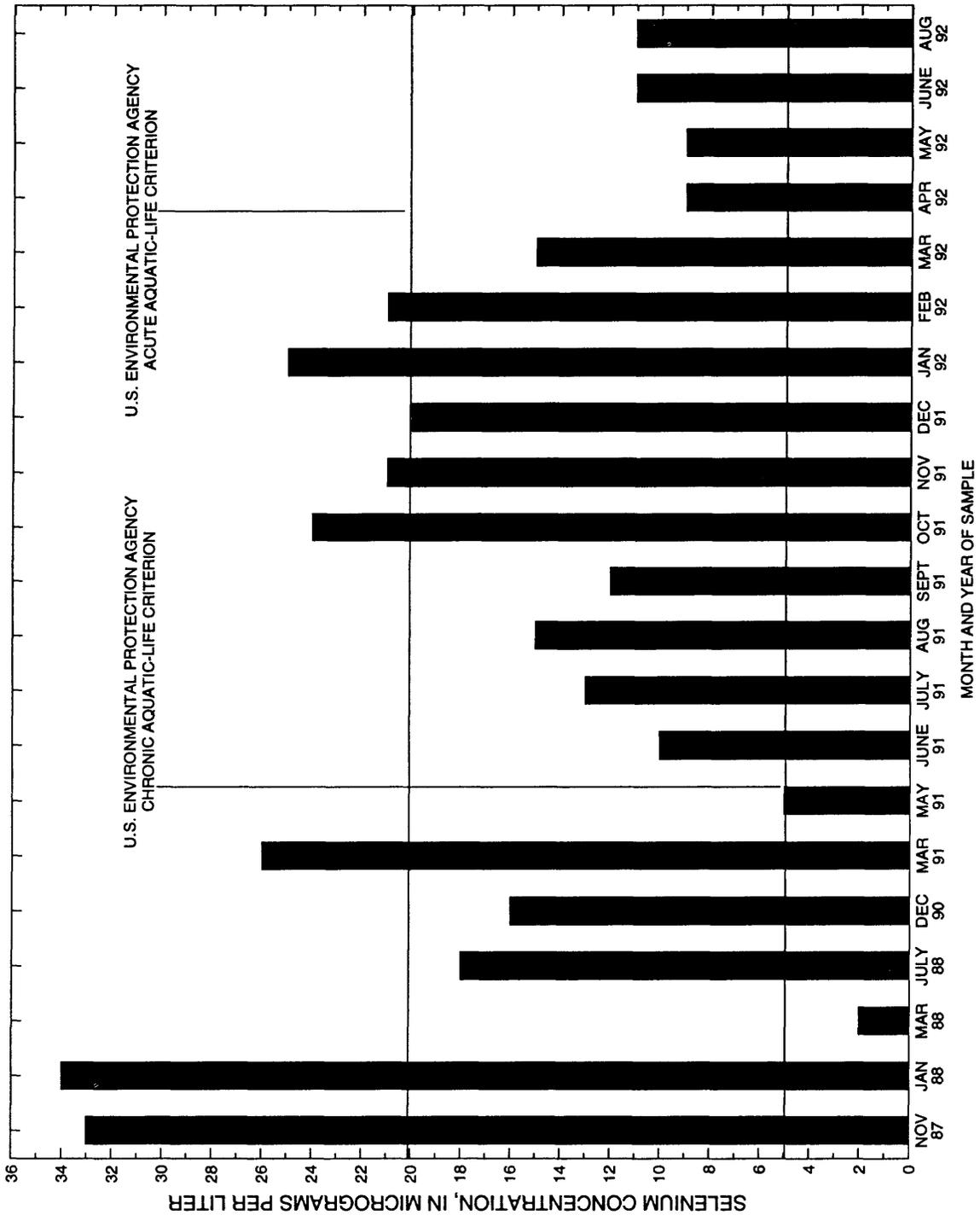


Figure 28. Selenium concentrations in the Uncompahgre River at Delta (site UC16), 1987-92.

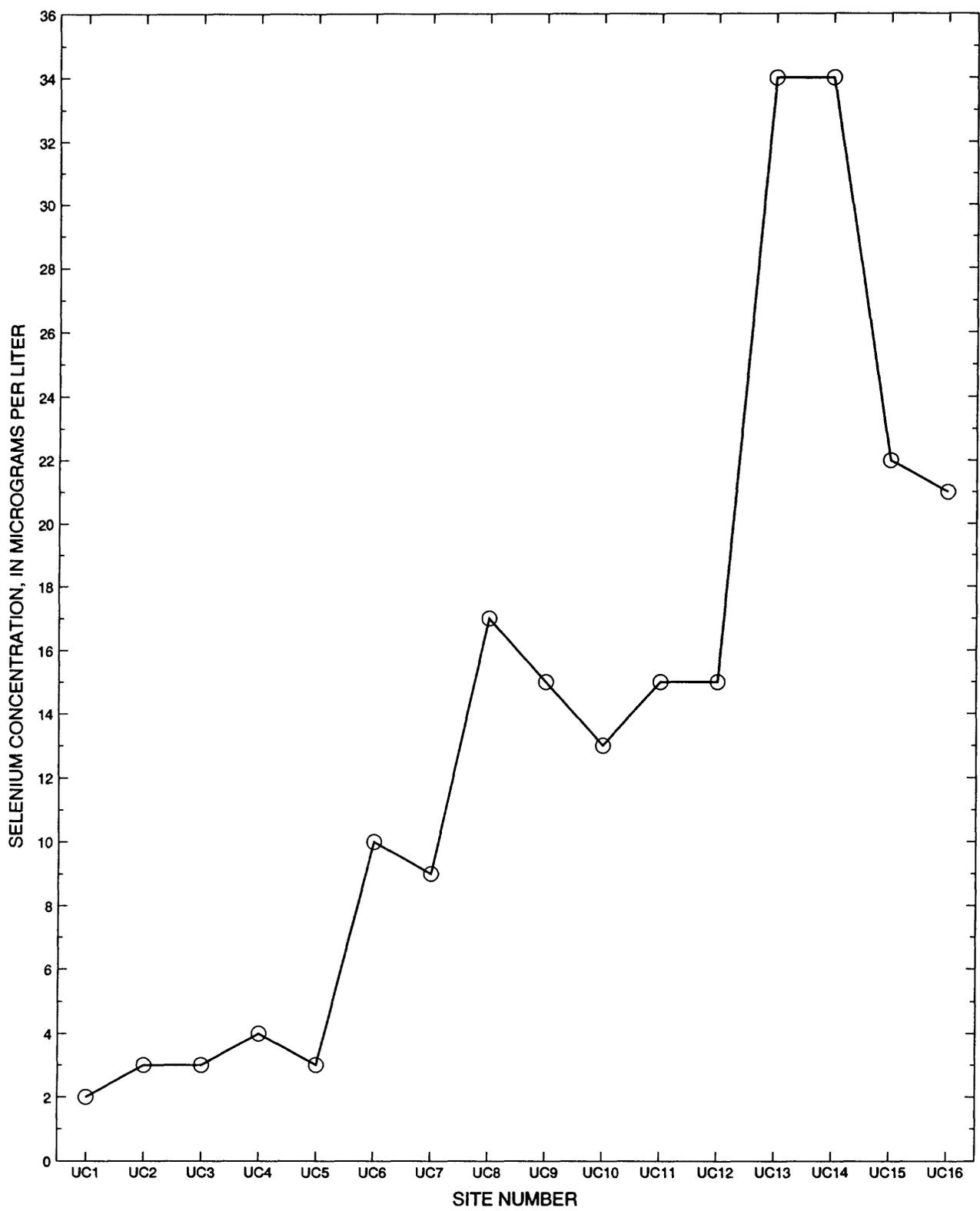


Figure 29. Selenium concentrations in the Uncompahgre River, February 19–20, 1992.

Selenium concentrations in about 84 percent of the samples collected during the irrigation season exceeded the chronic criterion. Surface-water samples (excluding ponds) collected in the Grand Valley during the nonirrigation season probably are representative of irrigation-drainage discharge. Three water samples collected in June 1991 and 1992 from ponds RDP and MWP (fig. 30) had selenium concentrations equal to the chronic criterion of 5 µg/L.

Selenium concentrations were much higher in irrigation drainage than in the irrigation-supply water from the Colorado River or in water at reference sites, which are upstream from the irrigated area. The median selenium concentration was 1 µg/L in water samples from site COL2 on the Colorado River (table 15) upstream from the Grand Valley. Selenium concentrations ranged from 1 to 6 µg/L in five samples from reference sites on West Salt Creek (site WSC2), East Salt Creek (site ESC3), and Big Salt Wash (site BSW3) (site locations in fig. 30).

**Table 18.** Summary of selenium concentrations in irrigated areas in the Grand Valley and the number of samples that exceeded aquatic-life criteria of the U.S. Environmental Protection Agency

[Concentrations in micrograms per liter; irrigation-season samples collected in August through October 1991 and April through August 1992; nonirrigation-season samples collected in March 1991 and from November 1991 through March 1992; chronic aquatic-life criterion is 5 micrograms per liter, and the acute criterion is 20 micrograms per liter (U.S. Environmental Protection Agency, 1987); <, less than]

Season	Number of samples	Median	Range	Number of samples exceeding criteria	
				Chronic	Acute
Irrigation	44	10	<1-58	37	7
Nonirrigation	76	50	1-380	73	62

There are large differences in selenium concentrations between adjacent drainage basins in the Grand Valley. A comparison of the mean selenium concentrations in samples collected in March 1991 and in February and March 1992 for the 20 reconnaissance sites is shown in figure 32. Relative locations of the 20 sites are shown in figures 30 and 31. Some of the highest selenium concentrations were at outflow sites in some of the larger drainage basins within the irrigated area, such as sites SC (Salt Creek), site RW1 (Reed Wash), and site LC1 (Leach Creek). Larger streams also tended to have the largest stream discharges for the 20 reconnaissance sites.

The median concentration of the samples collected in March 1991 at the 20 sites was 28.5 µg/L, but the discharge-weighted mean concentration was 77 µg/L; for the samples collected in February and March 1992, the median concentration was 36.5 µg/L, but the discharge-weighted mean concentration was 74 µg/L.

The selenium concentrations in samples collected for synoptic surveys in February and March 1992 indicate a highly variable distribution of selenium concentrations in irrigation drainage in the Grand Valley. For the synoptic surveys of the Grand Valley in 1992, 44 sites were sampled, including the 20 reconnaissance sites that were sampled in 1991. The synoptic-survey data are shown in figures 30 and 31 and are summarized by geographical areas in table 19. The synoptic data are assumed to represent selenium concentrations in irrigation drainage in the Grand Valley. The synoptic samples were collected when natural runoff was nonexistent or minimal, and there were no diversions for winter water. On an areal basis, the highest median selenium concentrations in the Grand Valley were in the Salt Creek and Reed Wash Basins, which drain the western part of the irrigated area (fig. 30, table 19). The lowest median selenium concentrations were for the Redlands and Orchard Mesa areas (table 19). The Redlands area and Orchard Mesa are on terrace deposits overlying Mancos Shale, and there would be less selenium in the terrace deposits.

The synoptic-survey data indicated variable selenium concentrations within some of the major tributary basins. In the Salt Creek Basin, selenium concentrations in East Salt Creek (site ESC1) were more than twice as high as in West Salt Creek (site WSC1) or in Mack Wash (site MW1) (fig. 30). Water samples from the outflow site on Reed Wash (site RW1) represented mixtures of irrigation drainage in the Reed Wash Basin that had variable selenium concentrations. The selenium concentration of 260 µg/L for the East Branch of Reed Wash (site RWEB) was much higher than concentrations in Peck and Beede Wash (site RWPB) or in an unnamed tributary at site RWTR (fig. 30). The maximum selenium concentration reported in a Grand Valley surface-water sample was 380 µg/L in the sample collected in the nonirrigation season at site RW4 on upper Reed Wash. Site RW4 also had the largest selenium concentration of irrigation-season samples. However, the stream discharge at site RW4 was less than 1 percent of the stream discharge in Reed Wash at site RW1.

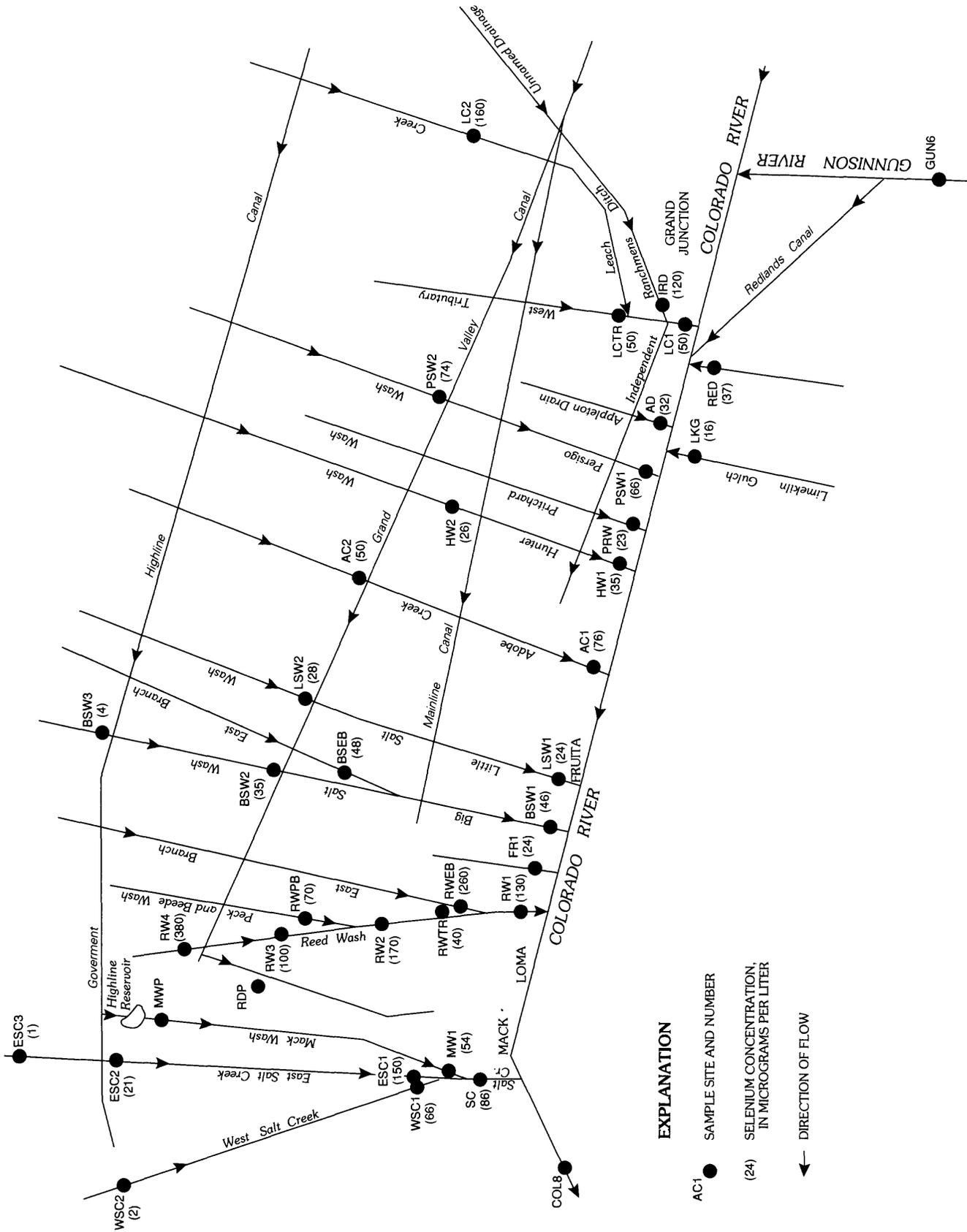


Figure 30. Schematic diagram showing the western part of the Grand Valley, relative locations of surface-water-sampling sites, and selenium concentrations in samples collected during synoptic surveys, February–March 1992.



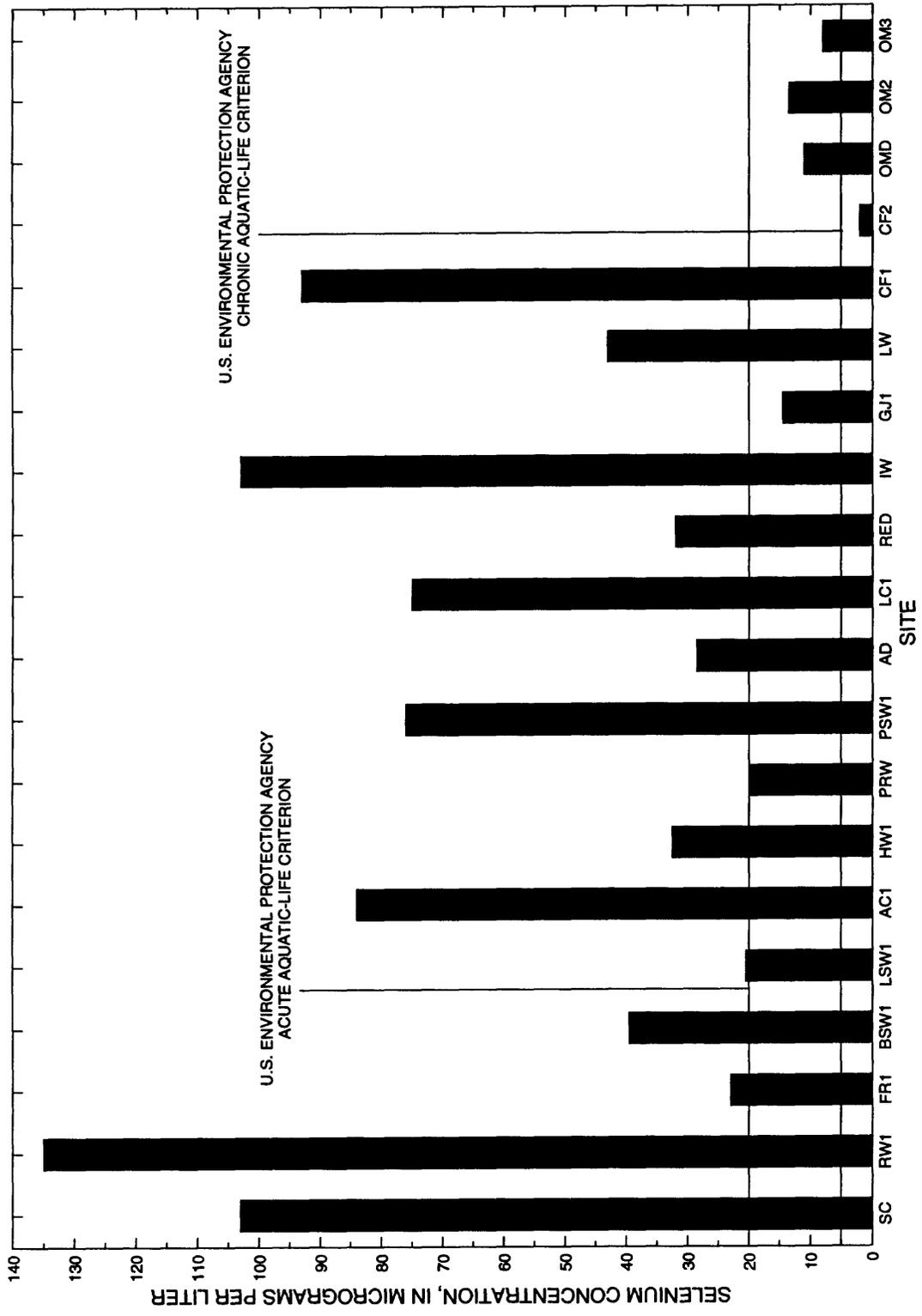


Figure 32. Mean selenium concentrations in irrigation-drainage samples collected in March 1991 and in February and March 1992 at the 20 reconnaissance sites in the Grand Valley.

**Table 19.** Summary of selenium concentrations in samples collected during the synoptic surveys of the Grand Valley, February and March 1992

[Concentrations in micrograms per liter; reference sites not included]

Drainage basin or area	Number of sites	Sites included (figs. 30 and 31)	Median	Range
Salt Creek and Reed Wash Basins	12	WSC1, ESC1, ESC2, SC, MW1, RW1–RW4, RWTR, RWPB, RWEB	115	21–380
Big Salt and Little Salt Wash Basins and miscellaneous ditches	6	FR1, BSW1, BSW2, BSEB, LSW1, LSW2	31.5	24–48
Area west of Grand Junction and east of Fruita	12	AC1, AC2, HW1, HW2, PRW, PSW1, PSW2, AD, LC1, LC2, LCTR, IRD	50	23–160
Redlands area	2	RED, LKG	26.5	16–37
Area east of Grand Junction to Clifton area	7	IW, GJ1–GJ3, LW, CF1, CF2	44	1–110
Orchard Mesa area	5	OMD, OM1–OM4	11	5–30

Another area of apparently higher selenium concentrations in the Grand Valley is drained by upper Leach Creek (site LC2) and by an unnamed wash (fig. 30) adjacent to the Leach Creek Basin. The unnamed wash becomes the Independent Ranchmens Ditch where the wash intersects the Grand Valley Canal, and the ditch discharges into Leach Creek at site IRD (fig. 30). Much of the eastern part of the Leach Creek Basin and the area drained by the unnamed wash are residential and commercial areas. Samples also were collected at multiple sites in several other drainage basins in the western part of the Grand Valley, but large differences among selenium concentrations were not apparent (fig. 30).

Selenium concentrations were variable in the sampled washes and ditches between Grand Junction and the Clifton area (fig. 31). Selenium concentrations in Indian Wash (site IW) were considerably higher than the concentrations in three unnamed drainage ditches (sites GJ1, GJ2, and GJ3 in fig. 31). Site CF2, on an unnamed drainage ditch east of Clifton, had the lowest selenium concentrations in surface-water samples from irrigated areas in the Grand Valley; however, selenium concentrations were much higher in another unnamed drainage ditch at site CF1, which is located about 2 mi southwest of site CF2 (fig. 31).

Selenium concentrations were much lower in irrigation-season samples compared to the nonirrigation-season samples in the Grand Valley; these seasonal differences were similar to the seasonal differences in selenium concentrations for surface water on the eastern side of the Uncompahgre Project. Seasonal distribution of selenium concentrations are shown for three frequently sampled sites in the Grand Valley in figure 33. Large quantities of surface-return flow from canals, laterals, ditches, and field runoff are discharged into streams and washes during the irrigation season, which dilute selenium concentrations in irrigation-drainage water. Historical stream-discharge data for discontinued gaging stations on eight streams and washes in the Grand Valley (data collected in water years 1973–83) indicated that 86 to 95 percent of the annual stream discharge occurred during the irrigation season (April through October). The median selenium concentration for the irrigation-season samples collected from August 27 to September 4, 1991, at the 20 reconnaissance sites was 8.5 µg/L, compared to 28.5 µg/L for nonirrigation-season samples collected in March 1991 and 36.5 µg/L for nonirrigation-season samples collected in February 1992 at the same 20 sites. Despite dilution during the irrigation season, selenium concentrations in most surface-water samples collected during the irrigation season in the Grand Valley exceeded the chronic aquatic-life criterion (table 18). Four of the eight samples collected at site RW1 on

Reed Wash (fig. 33) during the irrigation season exceeded the acute aquatic-life criterion of 20 µg/L (U.S. Environmental Protection Agency, 1987).

At least 96 percent of the dissolved selenium in samples collected on March 24, 1992, from five streams in the Grand Valley was selenate (table 20). Selenate is the most soluble form of selenium and is stable in alkaline and oxygenated conditions (Presser and others, 1990). Field measurements of pH were greater than 7.5, and dissolved oxygen usually was near saturation in all water samples from streams, washes, and ditches in the Grand Valley. The selenium-speciation results infer that once selenium is discharged by ground water (irrigation drainage) into the oxygenated environment of the streams, selenium remains in solution as selenate

and is transported out of the irrigated areas into the Colorado River. The selenate and selenite data for the five Grand Valley tributaries were used for risk-assessment analysis for endangered fish (described later in the report in the "Risk Assessment for Endangered Fish from Selenate and Selenite" section).

### Magnitude and Variation of Selenium loads

The magnitude and variation of selenium loads in irrigated areas of the Uncompahgre Project and in the Grand Valley are discussed in this section. Selenium-load data are used to describe major source areas of selenium from the irrigated areas.

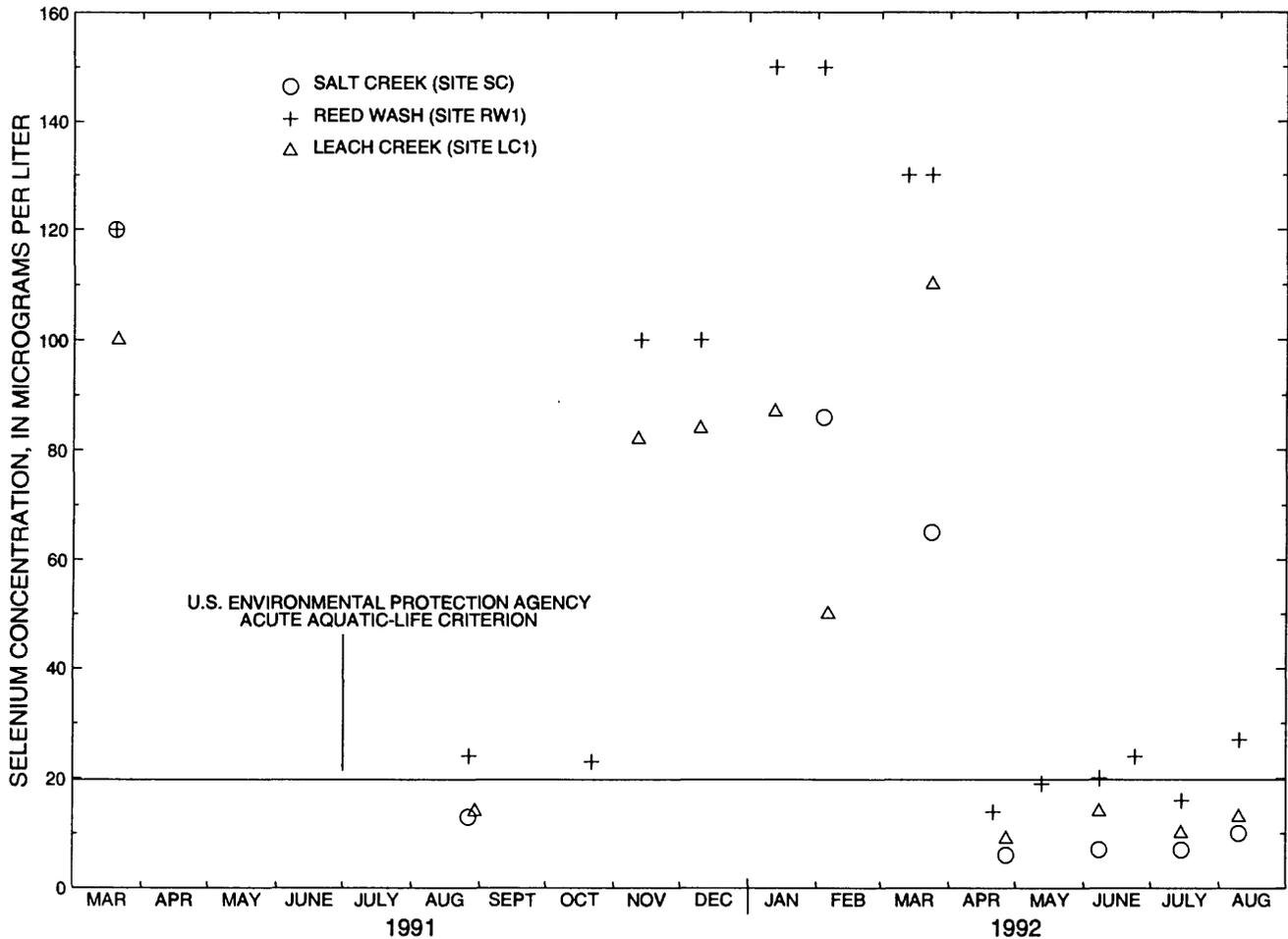


Figure 33. Selenium concentrations in samples from Salt Creek at site SC, Reed Wash at site RW1, and Leach Creek at site LC1, March 1991–August 1992.

**Table 20.** Concentrations of dissolved selenium, selenate, and selenite in water samples collected from five streams in the Grand Valley, March 24, 1992

[Concentrations in micrograms per liter; data from Roger Fujii (U.S. Geological Survey, written commun., 1992); sites shown in figs. 30 and 31]

Site number	Stream name	Dissolved selenium	Selenate selenium	Selenite selenium	Percent selenate
SC	Salt Creek	72.8	71.7	1.1	98.5
RW1	Reed Wash	126.2	126.2	0	100.0
AC1	Adobe Creek	74.8	72.5	2.3	96.9
LC1	Leach Creek	85.6	83.4	2.2	97.4
IW	Indian Wash	86.1	82.8	3.3	96.2

### Uncompahgre Project Area

The gain-loss study of the Uncompahgre River on February 19–20, 1992, indicated that the selenium load increased 13.4 lb/d between Colona (site UC1) and Delta (site UC16), which was 96 percent of the load at Delta (fig. 34). Relative locations of the sampling sites on the Uncompahgre River and on tributaries are shown in figures 25 and 26. The actual gain in selenium load probably was greater than 13.4 lb/d because some of the selenium load in winter water that was diverted from the Uncompahgre River was not measured at site UC16. Winter water is lost by consumptive use, canal and lateral seepage, and part of the unused winter water was discharged into the Gunnison River between Cummings Gulch and Roubideau Creek (fig. 26). Winter-water diversions were made upstream from site UC2 (West Canal) and immediately downstream from site UC3 (Montrose and Delta Canal), site UC7 (Selig Canal), and site UC9 (Ironstone Canal).

Much of the increase in selenium load in the Uncompahgre River between Colona and Delta occurred in 4 of the 15 sampled reaches. Much of the gain in selenium load in reach UC5–UC6 (fig. 34) is from Dry Cedar Creek (site DCC1 in fig. 25), which accounted for about 50 percent of the load at UC6. Cedar Creek (site CD1) accounted for about 93 percent of the increase in selenium load between sites UC7 and UC8 and for about 74 percent of the selenium load at site UC8. The largest increase in selenium load occurred in the reach between sites UC12 and UC13. Loutsenhizer Arroyo (site LZAM in fig. 26) discharges into the

Uncompahgre River between sites UC12 and UC13, and the load at site LZAM was 1.7 lb/d greater than the difference in loads between sites UC13 and UC12. That difference could result from errors in discharge measurements or in the selenium analyses. Loutsenhizer Arroyo accounted for about 90 percent of the gain in dissolved-solids load in reach UC12–UC13; a reasonable assumption is that at least 90 percent of the gain in selenium load in reach UC12–UC13 was from Loutsenhizer Arroyo. The selenium load from Dry Creek (site DRY1) accounts for much of the gain in reach UC14–UC15. Some of the selenium load in Dry Creek in February 1992 was from return flow of winter water that was discharged from the Ironstone Canal and its laterals.

Selenium loading into other reaches of the Uncompahgre River were relatively small. Stream reaches that had a decrease in selenium load (fig. 34) either lost water to alluvium or had winter-water diversions. Based on mass-balance calculations for reaches where selenium loads increased, unaccounted inflow of water containing higher selenium concentrations might be discharging into reaches UC8–UC9, UC10–UC11, and UC13–UC14. The selenium concentrations computed by mass-balance differences ranged from 23 to 52  $\mu\text{g/L}$  in unaccounted inflows for these three reaches. Those concentrations were higher than selenium concentrations in winter water, which infers that part of the gain of selenium load in the three reaches was from ground-water discharge into the Uncompahgre River and not from return flow of winter water.

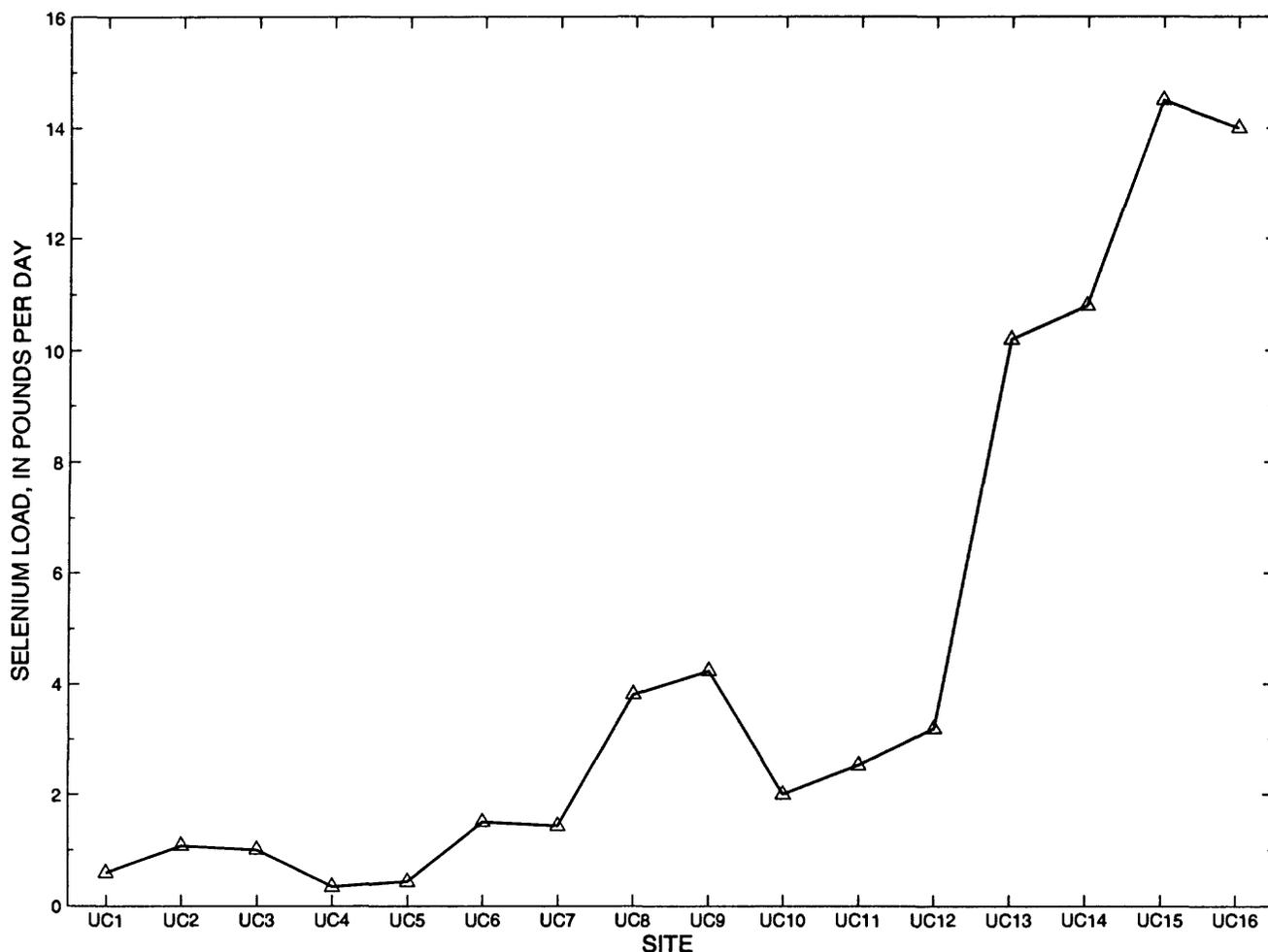


Figure 34. Selenium loads in the Uncompahgre River, February 19–20, 1992.

The mean selenium load in the Uncompahgre River at site UC16 for 20 samples collected in water years 1991–92 was 18.7 lb/d. A seasonally weighted mean was computed by weighting the mean selenium load for irrigation-season samples (April through October) and the mean load for the nonirrigation-season samples (November through March) according to the fraction of the year that each season composes (0.59 for irrigation, 0.41 for nonirrigation). The seasonally weighted mean selenium load was equal to the mean selenium load for the Uncompahgre River at site UC16 (water years 1991–92), which indicates that there were no large differences in selenium loads between the irrigation season and nonirrigation season in the Uncompahgre River.

The largest selenium loads in tributary streams are on the eastern side of the Uncompahgre Project, and the largest seasonally weighted mean selenium load was 14.0 lb/d for Loutsenhizer Arroyo at site LZA1. The seasonally weighted mean selenium loads for all samples collected at outflow sites on 12 tributary streams or canals draining the Uncompahgre Project are shown in figure 35. Because of canal diversions on the Uncompahgre River, part of the selenium load discharging from the Dry Cedar and Cedar Creek Basins on the eastern side of the project is rediverted into canals near or downstream from Montrose (figs. 25 and 26). The rediversion of considerable quantities of surface-return flow and irrigation drainage from the Uncompahgre River for

irrigation-supply water complicates the determination of the total-selenium load from the Uncompahgre Project. Perhaps a more accurate measure of selenium load from the project would be to determine selenium loads in all streams, canals, and ditches that discharge into the southern side of the Gunnison River between Peach Valley Arroyo and Roubideau Creek.

Water from Loutsenhizer Arroyo is used to supplement the water supply for the Garnet Canal; therefore, some of the selenium load from the arroyo is redistributed by the Garnet Canal system into areas east of Delta. The diversion structure on the arroyo is between site LZA1 and the Uncompahgre River. The fraction of the selenium load in the Garnet Canal that came from Loutsenhizer Arroyo was not determined. A small fraction of the annual flow of the Garnet Canal is diverted into Sweitzer Lake; therefore, a small fraction of the selenium load from

Loutsenhizer Arroyo might eventually be incorporated into Sweitzer Lake bottom sediment through chemical and biological processes. Tail water from the Garnet Canal discharges into the Relief Canal at site GAR4 (fig. 26), which discharges into the Bonafide Ditch. The Bonafide Ditch discharges into the Gunnison River immediately upstream from site GUN4 (figs. 23 and 26).

Much of the selenium load from the western side of the Uncompahgre Project apparently discharges from the northern part of the area, primarily from Dry Creek, Cummings Gulch, Seep Creek, and Roubideau Creek (fig. 26). Mass-balance calculations and synoptic-survey data indicate an unknown fraction of the selenium loads in those streams during the nonirrigation season of 1991–92 probably came from winter water transported by the Ironstone Canal and its laterals into these basins. It also is likely that

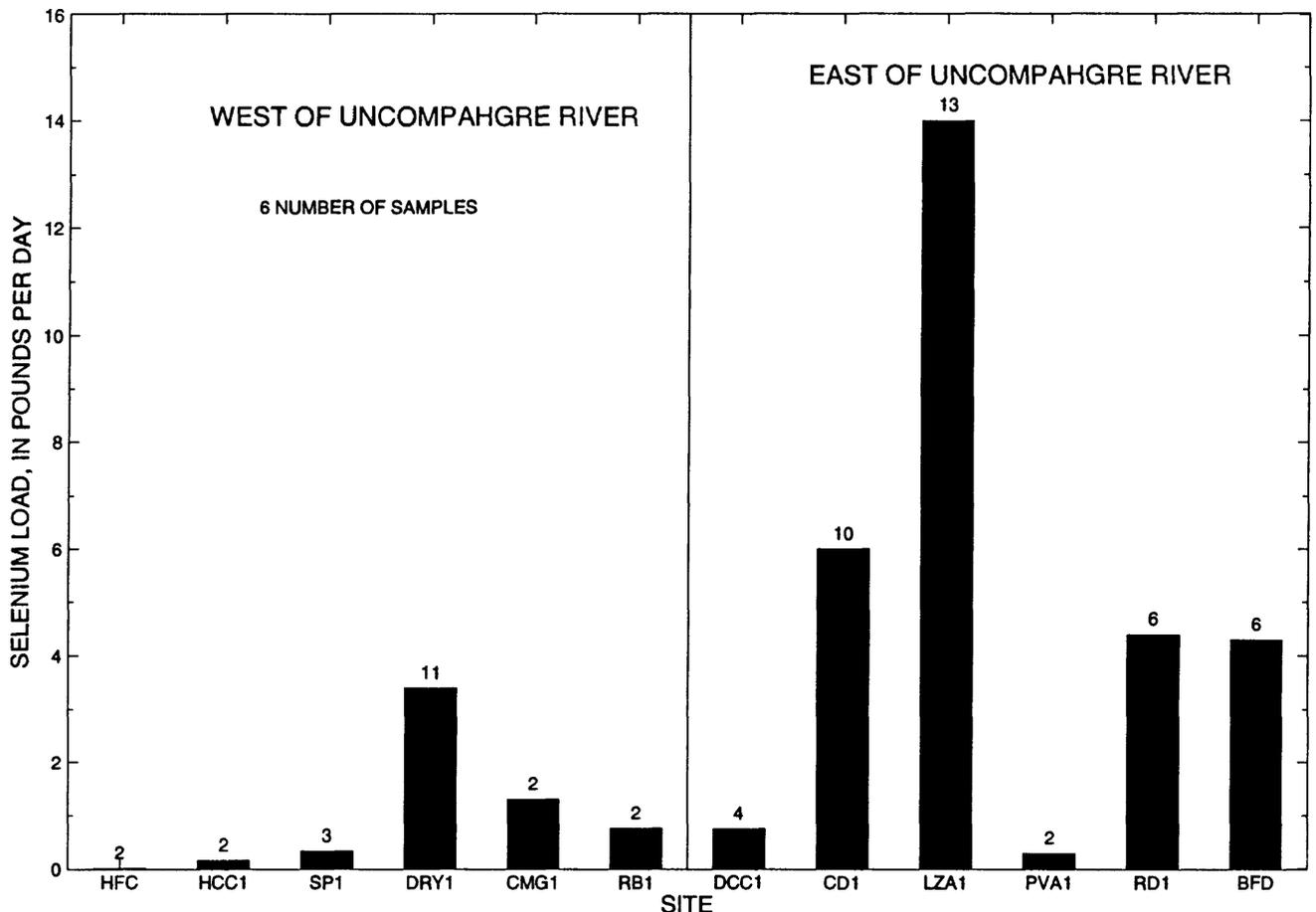


Figure 35. Seasonally weighted mean selenium loads for 12 sites in the Uncompahgre Project, 1991–92.

irrigation-supply water from the Ironstone Canal is a source of selenium loading to the western side of the project during the irrigation season.

Selenium loads within major drainage basins on the eastern side of the Uncompahgre Project were variable based on the synoptic-survey data collected in 1992 and on data collected in water year 1993. For four sets of samples, about 35 to 42 percent of the selenium load discharging from Cedar Creek (at site CD1) was from Montrose Arroyo (fig. 25), although Montrose Arroyo accounted for less than 20 percent of the stream discharge in Cedar Creek. The unnamed west tributary of Loutsenhizer Arroyo (at site WLZ1 in fig. 26) accounted for about 40 percent of the stream discharge, but only about 20 percent of the selenium load in Loutsenhizer Arroyo at site LZA1 in March 1992. About 90 percent of the selenium load in the unnamed drainage near Read at site RD1 in March 1992 was discharged into the reach between sites RD2 and RD3 (fig. 26).

Selenium data collected during 1991–93 in the Cedar Creek and Loutsenhizer Arroyo Basins (figs. 25 and 26) indicate that some of the selenium load measured at outflow sites CD1 and LZA1 originated outside the irrigated area of the Uncompahgre Project. There are some areas that are irrigated with non-project water in both drainage basins that are upstream from the Uncompahgre Project. There are extensive areas of Mancos Shale in the upper Cedar Creek and Loutsenhizer Arroyo Basins. Irrigation drainage from the nonproject areas might contribute a small selenium load to Cedar Creek and Loutsenhizer Arroyo throughout the year. Natural runoff in the Cedar Creek and Loutsenhizer Arroyo Basins also might contribute to the selenium load in these streams. Natural runoff in Loutsenhizer Arroyo probably is limited to brief periods of snowmelt runoff in spring and runoff associated with heavy rainstorms. In addition to natural runoff associated with snowmelt and rain, there seems to be a small natural base-flow discharge into upper Cedar Creek. Three sets of samples were collected in March 1992 and March 1993 during periods of snowmelt runoff from Mancos Shale areas in the upper Cedar Creek and Loutsenhizer Arroyo Basins. For those samples, about 24 to 45 percent of the selenium load in Cedar Creek and about 13 to 36 percent of the selenium load in Loutsenhizer Arroyo were accounted for at

the most upstream sampling site. Apparently, some of the selenium load measured at outflow sites on both streams was caused by snowmelt in the drainage basins upstream from the Uncompahgre Project. The selenium load resulting from snowmelt on Mancos Shale would be highly variable from year to year, depending on weather conditions. There was an accumulation of snow at low elevations in the Cedar Creek and Loutsenhizer Arroyo Basins in the winter of 1992. In some winters, snow accumulation at lower elevations in the Uncompahgre Project area is minimal, and the resulting snowmelt runoff from the Mancos Shale areas would be minimal.

The fraction of the selenium load in Cedar Creek and Loutsenhizer Arroyo from nonproject sources might be less in the irrigation season than in the nonirrigation season. Nonproject sources of selenium accounted for less than 5 percent of the selenium load in Loutsenhizer Arroyo and about 10 to 15 percent of the selenium load in Cedar Creek based on samples collected during the irrigation seasons in 1991 and 1993. During periods when the irrigation-season samples were collected, irrigation drainage from nonproject land probably was the sole source of selenium load to upper Loutsenhizer Arroyo, and non-project irrigation drainage and perhaps a small quantity of natural ground-water discharge were potential selenium sources to upper Cedar Creek.

The synoptic-survey results for March 1992 indicated that the Garnet Canal gained 1.1 lb/d of selenium between sites GAR1 and GAR2 (fig. 26). Most of the gain in selenium probably was from the drainage ditches at sites DR1 and DR2 (fig. 26) and from diffuse seepage of irrigation drainage into the canal. Essentially all the increase in selenium load in the Garnet Canal downstream from Sweitzer Lake (between sites GAR2 and GAR4) was from irrigation-drainage discharge from an unnamed natural drainage downstream from site UNGR (fig. 26). The selenium load discharged from the Garnet Canal (site GAR4 in fig. 26) accounted for almost all the selenium load in the Bonafide Ditch at site BFD in the samples collected on March 12, 1992.

Analysis of selenium loads for the more frequently sampled surface-water sites (the sites shown in fig. 35) indicated variable seasonal differences in mean selenium loads between irrigation and nonirrigation seasons. The mean selenium

load for seven irrigation-season samples for Cedar Creek at site CD1 was 7.3 lb/d, compared to the mean load of 4.1 lb/d for three nonirrigation-season samples. The mean selenium load of 14.7 lb/d for eight irrigation-season samples from Loutsenhizer Arroyo at site LZA1 is only slightly greater than the mean load of 13.0 lb/d for five nonirrigation-season samples. The seasonal differences between selenium loads for an unnamed drainage near Read at site RD1 and Dry Creek at site DRY1 were not large.

In July 1991, water samples were collected from the Gunnison River at sites GUN3 and GUN4 and from four tributaries draining irrigated areas adjacent to or upstream from the Uncompahgre Project (fig. 23). The selenium load in the Gunnison River at site GUN3, which is upstream from all irrigation drainage from the Uncompahgre Project, was 5.6 lb/d. About 50 percent of the load at site GUN3 was accounted for by the North Fork of the Gunnison River (site NFK1 in fig. 23). The sum of the selenium loads from the four other tributaries that drain nonproject irrigated areas (fig. 23)—the Smith Fork (site SMF), Currant Creek (site CRC), Alfalfa Run (site AFR), and Tongue Creek (site TGC)—was only 0.2 lb/d in July 1991. When compared to selenium loading from streams draining the irrigated areas of the Uncompahgre Project, selenium loading from other drainage basins in the lower Gunnison River Basin were small. However, the basins outside the project were sampled only once, and the selenium loads might not be representative of the selenium loads throughout the year.

## Grand Valley

The largest mean selenium loads in tributary streams draining the Grand Valley were for Salt Creek (site SC), Reed Wash (site RW1), Big Salt Wash (site BSW1), and Leach Creek (site LC1). Mean selenium loads for the 20 reconnaissance sites in the Grand Valley are compared in figure 36. The loads shown in figure 36 are arithmetic means of the selenium loads for the three sets of samples collected in March 1991, in late summer of 1991, and in February or March 1992. The greatest mean selenium load shown in figure 36 is 11.2 lb/d for site RW1; however, the seasonally weighted mean selenium load for site RW1, based on the 15 samples collected during 1991–92, was 12.8 lb/d. The selenium loads for the 20 sites might represent much of the selenium

load discharging from tributary streams into the Colorado River. However, the selenium loads from numerous, small washes and drainage ditches were not measured. There probably is discharge of irrigation drainage directly into the Colorado River in ground water that is not intercepted by tributary streams, washes, and drainage ditches. Ground-water studies by BOR (1986a) indicate that the cobble aquifer discharges directly into the Colorado River in the Fruita area. The cobble aquifer probably is of sufficient depth in many areas in the Grand Valley so that surface streams and drainage ditches might not intercept appreciable quantities of water from the cobble aquifer

Most of the irrigation-induced selenium load from the Grand Valley is from irrigated areas west of the Gunnison River and north of the Colorado River. Ninety-three percent of the sum (33.3 lb/d) of the mean selenium loads for the 20 sites shown in figure 36 was accounted for in the drainage basins in the western part of the Grand Valley between Salt Creek and Leach Creek (fig. 3). About 70 percent of the irrigated land in the Grand Valley is west of Grand Junction and north of the Colorado River (Bureau of Reclamation, 1986b). Most of the irrigated land in the western part of the Grand Valley is on soils derived from alluvium on Mancos Shale or shale residuum.

Selenium loads for sites on the Redlands area, the area east of the Gunnison River and north of the Colorado River, and on Orchard Mesa generally were smaller than loads in the streams and washes west of Grand Junction (figs. 30, 31, and 36). Except for Indian Wash and an unnamed drainage near Clifton at site CF1, selenium loads in washes and ditches in those areas generally ranged from 0.01 to 0.20 lb/d (fig. 36). One reason for smaller selenium loads in these areas is that the washes and drainage ditches have small drainage-basin areas, and subsequently the stream discharges are smaller compared to stream discharges in larger basins. The Redlands and Orchard Mesa areas primarily are on terrace deposits. Soils derived from terrace deposits should contain less material derived from the Mancos Shale, and consequently, irrigation drainage from terrace deposits generally had lower selenium concentrations compared to other areas in the Grand Valley (table 19). The Redlands area accounts for about 6 percent, the area east of Grand Junction to

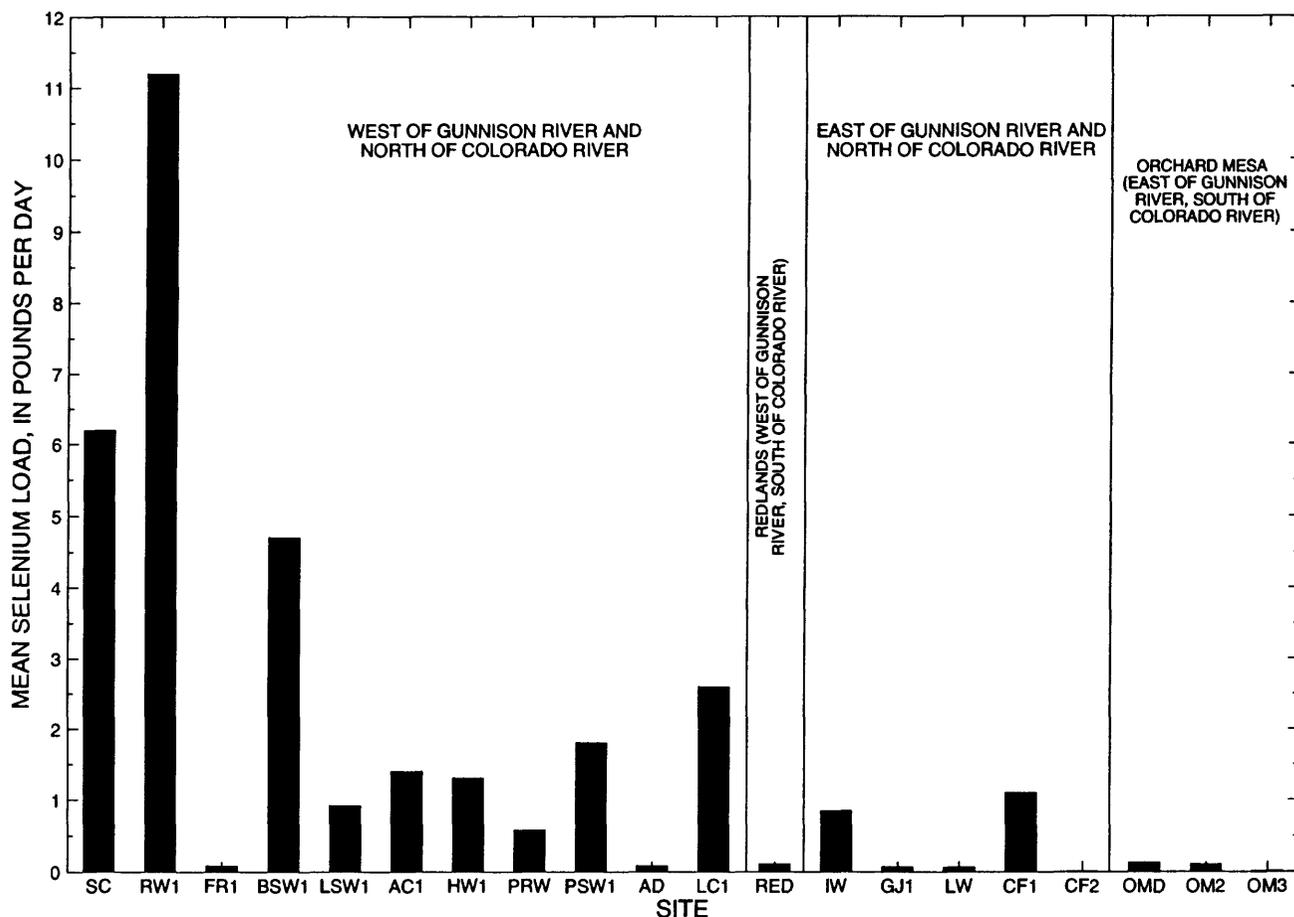


Figure 36. Mean selenium loads of three sets of samples collected in 1991–92 for 20 sites in the Grand Valley.

the east end of the valley (north of the Colorado River) accounts for about 16 percent, and Orchard Mesa about 11 percent of the irrigated area in the Grand Valley. Large sections of the Redlands, the area between Grand Junction and Clifton, and western Orchard Mesa are residential and commercial areas.

The synoptic data collected during the nonirrigation season in early 1992 were used to examine selenium-loading differences within the major streams that drain the Grand Valley. In Reed Wash in March 1992, about one-half the selenium load at the outflow site (RW1 in fig. 30) was from the East Branch (site RWEB). Surveys on Big Salt Wash, Little Salt Wash, Adobe Creek, Hunter Wash, and Persigo Wash (fig. 30) indicated that 67 to 81 percent of the selenium load at the outflow sites was gained in the lower reaches of the streams. Much of the increase in selenium loads

in those five streams was caused by increases in stream discharge rather than by downstream increases in selenium concentrations.

Selenium loads in some streams and drains in the Grand Valley were higher in the irrigation season (April through October) than in the nonirrigation season (November through March). For the 20 reconnaissance sites (fig. 36), the sum of selenium loads for the samples collected March 20–22, 1991, was 18.0 lb/d, compared to 60.0 lb/d for samples collected August 27–September 4, 1991, at the same sites. Four sites were sampled at least five times, and the selenium loads for each sample are shown in figure 37. For Reed Wash at site RW1, the mean selenium load for irrigation-season samples (16.6 lb/d) is more than twice the mean load of nonirrigation-season samples (7.5 lb/d). Greater irrigation-season selenium loads also were indicated for Salt Creek (site SC) and Big Salt Wash

(site BSW1) (fig. 37). By contrast, the mean selenium load for irrigation-season samples for Leach Creek at site LC1 was about 25 percent less than the mean load for the nonirrigation-season samples. During the nonirrigation season, irrigation drainage from the Independent Ranchmens Ditch is discharged into Leach Creek at site IRD. During the irrigation season, most of the water in the Independent Ranchmens Ditch flows in a pipe over Leach Creek to irrigate fields west of Leach Creek. Therefore, most of the selenium load in the Independent Ranchmens Ditch was not discharged into Leach Creek during the irrigation season.

Although the discharges in Grand Valley streams and washes are much higher in the irrigation season than in the nonirrigation season, the increase in

discharge does not account for all of the increase in selenium loads during the irrigation season. The range of stream-discharge measurements for the 15 water samples collected from Reed Wash at site RW1 was 7.0 to 168 ft<sup>3</sup>/s, and the range for 8 samples from Salt Creek at site SC was 7.1 to 203 ft<sup>3</sup>/s. In the Grand Valley, a large quantity of unused irrigation water is discharged from canals and laterals into the washes during the irrigation season. However, selenium concentrations in the irrigation-supply water are too small to be the sole cause of higher selenium loads in streams and washes during the irrigation season. In drainage basins, such as Reed Wash, either groundwater (irrigation-drainage) discharge had to increase or selenium concentrations in ground water had to increase to account for the higher selenium loads

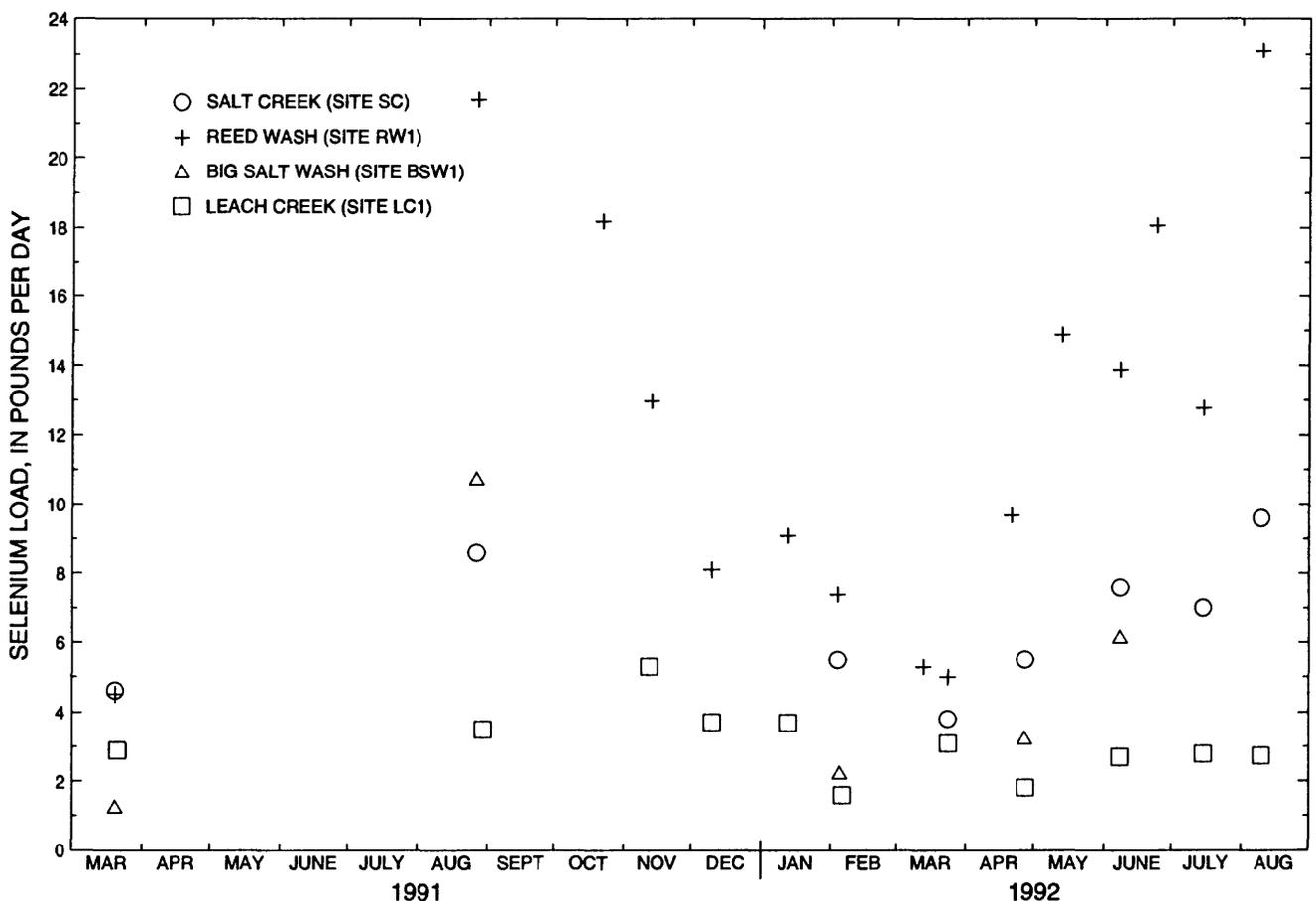


Figure 37. Selenium loads in Salt Creek at site SC, Reed Wash at site RW1, Big Salt Wash at site BSW1, and Leach Creek at site LC1, March 1991–August 1992.

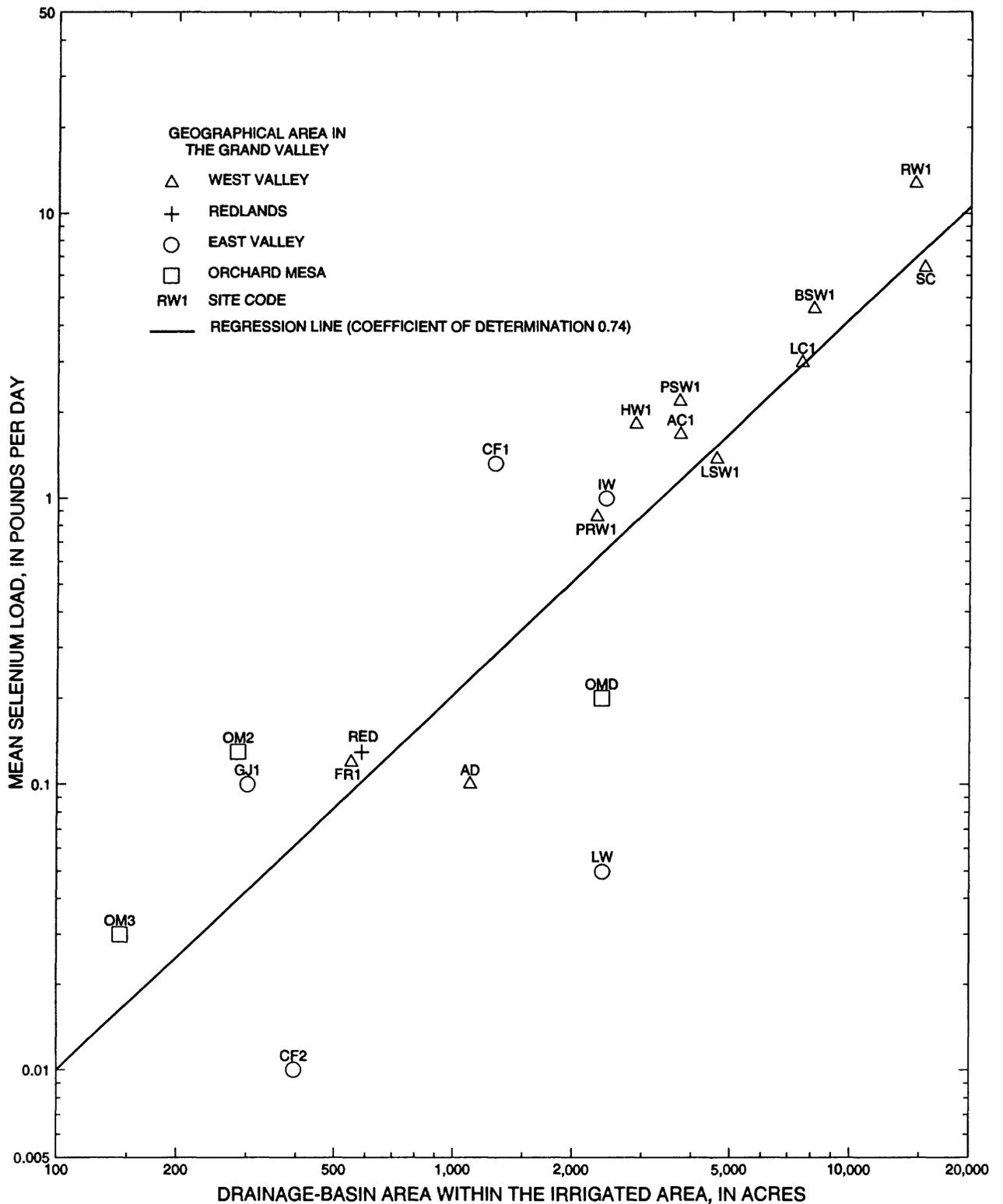
at site RW1 during the irrigation season. Water levels in shallow wells in the Grand Valley are higher during the irrigation season than during the nonirrigation season, which indicates the potential for increased ground-water discharge into tributary streams, washes, and drainage ditches that dissect the valley. Higher selenium concentrations could occur during the irrigation season because of more oxidizing conditions in ground water or by the flushing of soluble salts that contain selenium. Water samples collected from Reed Wash during this study were not affected by surface runoff from precipitation or snowmelt; therefore, seasonal differences in selenium loads were not caused by natural runoff.

There is a statistically significant (significance level less than 0.001) relation of seasonally weighted mean selenium load to drainage-basin area within the irrigated area for the 20 reconnaissance sites in the Grand Valley (fig. 38). The coefficient of determination of the relation shown in figure 38 is 0.74. The four streams with the largest selenium loads in the Grand Valley also have the largest drainage areas within the irrigated area of the Grand Valley. That relation is not surprising because the larger drainage basins would tend to have more miles of canals, laterals, and ditches and more irrigated acreage than smaller basins; therefore, the large basins would have greater recharge to shallow ground water from distribution-system losses and deep percolation. The selenium yield, in pounds per day per 100 acres of drainage area, was determined for the 20 sites in figure 38 by dividing the seasonally weighted mean selenium load of all the samples collected at a site by the drainage-basin area within the irrigated boundaries (bounded by the Government Highline Canal) and multiplying by 100. The largest selenium yields were 0.115 (lb/d)/100 acres for the drain near Clifton at site CF1 and 0.088 (lb/d)/100 acres for Reed Wash at site RW1. Most basins had selenium yields between 0.020 and 0.060 (lb/d)/100 acres. The selenium yields were less than 0.01 (lb/d)/100 acres for Appleton Drain (site AD in fig. 30), Lewis Wash (site LW in fig. 31), an unnamed drainage east of Clifton at site CF2, and Orchard Mesa Drain (site OMD).

General surficial geology does not seem to explain differences in selenium loads in the Grand Valley. For example, the selenium load for Reed Wash at site RW1 is about twice the selenium load for the Salt Creek Basin at site SC (fig. 38), although the drainage-basin areas within the irrigated area are about equal for both basins. General geologic differences between the basins are not readily apparent because most of the irrigated soil in both basins is derived either from alluvium on Mancos Shale or Mancos Shale residuum (fig. 5A). However, based solely on field observations, a higher percentage of the Reed Wash Basin is irrigated compared to the Salt Creek Basin, which could explain some of the difference in selenium loads between the basins. Land-use factors and small-scale geologic differences might explain some of the differences in selenium loads among tributary streams in the Grand Valley.

## **Dissolved Solids and Major Constituents and Relations to Selenium**

The irrigated areas in the Uncompahgre Project and in the Grand Valley have been identified in salinity studies by the BOR (1978, 1982) as major sources of salt (dissolved solids) to the upper Colorado River. These studies indicated that the Uncompahgre Project contributes about 360,000 tons/yr and the Grand Valley about 580,000 tons/yr of salt to the Colorado River. Because of previous, ongoing, and proposed salinity-control projects in the Uncompahgre Project and in the Grand Valley, there is an interest in determining if there are relations of selenium to dissolved solids and if projects designed to decrease dissolved-solids loading could affect selenium loading. Relations of selenium concentrations and loads to dissolved-solids concentrations and loads were analyzed to determine if source areas of selenium also are source areas of dissolved solids. The major ions that compose dissolved solids and their relations to selenium also are discussed.



**Figure 38.** Relation of seasonally weighted mean selenium load to drainage-basin area within the irrigated area for 20 basins in the Grand Valley.

## Dissolved Solids

Irrigation water from the Gunnison River (through the Gunnison Tunnel) into the Uncompahgre Project had dissolved-solids concentrations less than 150 mg/L and was a calcium bicarbonate water. Dissolved-solids concentrations in the Uncompahgre River at Colona during 1991–92 ranged from about 250 to 450 mg/L and was a calcium sulfate bicarbonate water. Both rivers are regulated by reservoirs, and dissolved-solids concentrations in the Gunnison and Uncompahgre Rivers upstream from the Uncompahgre Project had less seasonal variation than is typical of streams in western Colorado. There is considerable variability in the quality of irrigation water delivered within the Uncompahgre Project. Water into the South and West Canals (fig. 25) is directly from the Gunnison Tunnel, and this irrigation water had low dissolved-solids and major-ion concentrations. Water diverted from the Uncompahgre River into the six canals downstream from the South Canal (figs. 25 and 26) has increasing dissolved-solids and major-ion concentrations in the downstream direction compared to the original irrigation water because of the effects of surface-return flow, irrigation drainage, and consumptive losses.

The median dissolved-solids concentration for nonirrigation-season samples from the western side of the Uncompahgre Project was 1,160 mg/L, and concentrations ranged from 648 to 4,840 mg/L. The median dissolved-solids concentration for nonirrigation-season samples from the eastern side was 4,110 mg/L, and concentrations ranged from 1,470 to 6,380 mg/L. Water composition generally was a mixed-cation sulfate water. Sulfate composed more than 70 percent of the anion concentration in most nonirrigation-season samples, and sulfate was greater than 80 percent of the anion composition in most nonirrigation-season samples from the eastern side.

Water samples collected from the Colorado River near Cameo at site COL2 (fig. 31) are representative of water quality of the irrigation-supply water for all irrigated areas in the Grand Valley, except the Redlands area, which is irrigated by water from the Gunnison River. During 1991–92, dissolved-solids concentrations in discrete samples collected at site COL2 ranged from 196 to 654 mg/L during April through October. Water composition at

site COL2 varied during the irrigation season and had higher ion percentages of calcium bicarbonate during snowmelt runoff and higher percentages of sodium chloride during low flow. Water samples from the Gunnison River at site GUN6, about 7 mi upstream from the irrigation diversion for the Redlands area, had slightly higher dissolved-solids concentrations than samples from site COL2 and was a calcium sulfate water.

The median dissolved-solids concentration was 3,600 mg/L for nonirrigation-season samples in the Grand Valley, and concentrations ranged from 1,760 to 6,170 mg/L. There were no winter-water diversions in the Grand Valley when nonirrigation-season samples were collected; therefore, nonirrigation-season samples from streams probably consisted of shallow ground-water discharge from irrigated areas. The nonirrigation-season samples were a mixed-cation sulfate water, and sulfate accounted for more than 70 percent of the anion equivalent concentration. The nonirrigation-season samples often had higher percentages of magnesium and sulfate and lower percentages of sodium, chloride, and bicarbonate compared to irrigation water from the Colorado River.

The Pearson correlation coefficients of selenium concentration to specific conductance, dissolved-solids, major-ion, boron, and uranium concentrations in surface-water samples collected within the irrigated areas, separated by irrigation and nonirrigation seasons, are listed in table 21. The Uncompahgre Project data were separated into the western and the eastern sides of the Uncompahgre River, and the Grand Valley data were separated into areas north and south of the Colorado River. Irrigation on the western side of the Uncompahgre Project and in the Grand Valley south of the Colorado River primarily is on terrace deposits; irrigation on the eastern side of the Uncompahgre Project and in the Grand Valley north of the Colorado River primarily is on Mancos Shale or on alluvium containing substantial amounts of shale.

Many of the correlation coefficients of selenium to the variables listed in table 21 were less than 0.50 for samples collected in Mancos Shale areas (eastern side of Uncompahgre Project; north of Colorado River). In some instances, relatively large sample sizes (more than 30 samples) probably improved the chance that the correlations of selenium

with other water-quality constituents would be statistically significant. Most of the correlations for the irrigation-season samples from the eastern side of the Uncompahgre Project and for the nonirrigation-season samples from the Grand Valley north of the Colorado River were not statistically significant (at a significance level of 0.05). Specific conductance usually is highly correlated with dissolved-solids concentrations, and because it can be measured in the field, specific conductance can be used to monitor dissolved-solids concentrations. Selenium concentrations seemed to have greater variability than specific conductance in irrigated areas on Mancos Shale, which results in the relatively low correlations of selenium and specific conductance (table 21). For that reason, specific conductance probably is not an accurate indicator of selenium concentration for irrigated areas on Mancos Shale for broad geographical areas.

If data for specific sites are used, relations of selenium to dissolved-solids concentrations and specific conductance improved markedly because the variance in selenium concentrations between sites or drainage basins was removed. Some of the variance between drainage basins could be

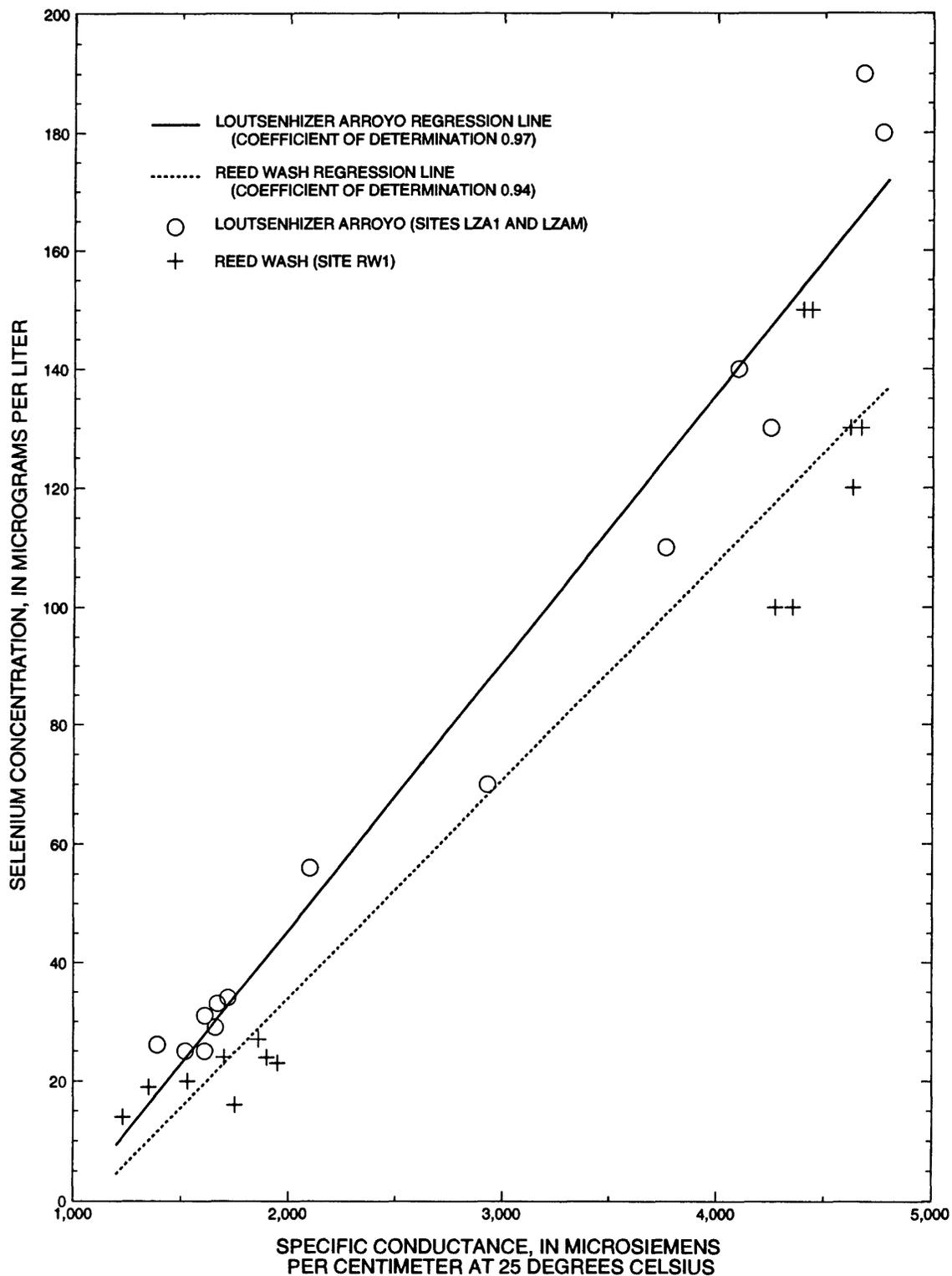
caused by differences in geology and land use. Relations of selenium concentration to specific conductance for samples collected during 1991–92 from Loutsenhizer Arroyo (sites LZA1 and LZAM) and Reed Wash (site RW1) are shown in figure 39. Specific conductance was used instead of dissolved-solids concentrations because there were more data for specific conductance, but regressions using dissolved-solids concentrations would have essentially the same relations. The coefficients of determination were 0.97 for the Loutsenhizer Arroyo relation and 0.94 for the Reed Wash relation. Coefficients of determination were greater than 0.89 for relations of selenium to specific conductance for Cedar Creek (site CD1), Salt Creek (site SC), and Leach Creek (site LC1). For Dry Creek (site DRY1), which does not drain Mancos Shale lands to a great extent, the coefficient of determination was only 0.65.

The salinity-control projects, which are designed to decrease dissolved-solids loads, could have an effect on selenium loads in the irrigated areas of the Uncompahgre Project area and the Grand Valley. The salinity-control projects are designed to decrease distribution-system losses and deep percolation of applied water, which would result in less recharge to shallow aquifers in the Mancos Shale.

**Table 21.** Pearson correlation coefficients of selenium concentration to specific conductance and to dissolved-solids, major-ion, boron, and uranium concentrations for the Uncompahgre Project and the Grand Valley

[Areas of the Uncompahgre Project are west or east of the Uncompahgre River; areas of the Grand Valley are north or south of the Colorado River; irr, irrigation season; non, nonirrigation season; \*, correlation not significant at 0.05 probability level; --, correlation not reported for sample sizes less than 6; samples from mainstem rivers and reference sites were not included]

Area	Season	Specific conductance	Dissolved solids	Calcium	Magnesium	Sodium	Sulfate	Alkalinity	Chloride	Nitrate plus nitrite	Boron	Uranium
<b>UNCOMPAHGRE PROJECT</b>												
West	Irr	0.77	0.78	0.75	0.69	0.57	0.79	-0.03*	-0.11*	0.91	0.23*	0.42*
West	Non	.84	.85	.69	.74	.86	.86	.41	.27*	.57	.88	--
East	Irr	.20*	.19*	.49	-.12*	-.22*	-.11*	.36*	-.04*	.82	-.04*	-.17*
East	Non	.50	.45	.47	.15*	.48	.42	-.07*	.27*	.71	.43	--
<b>GRAND VALLEY</b>												
North	Irr	.71	.77	.85	.68	.25*	.75	.44	.17*	.80	.50	.54
North	Non	.13*	.15*	.44	.17*	-.08*	.14*	-.08*	-.09*	.61	.08*	.65
South	Irr	--	--	--	--	--	--	--	--	--	--	--
South	Non	-.02*	-.16*	-.36*	.36*	.39*	-.24*	.43*	-.51*	.93	.46*	--



**Figure 39.** Relations of selenium concentration to specific conductance for Loutsenhizer Arroyo and Reed Wash.

Less recharge to aquifers in the Mancos Shale would decrease the quantity of irrigation-drainage discharge, which should decrease dissolved-solids loads. Linear-regression relations of selenium loads to dissolved-solids loads were determined for major tributary streams in the Uncompahgre Project and the Grand Valley. The relations of selenium and dissolved-solids loads among drainage basins are highly variable, and coefficients of determination range from about 0.32 to 0.90. For some streams, additional variables apparently are needed to relate selenium load to dissolved-solids load. The load relations for the two tributary streams that had the largest selenium loads in the study area, Loutsenhizer Arroyo and Reed Wash, are shown in figure 40. The load relation for Loutsenhizer Arroyo (coefficient of determination 0.36) was much weaker than the relation for Reed Wash (coefficient of determination 0.82). Reasons why the relation is less well defined for Loutsenhizer Arroyo are not known. Loutsenhizer Arroyo and Reed Wash drain irrigated areas that are predominately on soils derived from shale, and the major land use in both drainage basins is irrigated agriculture. Neither basin had been substantially affected by urbanization.

The relations of selenium and dissolved-solids loads for tributary streams had positive slopes, which might indicate that a decrease in dissolved-solids load in a particular drainage basin could be accompanied by a decrease in selenium load. Such relations could imply that the salinity-control projects, which are designed to decrease dissolved-solids loads from irrigated areas, also could decrease selenium loads. Potential decreases in dissolved-solids loads and selenium loads resulting from salinity-control projects assume that the projects decrease the quantity of ground-water discharge (irrigation drainage) and that the concentrations of dissolved solids and selenium in ground water are relatively unchanged. Actual effects of salinity-control projects on selenium loads have not been measured in field studies in the Uncompahgre Project or in the Grand Valley.

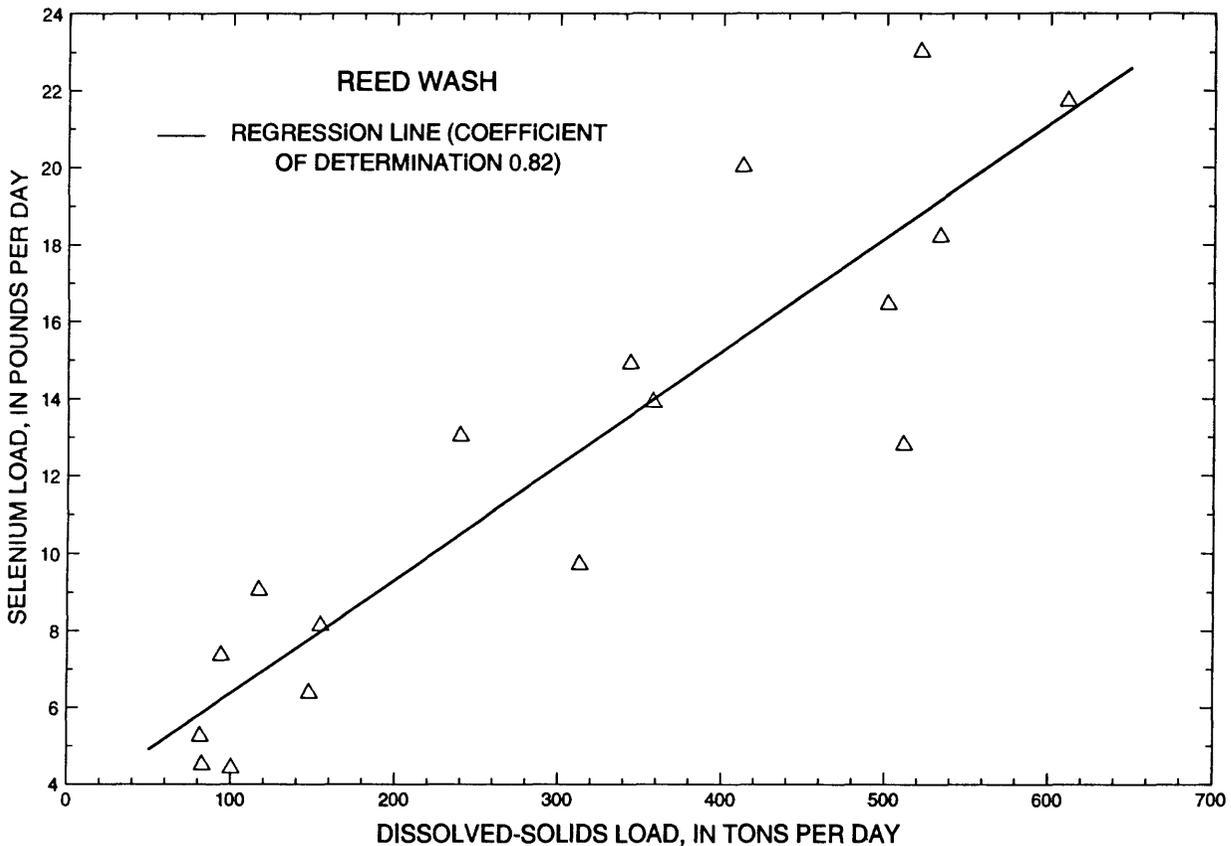
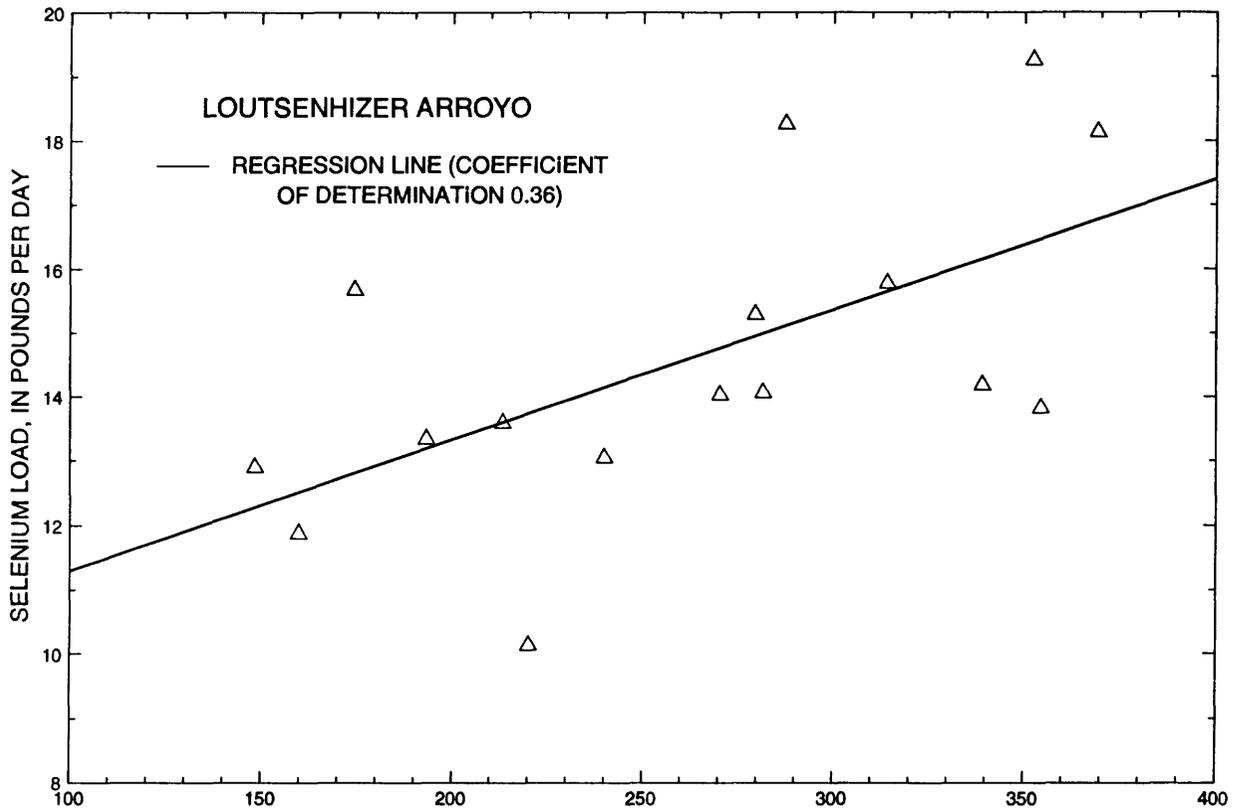
Gains and losses of dissolved-solids loads in the Uncompahgre River in February 1992 had a similar pattern as selenium loads. Dry Creek discharged the largest dissolved-solids load into the river, and Loutsenhizer Arroyo contributed the second largest load to the river. Dry Creek had about four times greater stream discharge than Loutsenhizer

Arroyo (at site LZAM downstream from the Garnet Canal diversion). Part of the dissolved-solids load in Dry Creek in February 1992 probably was from winter water that was diverted from the Uncompahgre River.

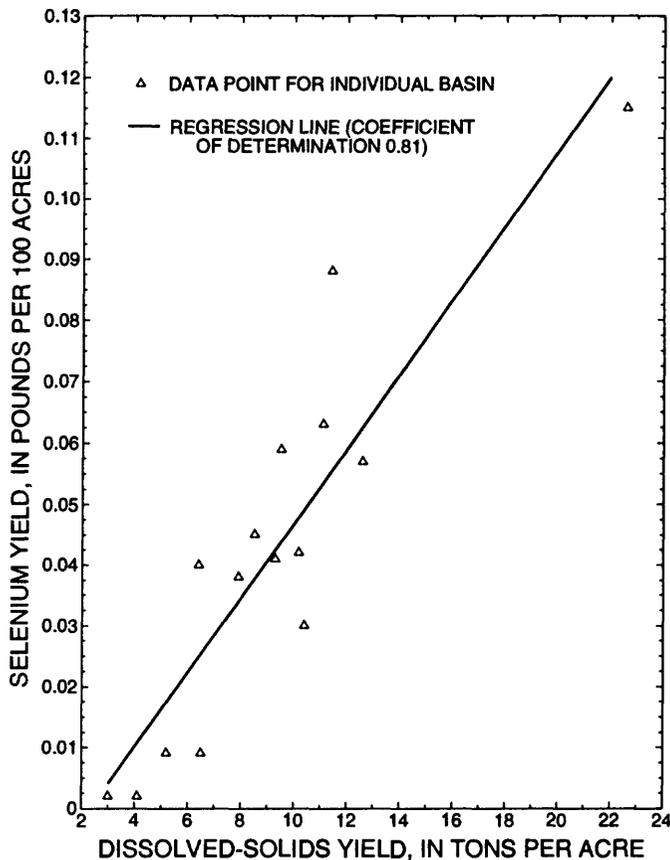
For the 20 reconnaissance sites in the Grand Valley, streams that had the largest selenium loads (fig. 36) also had the largest dissolved-solids loads. The largest seasonally weighted mean dissolved-solids loads for 1991–92 were 318 tons/d for Reed Wash at site RW1 (13 samples) and 271 tons/d for Salt Creek at site SC (6 samples). Generally, the relative differences in dissolved-solids loads among the 20 sites were less pronounced than were differences in selenium loads. The dissolved-solids load per unit drainage-basin area is the dissolved-solids yield. Data for 15 of the basins in the Grand Valley shown in figure 36 have dissolved-solids yield data listed in a BOR report (1978), and a plot of the relation of estimated selenium yield to estimated dissolved-solids yield for these 15 basins is shown in figure 41. The selenium and dissolved-solids yields are based on the total drainage-basin area within the irrigated area and not on irrigated acreage within the basin. The highly significant coefficient of determination of 0.81 (significance level less than 0.001) for the relation of selenium yield to dissolved-solids yield for the 15 basins shown in figure 41 implies that drainage basins in the Grand Valley that have high dissolved-solids yields have high selenium yields.

### **Chloride and Evaporative Concentration**

By assuming chloride is a conservative ion, a relation of selenium and chloride concentrations was used to analyze possible effects of evaporative concentration on selenium concentrations in the Grand Valley. Mass-balance methods were used to estimate a chloride budget for the Grand Valley for water years 1976–92. The flow-weighted chloride concentration of the Colorado River downstream from the Grand Valley (site COL8) was 54 mg/L, compared to 51 mg/L for the combined inflow of the Colorado and Gunnison Rivers into the Grand Valley. The small increase in chloride concentration could result from consumptive water loss in the Grand Valley by evaporative concentration of the irrigation water or from computational errors.



**Figure 40.** Relations of selenium load to dissolved-solids load for Loutsenhizer Arroyo (site LZA1) and Reed Wash (site RW1).

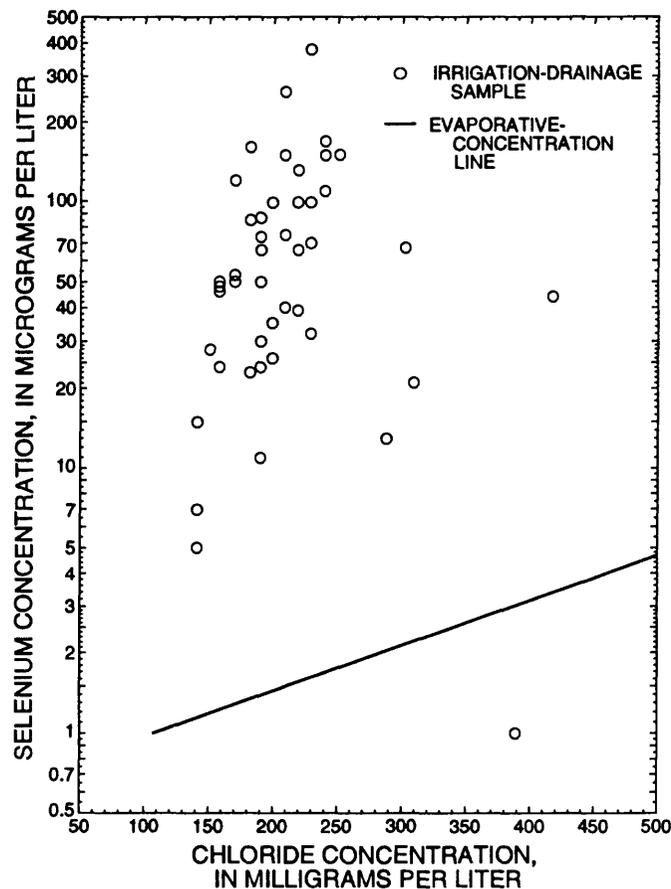


**Figure 41.** Relation of estimated selenium yield based on sampling during 1991–92 to estimates of dissolved-solids yield by the Bureau of Reclamation for 15 basins in the Grand Valley.

Selenium and chloride concentrations in irrigation drainage from the Grand Valley are plotted with the evaporative-concentration line in figure 42. The evaporative-concentration line is constructed by projecting mean irrigation-season concentrations of 1 µg/L for selenium and 107 mg/L for chloride for irrigation water from the Colorado River along a 1:1 line. Because the chloride concentrations predicted from the evaporative-concentration line are in the same range as the chloride concentrations of the samples (fig. 42), the chloride concentrations in irrigation drainage could be caused by simple evaporation. The selenium concentrations of the samples are much greater than the selenium concentrations predicted from the evaporative-concentration line; therefore, simple evaporation of irrigation water does not account for the selenium concentrations in the Grand Valley (fig. 42). Many selenium concentrations were about 5 to 100 times greater than the concentrations predicted by evaporative concentration, implying that the Grand Valley is a source area for selenium.

### Other Major Constituents

Much of the gain in dissolved solids in irrigation water in the Uncompahgre Project and in the Grand Valley was from gain in calcium, magnesium, sodium, and sulfate ions. Weathering of shale detritus or of evaporite sulfate minerals would contribute calcium, magnesium, sodium, and sulfate. Dissolution of carbonate minerals by irrigation drainage could result in a gain in calcium, magnesium, and sodium. Cation exchange on clay minerals could substitute calcium and magnesium ions for sodium ions, or vice versa. Dissolution of gypsum and oxidation of sulfides, such as pyrite, would produce sulfate. Only a small part of the increase in dissolved solids was the result of increases in alkalinity concentrations (almost all the alkalinity was bicarbonate ions based on the pH of samples).



**Figure 42.** Selenium and chloride concentrations in irrigation-drainage samples from the Grand Valley, November 1991–March 1992, and the estimated evaporative-concentration line.

Nonirrigation-season samples from the Uncompahgre Project and the Grand Valley were supersaturated with the carbonate minerals calcite and dolomite. The computer program WATEQ4F (Ball and Nordstrom, 1991) was used to compute ion speciation, mineral saturation, and mineral-saturation indices for selected samples collected from tributary streams and ditches during February and March 1992. Alkalinity concentrations were limited because equilibrium solubilities controlled the carbonate and bicarbonate concentrations. The irrigation water coming into the Uncompahgre Project and into the Grand Valley was undersaturated with gypsum (calcium sulfate). More than 50 percent of the samples from the Mancos Shale areas (the eastern side of the Uncompahgre Project and most of the Grand Valley) were approximately at equilibrium with gypsum, and the remainder of the samples was slightly undersaturated with gypsum. The change in saturation indices for gypsum from undersaturated in the irrigation-supply water to saturation or near saturation in irrigation drainage from Mancos Shale areas could imply that dissolution of gypsum is occurring in the study area. Dissolution of other evaporite minerals formed by weathering of Mancos Shale, such as epsomite and thenardite, would produce magnesium, sodium, and sulfate.

Sulfate concentrations were much higher in water samples from the irrigated areas compared to sulfate concentrations in irrigation-supply water for the Uncompahgre Project and in the Grand Valley. Sulfate concentrations were about 20 mg/L in irrigation water diverted through the Gunnison Tunnel, based on six samples collected during 1987–92 from the Gunnison River downstream from the tunnel diversion (site GUN1 in fig. 23) and from the South Canal. Sulfate concentrations were about 150 to 250 mg/L in samples collected during the irrigation season from the Uncompahgre River upstream from the Uncompahgre Project (site UC1 in fig. 25). For samples collected during the nonirrigation season, sulfate concentrations ranged from 200 to 3,100 mg/L for the western side of the Uncompahgre Project and from 790 to 4,200 mg/L for the eastern side of the project. Sulfate concentrations in irrigation-supply water from the Colorado River upstream from the Grand Valley (site COL2)

generally ranged from about 50 to 175 mg/L. Sulfate concentrations in non-irrigation-season samples collected in the Grand Valley ranged from 760 to 3,900 mg/L.

Differences in the distribution of selenium and sulfate might indicate differences in source areas, mobility, deposition, and transport of these constituents (Izbicki, 1989). Ratios of the concentrations of sulfate to selenium were computed for water samples from the study area. Lower ratios of sulfate to selenium concentrations in water samples could imply that selenium was enhanced in the water compared to sulfate and might indicate the most important selenium-source areas. In samples from the Uncompahgre Project, sulfate to selenium ratios generally were greater than 100,000 for samples from reference sites (sites outside the irrigated area) and for samples of irrigation-supply water from the Gunnison and Uncompahgre Rivers. Ratios also were greater than 100,000 for irrigated areas that had low selenium concentrations on the western side of the project, such as in the Happy Canyon Creek, Spring Creek, and Roubideau Creek Basins (figs. 25 and 26). Sulfate to selenium ratios were about 40,000 to 70,000 in samples from lower Dry Creek, Cummings Gulch, and Seep Creek, and these lower ratios might partly be the result of selenium-enhanced water from the Uncompahgre River being transported into these basins by the Ironstone Canal. Sulfate to selenium ratios were lower for samples collected in the nonirrigation season from the eastern side of the project and generally ranged from 10,000 to 30,000. The lowest ratios were for samples from areas having some of the higher selenium concentrations, such as the Loutsenhizer Arroyo Basin, an unnamed drainage near Read (upstream from site RD1), and from sites GAR2 and UNGR in the Garnet Canal area.

The irrigation-supply water from the Colorado River upstream from the Grand Valley had sulfate to selenium ratios greater than 100,000. Most irrigation-drainage samples from the Grand Valley had ratios between 10,000 and 60,000, and the lowest ratios were for water samples from areas that had the higher selenium concentrations, such as East Salt Creek, upper Reed Wash, the East Branch of Reed Wash, sites IRD and LC2 in the Leach Creek Basin, and Indian Wash (figs. 30 and 31). The only samples collected in irrigated areas of the Grand Valley that

had sulfate to selenium ratios greater than 100,000 were samples from areas of lower selenium concentrations, such as the ditches and washes represented by sites GJ1 and CF2 and sites on Orchard Mesa. The sulfate to selenium ratios for four of the five samples from reference sites on West Salt Creek, East Salt Creek, and Big Salt Wash were greater than 1,000,000, which implies that, in nonirrigated areas on Mancos Shale, sulfate was easily mobilized, but selenium was not readily mobilized.

The ratios of sulfate to selenium for pond-water samples were greater than the ratios for stream samples from Mancos Shale areas in the Uncompahgre Project area and in the Grand Valley. Six water samples from ponds in the Uncompahgre Project area had ratios between 110,000 and 400,000. The ratios of sulfate to selenium were 118,000 and 74,000 for samples from Reid Pond (site RDP in fig. 30) in the Grand Valley. The ponds are all located in Mancos Shale areas and probably receive some inflow of subsurface-irrigation drainage. Higher ratios for pond-water samples could indicate that chemical and biological processes were removing some of the selenium from ponds, but were not appreciably affecting sulfate concentrations.

Selenium and nitrite-plus-nitrate concentrations were significantly correlated (table 21) in the Uncompahgre Project and in the Grand Valley. Water samples from irrigated areas had considerably higher nitrite-plus-nitrate concentrations than irrigation-supply water, which is not unusual for agricultural areas where fertilizers are used on fields and where there are numerous small dairy and cattle-feeding operations. Nitrite-plus-nitrate concentrations in irrigation-supply water and in samples from reference sites usually were less than 0.2 mg/L. The median nitrite-plus-nitrate concentrations for nonirrigation-season samples collected in 1991–92 were 2.9 mg/L for the western side of the Uncompahgre Project, 7.6 mg/L for the eastern side, and 5.2 mg/L for the Grand Valley. Median concentrations do not include selenium data for reference sites, ponds, or mainstem rivers. The maximum nitrite-plus-nitrate concentrations for 1991–92 for the Uncompahgre Project were 14 mg/L (selenium concentration 23 µg/L) for the western side at site SEP2 (fig. 26) and 21 mg/L

(selenium concentration 240 µg/L) for the eastern side at site GAR2. However, a sample from a drainage ditch at site DR2 (fig. 26) had a nitrite-plus-nitrate concentration of 73 mg/L in March 1993. That sample also had a selenium concentration of 600 µg/L, which was the maximum selenium concentration in surface-water samples from the study area. The maximum nitrite-plus-nitrate concentration for 1991–92 in the Grand Valley was 46 mg/L (selenium concentration 100 µg/L) for a drainage ditch near Clifton at site CF1 (fig. 31). However, site CF1 is near sewage-treatment ponds, and perhaps much of the nitrogen at site CF1 was from nonagricultural sources. Excluding site CF1, the maximum nitrite-plus-nitrate concentration in Grand Valley surface water was 19 mg/L at site RW4 on upper Reed Wash (fig. 30). The selenium concentration of 380 µg/L associated with that sample from site RW4 was the maximum selenium concentration in surface-water samples from the Grand Valley.

Because laboratory experiments have indicated that nitrate can oxidize selenium from Mancos Shale samples (Wright and McMahon, 1994; Wright, 1995), relations of selenium and nitrite-plus-nitrate concentrations in surface water in irrigated areas on Mancos Shale were examined. In the oxidized environment of surface water (excluding ponds), almost all of the nitrite-plus-nitrate determination represents nitrate. In surface-water samples from Mancos Shale areas, high selenium concentrations often were associated with high nitrite-plus-nitrate concentrations, although there were some samples with high selenium concentrations that did not contain unusually high nitrite-plus-nitrate concentrations. Also, a number of the samples from Mancos Shale areas that had some of the lower selenium concentrations were associated with some of the lower nitrite-plus-nitrate concentrations. The linear relations between selenium and nitrite-plus-nitrate concentrations were examined using samples collected from tributary streams and ditches on the eastern side of the Uncompahgre Project and in the Grand Valley north of the Colorado River. Irrigation in these areas primarily is on soils derived from alluvium that contain variable quantities of shale detritus or is on soils derived from shale residuum. Samples collected only during the nonirrigation season (November through March) were used in

the regression analysis, and most of those samples were representative of subsurface-irrigation drainage from shale areas. The relations shown in figure 43 are statistically significant (significance level 0.05), although the coefficients of determination for both relations do not exceed 0.50. The relations in figure 43 indicate that higher selenium concentrations generally are accompanied by higher nitrite-plus-nitrate concentrations. Statistical correlations between selenium and nitrite-plus-nitrate concentrations does not prove that a cause-and-effect mechanism actually exists in the field (that nitrate oxidizes selenium). If there are significant sources of selenium and nitrogen available, oxidizing conditions could cause high concentrations of both constituents, which could result in positive correlations between constituent concentrations in the ground water that is discharged into streams, washes, and ditches. However, there seems to be an association between high selenium concentrations and high nitrite-plus-nitrate concentrations in some surface-water samples collected in Mancos Shale areas in the Uncompahgre Project and in the Grand Valley.

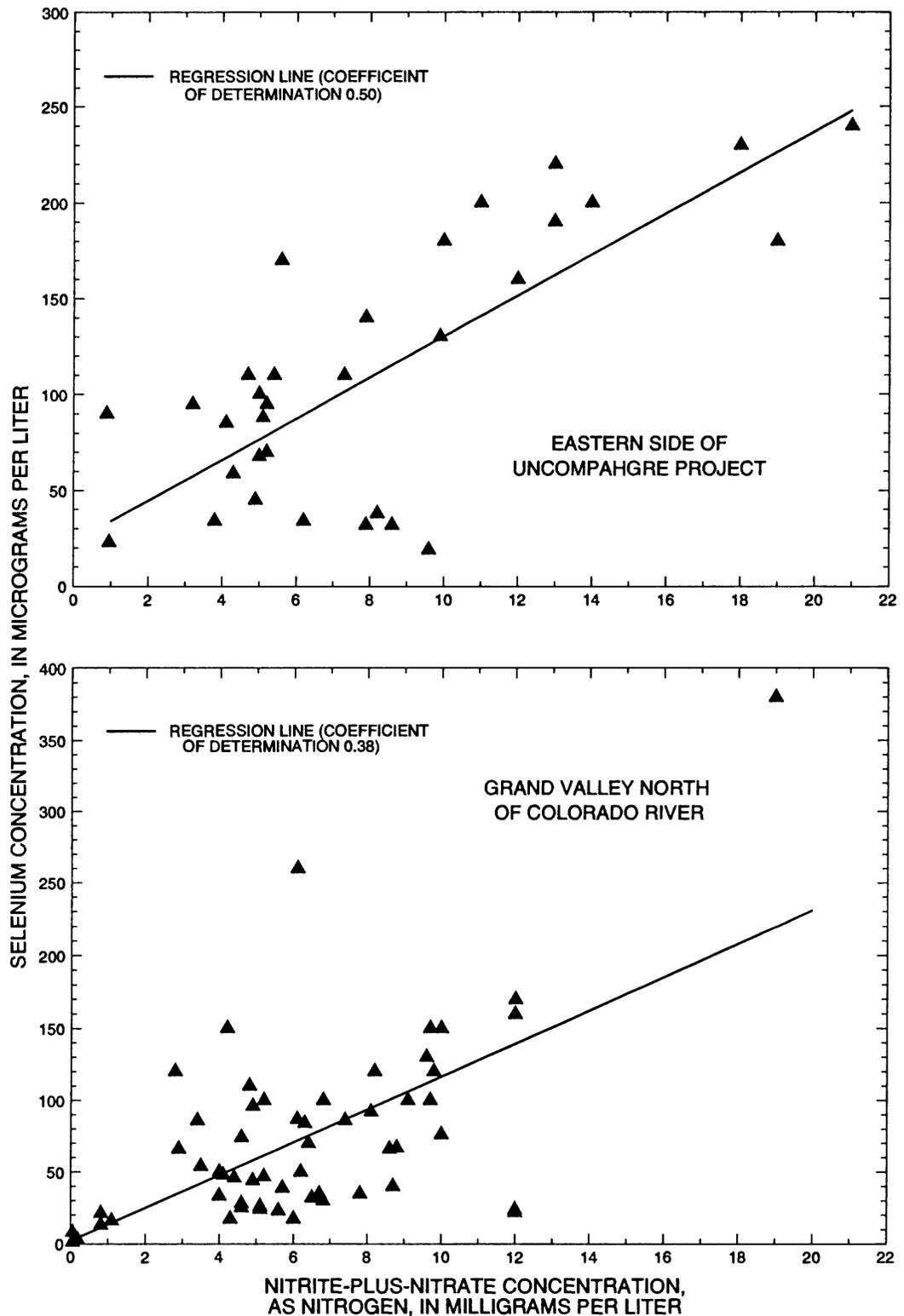
### Other Trace-Constituent Concentrations

Many concentrations of trace constituents potentially toxic to biota, such as arsenic, cadmium, copper, lead, mercury, and zinc, were about equal to or less than analytical reporting limits (table 22). In addition to selenium, Colorado has aquatic-life criteria (Colorado Department of Health, 1989) for arsenic, cadmium, chromium, copper, lead, mercury, uranium, and zinc. Except for mercury, concentrations of these trace constituents in surface-water samples were less than the chronic criteria established by the State. The criterion for mercury is 0.01 µg/L, but the analytical reporting limit was 0.1 µg/L; therefore, it is unknown if mercury concentrations exceeded the aquatic-life criterion. Cadmium was detected in only two samples, and mercury was detected in only one sample (table 22).

There was a substantial increase in boron concentrations from the applied irrigation water to irrigation-drainage water in the study area. Boron concentrations were about 10 to 50 µg/L in the irrigation-supply water for the Uncompahgre Project and the Grand Valley. In the Uncompahgre

Project area, the maximum boron concentration was 1,600 µg/L (table 22) in a drainage ditch at site ASH (fig. 26). In the Grand Valley, the maximum boron concentration was 790 µg/L in a drainage ditch at site GJ2 (fig. 31). In the Grand Valley, some of the highest boron concentrations were in smaller basins or drainage ditches. Boron concentrations generally ranged from about 250 to 600 µg/L in nonirrigation-season samples from the Uncompahgre Project and the Grand Valley.

Uranium was detected in all surface-water samples collected in the study area (table 22). The median uranium concentrations are lower for the Uncompahgre Project area than for the Grand Valley. All the samples from the Uncompahgre Project area that had uranium analysis were collected during the irrigation season, whereas almost one-half of the uranium data for the Grand Valley were obtained during the nonirrigation season. Many constituent concentrations are lower in the irrigation season compared to the nonirrigation season because of dilution by surface return flows. Median uranium concentrations of samples collected at the 20 reconnaissance sites in the Grand Valley were much higher for March 1991 (31 µg/L) than for August and September 1991 (8.8 µg/L). The two highest uranium concentrations from the Uncompahgre Project area were in samples from ponds—62 µg/L at Ferrier Pond near Austin (site FRP in fig. 23) and 16 µg/L from Markley Pond (site MKP in fig. 26). Ferrier Pond was a reference site located outside of the irrigated area served by the Uncompahgre Project; the pond is located in Mancos Shale terrain and might receive irrigation drainage from mesas north of the pond. In the Grand Valley, the maximum uranium concentration was 83 µg/L (table 22) in a sample collected at site BSW3 (fig. 30), a reference site located on Big Salt Wash upstream from the Government Highline Canal. Surface-water samples that had some of the highest uranium concentrations in the Grand Valley were from sites that had high selenium concentrations, such as upper Reed Wash (site RW4) and Indian Wash (site IW). However, there also were high uranium concentrations in samples that had some of the lower selenium concentrations, such as samples from Orchard Mesa Drain (site OMD in fig. 31).



**Figure 43.** Relations of selenium to nitrite-plus-nitrate concentrations in water samples collected during the nonirrigation season from streams and ditches on the eastern side of the Uncompahgre Project and in the Grand Valley north of the Colorado River, 1991–92.

**Table 22.** Summary of dissolved trace-constituent concentrations in surface-water samples from the Uncompahgre Project area and from the Grand Valley, 1991–92

[Concentrations in micrograms per liter; number detected is the number of samples reported as equal to or greater than the reporting limit; <, less than; includes samples collected from irrigated areas, reference sites, and mainstem rivers]

Trace constituent	Reporting limit(s)	Number of samples	Number detected	Median	Maximum	Minimum
<b>UNCOMPAHGRE PROJECT AREA</b>						
Arsenic	1	37	30	1	3	<1
Boron	10	168	168	180	1,600	10
Cadmium	1	61	1	<1	1	<1
Chromium	1	37	7	<1	3	<1
Copper	1	61	56	2	6	<1
Lead	1	61	6	<1	4	<1
Mercury	.1	61	0	<.1	<.1	<.1
Molybdenum	1	38	30	3	10	<1
Selenium	1	197	177	9	260	<1
Uranium	.6	37	37	6.2	62	1.5
Vanadium	1.0	38	37	2.7	7.7	<1.0
Zinc	3, 10	61	45	6	59	<3
<b>GRAND VALLEY</b>						
Arsenic	1	45	19	<1	2	<1
Boron	10	122	122	280	790	20
Cadmium	1, 2	45	1	<1	2	<1
Chromium	1	45	16	<1	3	<1
Copper	1	45	43	1	4	<1
Lead	1	45	0	<1	<1	<1
Mercury	.1	45	1	<.1	.2	<.1
Molybdenum	1	54	54	7.5	70	1
Selenium	1	125	124	24	380	<1
Uranium	.6	54	54	15.5	83	3.5
Vanadium	1.0	54	54	4.5	15	2.4
Zinc	3, 10	45	33	9	30	<10

## Insecticides in the Grand Valley

Pesticide data were collected in 1988 for the reconnaissance investigation of the Uncompahgre Project (Butler and others, 1991). Insecticide samples were collected at 11 outflow sites on tributaries and at two sites on the Colorado River in the Grand Valley in the summer of 1991. Samples were analyzed for 15 organophosphate and 11 carbamate insecticides. Analytical results indicated that most compounds were not detected or were detected at low concentrations. Nine organophosphate concentrations equaled or exceeded the reporting limit of 0.01 µg/L.

Chlorpyrifos was detected in two samples at concentrations of 0.06 and 0.01 µg/L. Diazinon was detected in five samples at concentrations of 0.01 to 0.12 µg/L, and the maximum concentration was in the sample from Hunter Wash (site HW1 in fig. 30). Parathion was detected in two water samples at concentrations of 0.01 µg/L in Reed Wash (site RW1) and 0.09 µg/L in Persigo Wash (site PSW1). The aquatic-life criterion for parathion is 0.04 µg/L (U.S. Environmental Protection Agency, 1986). Butler and others (1991) reported parathion concentrations greater than 0.04 µg/L in the Gunnison and Uncompahgre Rivers

in samples collected in July 1988. The only carbamate insecticide detected in water samples from the Grand Valley was a concentration of 0.8 µg/L (reporting limit 0.5 µg/L) of 3-hydroxycarbofuran in a sample from Hunter Wash.

The insecticide data were collected in 1991 as a one-time reconnaissance of some of the pesticides used in the Grand Valley. A wide variety of crops are grown in the Grand Valley, and pesticide usage can vary depending on the type of crops grown and on the weeds and insects associated with the crops. Pesticides are applied at different times of the year. A much more comprehensive sampling program than was possible for the detailed study would be needed to more adequately assess pesticide concentrations in surface water in the study area.

## SELENIUM AND OTHER CONSTITUENTS IN BOTTOM SEDIMENT

Bottom-sediment samples were collected from eight streams and washes and from four ponds at wetland sites in the study area for analysis of total selenium. Samples from streams were collected in March 1992, and samples from ponds were collected in June 1992. A sample was collected from a salt crust near an avocet nesting area adjacent to Brozina Pond in the northeast part of the Uncompahgre Project. A soil sample was collected on a hillside adjacent to Reid Pond in the Grand Valley where prince's plume (*Stanleya pinnata*), a selenium-indicator plant, was growing. Soluble and adsorbed selenium concentrations and the percent selenite were determined for the eight bottom-sediment samples collected from streams to provide additional information about selenium in bottom sediment.

### Sample Collection and Analytical Methods

A BMH-53 sampler (Ward and Harr, 1990) was used to collect bottom-sediment samples from pool and backwater areas in streams where sediment deposits were sufficient for collection of samples. A minimum of six to eight cores were collected and composited in a stainless-steel bucket using a stainless-steel spoon. The salt-crust sample was a

surficial sample collected using a spoon, and the soil sample was collected using a spoon and shovel at the base of prince's plume plants at shallow depths (less than 6 in.). Bottom-sediment and soil samples were analyzed by the Geologic Division of the USGS in Lakewood, Colo. For bottom sediment, the less-than 0.0625-mm size fraction was analyzed for selenium, uranium, 40 trace constituents, total carbon, and organic carbon by methods described by Harms and others (1990). The samples for total-selenium analysis were digested in a mixture of nitric, perchloric, and hydrofluoric acids; dried; and redissolved in hydrochloric acid (Harms and others, 1990). The salt-crust and soil samples were analyzed for the same constituents on the less-than 2-mm size fraction.

A subsample of the bottom-sediment samples collected from streams was used for the analysis of soluble and adsorbed selenium and selenite. The subsamples were placed in glass jars, were frozen, and were shipped in dry ice. The soluble and adsorbed selenium were determined by sequential extractions on the bottom-sediment samples using potassium chloride (KCl) and potassium phosphate ( $K_2HPO_4$ ) on the same sample (Fujii and others, 1988). The KCl extract was considered an approximation of soluble selenium, and the  $K_2HPO_4$  extract an approximation of the adsorbed selenium on the sediment. Selenite concentrations were determined in each extract by methods described by Fio and Fujii (1990). Most of the selenate selenium probably was extracted by KCl; therefore, the nonselenite fraction in the KCl extract was assumed to be selenate. The analyses of soluble and adsorbed selenium and selenite for bottom-sediment samples were done by the U.S. Geological Survey in Sacramento, Calif. (Roger Fujii, U.S. Geological Survey, written commun., 1992).

### Selenium Concentrations

In general, selenium concentrations were greater in bottom-sediment samples from ponds than in samples from streams (table 23). All selenium concentrations listed in table 23 exceeded the upper base-line concentration of 1.4 µg/g for soils in the Western United States (Shacklette and Boerngen, 1984). Selenium concentrations greater than or equal

to 4 µg/g in sediment are a level of concern for fish and wildlife because of food-chain bioaccumulation (Lemly and Smith, 1987). Selenium concentrations in bottom-sediment samples from the four ponds and the samples from Loutsenhizer Arroyo (site LZA1), Reed Wash (site RW1), Leach Creek (site LC1), and Indian Wash (site IW) exceeded 4 µg/g (table 23). The selenium concentration of 47 µg/g in the bottom-sediment sample from Brozina Pond (site BZP) was similar to the selenium concentration of 41 µg/g reported for a bottom-sediment sample from Sweitzer Lake (Butler and others, 1991). Brozina Pond is about 3 mi southeast of Sweitzer Lake in Mancos Shale terrain. Selenium is enriched in bottom sediment compared to water, but more so in ponds than in streams. The ratio of selenium concentrations in bottom-sediment samples to concentrations in water samples collected concurrently at each site ranged from 29 to 250 for streams and from 2,670 to 23,500 for ponds. The largest ratio of selenium concentrations was for Brozina Pond. The selenium concentrations in the salt crust collected adjacent to Brozina Pond and in the soil sample collected

among selenium-indicator plants near Reid Pond were similar to selenium concentrations in bottom sediment from streams (table 23).

Total-selenium concentrations in bottom sediment from the three streams in the Uncompahgre Project (table 23) were slightly higher than total-selenium concentrations in soil samples (data in Crock and others, 1994) that were collected from irrigated fields in the same drainage basin. The median total-selenium concentration for 11 soil samples collected in the Cedar Creek Basin was 2.9 µg/g, and the median for 15 soil samples collected in the Loutsenhizer Arroyo Basin was 3.5 µg/g. The bottom-sediment samples collected at the outflow sites for these basins (sites CD1 and LZA1 in table 23) had slightly higher selenium concentrations than median concentrations in soil. Most of the irrigated land in Cedar Creek and Loutsenhizer Arroyo Basins consists of soils derived from residual Mancos Shale or of alluvium derived primarily from shale. The total-selenium concentration in the bottom-sediment sample from Dry Creek is about twice the median concentration in irrigated soils in the Dry Creek Basin. Irrigated soils in Dry Creek

**Table 23.** Concentrations of selenium, uranium, total carbon, and organic carbon in bottom-sediment, salt-crust, and soil samples

[Sample types are: bot, bottom sediment; crust, sample from a salt crust adjacent to Brozina Pond; soil, a shallow soil sample from a hillside near Reid Pond where prince's plume, a selenium-indicator plant, was present; µg/g, micrograms per gram; bottom-sediment samples from streams were collected in March 1992 and samples from ponds in June 1992]

Site number	Stream or pond	Sample type	Selenium (µg/g)	Uranium (µg/g)	Total carbon (percent)	Organic carbon (percent)
<b>UNCOMPAHGRE PROJECT AREA (sites shown in figs. 25 and 26)</b>						
DRY1	Dry Creek	Bot	2.0	4.46	2.32	0.67
CD1	Cedar Creek	Bot	3.5	5.18	2.96	.88
LZA1	Loutsenhizer Arroyo	Bot	6.9	5.09	3.34	.60
MKP	Markley Pond	Bot	16	12.5	5.48	1.73
BZP	Brozina Pond	Bot	47	12.1	9.30	2.72
BZP	Brozina Pond	Crust	3.4	5.62	1.56	.56
<b>GRAND VALLEY (sites shown in figs. 30 and 31)</b>						
SC	Salt Creek	Bot	1.9	4.55	2.32	.51
MWP	Pond in Mack Wash	Bot	21	6.28	5.62	2.21
RDP	Reid Pond	Bot	15	7.39	3.79	1.95
RDP	Reid Pond	Soil	4.1	4.90	3.48	.94
RW1	Reed Wash	Bot	6.3	5.62	3.44	.62
AC1	Adobe Creek	Bot	3.9	6.45	3.37	.92
LC1	Leach Creek	Bot	5.6	5.45	3.35	.93
IW	Indian Wash	Bot	16	6.69	3.17	1.25

Basin primarily are derived from terrace deposits and the Dakota Sandstone. Bottom sediment in tributary streams does not seem to be accumulating appreciable quantities of selenium when compared to the selenium content of the parent soils.

Selenium can be removed from water and immobilized in sediment through chemical and bacterial reduction, adsorption, coprecipitation, and deposition of plant and animal tissue (Lemly and Smith, 1987). In reducing environments, selenide and elemental selenium are very insoluble in water (Elrashidi and others, 1989), and selenium can become incorporated into the bottom sediment. Reducing conditions are likely near the bottom of most ponds and lakes; therefore, selenium enrichment in bottom sediment in ponds is not unexpected. The ponds, lakes, and wetlands in the Uncompahgre Project area and the Grand Valley probably function as sinks for selenium. Because selenium concentrations and loads in water discharging into and out of ponds and lakes were not measured, the magnitude of selenium removal in ponds and lakes in the study area was not determined. However, probably much more selenium is discharged to streams, washes, and ditches and transported out of the study area by the Gunnison and Colorado Rivers compared to the amount of selenium that is immobilized in pond and lake sediment.

Total-selenium concentrations are compared to the soluble and adsorbed selenium for bottom-sediment samples from the eight streams in table 24. The soluble selenium (the KCl extract) accounted for about 1 percent or less of the total-selenium concentration in all samples (table 24). The surface-adsorbed selenium (the  $K_2HPO_4$  extract) accounted for about 2.5 to 16.9 percent of the total selenium. Except for site LC1, the soluble and adsorbed selenium extracted by KCl and  $K_2HPO_4$  accounted for less than 10 percent of the total selenium in the eight bottom-sediment samples (table 24). The unextracted selenium could be chemically bound in oxides by precipitation or coprecipitation; could be present in insoluble, reduced chemical forms; or might be bound in organic matter. Fujii and others (1988) reported that the proportion of adsorbed selenium to total selenium in soils in the San Joaquin Valley in California ranged from 1 to 11 percent, which is similar to the results for bottom sediment from streams in the study area.

The percent selenite in both selenium extracts was 25 percent or less, except for the sample from Salt Creek (site SC) in the Grand Valley (table 24). Fujii and others (1988) reported that most of the surface-adsorbed selenium in soils was selenite, which, except for the sample from site SC, was not

**Table 24.** Concentrations of total, soluble, and adsorbed selenium and the percent selenite in bottom-sediment samples from eight streams, March 1992

[Concentrations in micrograms per gram; KCl- (potassium chloride-) extractable selenium approximates the soluble selenium, and  $K_2HPO_4$ - (potassium phosphate-) extractable selenium approximates the adsorbed selenium; selenium-extract data from Roger Fujii (U.S. Geological Survey, written commun., 1992)]

Site number	Stream name	Total selenium	KCl-extractable (soluble) selenium		$K_2HPO_4$ -extractable (adsorbed) selenium	
			Concentration	Percent selenite	Concentration	Percent selenite
<b>UNCOMPAHGRE PROJECT AREA (sites shown in figs. 25 and 26)</b>						
DRY1	Dry Creek	2.0	0.010	0	0.054	25
CD1	Cedar Creek	3.5	.007	1.5	.181	18
LZA1	Loutsenhizer Arroyo	6.9	.038	10	.430	19
<b>GRAND VALLEY (sites shown in figs. 30 and 31)</b>						
SC	Salt Creek	1.9	.027	26	.128	90
RW1	Reed Wash	6.3	.057	15	.156	13
AC1	Adobe Creek	3.9	.048	12	.291	19
LC1	Leach Creek	5.6	.071	5.0	.944	11
IW	Indian Wash	16	.076	14	.813	10

true for the bottom-sediment samples collected from the eight streams in the study area. Geochemical conditions in soils from the San Joaquin Valley might be different than geochemical conditions for bottom sediment in streams in the Uncompahgre Project and the Grand Valley.

For the 12 bottom-sediment samples collected from streams and ponds (table 23), there were significant (significance level 0.05) positive correlations between selenium concentrations and concentrations of total carbon and organic carbon. The correlation coefficient for selenium and organic carbon was 0.95. Selenium was positively correlated with organic carbon in mining overburden in Wyoming (Naftz and Rice, 1989). Singh and others (1981) reported that organic carbon had a positive effect on selenate and selenite adsorption in semiarid soils. The sample from Brozina Pond that had the maximum selenium concentration of 47  $\mu\text{g/g}$  in bottom sediment also had the maximum organic carbon concentration of 2.72 percent. Perhaps the high organic-carbon content of the bottom-sediment sample from Indian Wash (site IW in table 23) might partly account for the high selenium concentration in Indian Wash bottom sediment compared to the other seven streams where bottom sediment was sampled.

## Other Trace-Constituent Concentrations

Most other trace-constituent concentrations in bottom sediment (Butler and others, 1994) were less than the upper base lines for soil in the Western United States (Shacklette and Boerngen, 1984). Uranium concentrations in 9 of the 14 samples listed in table 23 exceeded the upper base line for uranium of 5.3  $\mu\text{g/g}$  (Shacklette and Boerngen, 1984). The differences in uranium concentrations between pond bottom sediment and stream bottom sediment were considerably less than were the differences in selenium concentrations, especially in the Grand Valley (table 23). Molybdenum concentrations in three of the four bottom-sediment samples from ponds were slightly greater than the upper soils base line of 4  $\mu\text{g/g}$ . The salt-crust sample from Brozina Pond has unusually low concentrations of some trace constituents, such as barium, chromium, vanadium, and zinc, compared to bottom-sediment samples.

## BIOLOGICAL INVESTIGATIONS

### Sample Collection

Biological samples were collected by the FWS using standard equipment and techniques (U.S. Fish and Wildlife Service, 1986, 1990). Fish were collected using electroshocking equipment and seine or gill nets. Fish were rinsed, weighed, measured for length, and immediately frozen on dry ice until stored in a freezer. Whole-body fish samples from tributaries were composited by species into groups of three or more fish as directed by the sampling protocol. Fish samples from rivers were processed as individual samples for data-analysis purposes. Fish-fillet and -egg samples were taken from individual fish and were not composited. Fish samples for analyses of inorganic contaminants were frozen in plastic bags. Fish samples for analyses of organic compounds were wrapped in aluminum foil and placed in plastic bags.

Vascular plants and algae were collected by handpicking. These samples were placed in chemically cleansed jars, weighed, and frozen. Algae samples probably contained green algae (Chlorophyta) and blue-green algae (Cyanophyta). Stream invertebrates were collected using a kick screen. Several easily identifiable invertebrate groups were combined to obtain sufficient biomass for analysis. Crayfish were collected when present.

Birds were shot using steel shot, and livers were removed using stainless-steel dissecting equipment. Bird liver was considered to be the best organ for a general trace-element scan (Ohlendorf, 1993), although other tissues might be better indicators for specific elements (such as kidney for cadmium and bone for lead). Dissecting equipment was cleansed using water and soap and rinsed using distilled water and benzene prior to the removal of each liver. Bird livers and muscle tissue were placed in chemically cleansed jars, weighed, and frozen. Livers from each bird group were sometimes composited, which resulted in two or three livers constituting one sample.

After locating nests, bird eggs were removed, the egg volume was determined (by water displacement), and eggs were opened to examine embryos for possible developmental abnormalities. After examination, eggs were placed in chemically cleansed jars, weighed, and frozen. Small eggs, such as blackbird eggs, were composited to provide sufficient biomass for analysis.

The sampling period depended on availability of bird eggs and prefledgling birds. Because prefledglings generally are confined to a local area until they fledge, trace elements and pesticides in their tissues are obtained from food and water in the area where the birds are reared. An attempt was made to collect prefledglings immediately before fledging because older birds would have been exposed to any contaminants present in the area for a longer time period than younger birds. Such collections were not always possible because of time limitations in the sampling effort and because of considerable predation on young birds. Although developmental abnormalities among embryos in bird eggs cannot be detected before the eggs have reached one-half term (Ohlendorf and others, 1986), eggs were collected as soon as they were discovered because of the high risk of predation. Therefore, early collection to ensure that representative egg samples were available for contaminant analysis often outweighed the loss of pathological information related to field observations.

Because of high predation rates on bird eggs and hatchlings, incubation studies were conducted. For the incubation study, eggs were collected in the field and placed into egg cartons with Kleenex tissues to keep the pointed end down (Stromberg, 1975; Brown, 1979). The egg cartons were kept cool during transportation to the laboratory. Usually, the eggs were transferred from egg cartons to trays with the small end down and incubated at a temperature of 99°F and at a relative humidity of 55 percent (Stromberg, 1975; Brown, 1979). Eggs were mechanically turned at 4-hour intervals. Eggs were candled and a hatching date was projected by using a field guide for incubation lengths for each species (Harrison, 1979). Newly hatched young were examined for external deformities. Eggs that failed to hatch within a few days of their hatching date were opened and examined. All incubated specimens were frozen and sent to the laboratory for trace-element analysis.

## **Analytical Methods**

The quantitative analyses of trace constituents in biological samples were performed by the Environmental Trace Substances Research Center in Columbia, Mo. This laboratory was contracted by the FWS Patuxent Analytical Control

Facility in Laurel, Md. Biological samples were analyzed for selenium and selected trace constituents.

Analyses for most trace constituents in biota samples were performed using inductively coupled argon-plasma atomic-absorption spectrometry after complete digestion of the sample by strong acids. Analyses for selenium and arsenic in biota samples were performed using HGAAS, and analysis for mercury was performed using flameless cold-vapor atomic-absorption spectrometry.

Organochlorine pesticides were analyzed at Mississippi State University in Mississippi State, Miss. Methods consisted of solvent extraction and electron-capture gas chromatography. Polycyclic aromatic hydrocarbons (PAH's) were analyzed at Texas A&M University in College Station, Tex. The quantitative analyses were performed by using a mass spectrometer detector in the selected ion-monitoring mode.

## **Data Analysis**

Statistical analyses were conducted using a statistical software program called Statistical Analysis System (SAS Institute, 1982). Geometric mean, geometric deviation, maximum, and minimum concentrations were determined.

Fish data for the Gunnison, Uncompahgre, and Colorado Rivers were analyzed by using a General Linear Model (GLM) for unbalanced data. A two-way ANOVA and the Tukey-Kramer Honestly Significant Difference (HSD) (SAS Institute, 1982) were used to compare selenium residues in fish among the three rivers, among individual sites on the three rivers, and among three fish trophic groups.

## **Data Interpretation**

Many chemical, physical, and biological factors affect the toxicity of environmental contaminants to biological organisms. Chemical and physical factors include contaminant type, chemical species or form, pH, water temperature, dissolved oxygen, hardness, salinity, and multiple-chemical exposure (antagonism and synergism). Duration of exposure, quantity of contaminant, and exposure pathways from the environment to the organism also affect toxicity. Some trace constituents are beneficial to organisms

at small concentrations, but can be toxic at larger concentrations. Biological and physiological factors affecting toxicity are species, age, sex, and health of the organism. Interpretation of contaminant concentrations in biota is difficult and complex and often might not be possible, using the data collected in field studies. One of the best methods for interpreting contaminant data is by comparison with data collected from other field studies and from laboratory studies.

Concentrations of inorganic trace constituents in biological samples are extremely variable. Trace-constituent data can be interpreted by comparison to available literature to determine if constituent concentrations in biota samples exceed concentrations that could be harmful to fish and wildlife or exceed guidelines for human consumption. A frequently used index for interpreting contaminant data for fish samples is the National Contaminant Biomonitoring Program (NCBP) of the FWS. Schmitt and Brumbaugh (1990) reported the 85th-percentile concentrations for arsenic, cadmium, copper, lead, mercury, selenium, and zinc for fish samples collected during 1976–84 throughout the United States. The 85th percentile has been established by NCBP as an arbitrary concentration for distinguishing whole-body fish samples that have large concentrations for the seven trace constituents relative to a national data base. The 85th percentile is not necessarily an indicator of potential hazards to fishery resources nor can it be used in place of regulatory standards. The NCBP means and percentiles were calculated using combined fish species, and readers need to be aware that there can be substantial differences in selenium accumulation between species (Lemly, 1993). Nevertheless, NCBP data still are useful for comparison purposes. Concentrations listed in Schmitt and Brumbaugh (1990) are wet-weight concentrations; therefore, the dry-weight concentrations for biota samples collected for the detailed study (Butler and others, 1994) for the seven trace constituents were converted to wet-weight concentrations to facilitate comparison to the 85th-percentile concentrations. The NCBP also has collected data for organochlorine pesticides (Schmitt and others, 1990).

The NCBP 85th percentile was reported for several periods within the sampling period (1976–84) (Schmitt and Brumbaugh, 1990). The most recent

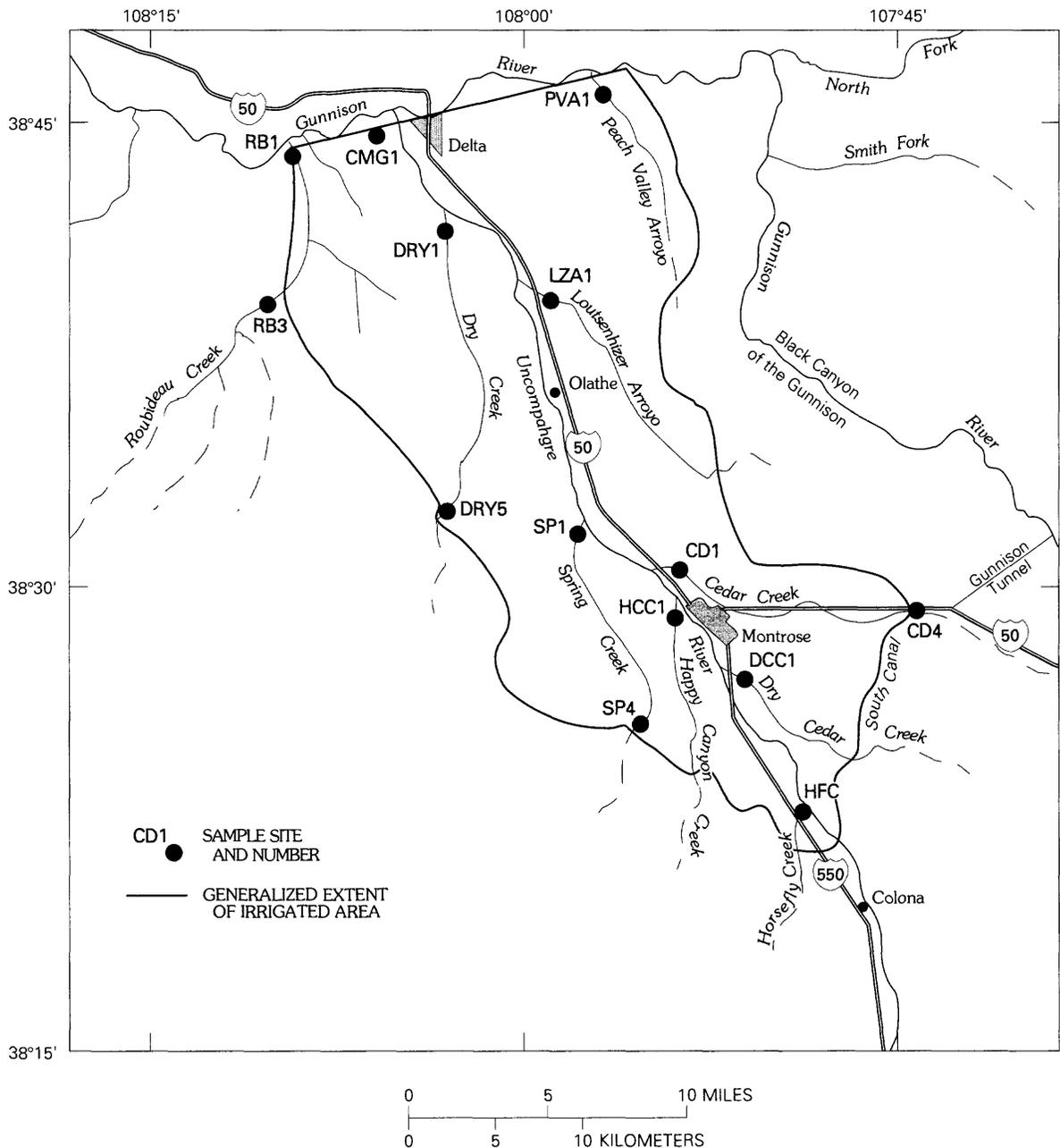
compilation was for fish samples collected during 1984, and the 85th percentiles reported for 1984 are used in this report. The previous DOI reconnaissance investigations used 85th percentiles based on earlier compilation periods.

## **Selenium Concentrations in Fish Samples and Their Food Items in Irrigated Areas**

### **Uncompahgre Project**

In general, selenium concentrations were higher in biota samples collected east of the Uncompahgre River than in samples collected west of the Uncompahgre River (Butler and others, 1994, tables 23–27). This pattern in selenium data in biota was similar to the pattern in surface-water samples. Biota-sampling sites within the irrigated area east of the Uncompahgre River include sites DCC1, CD1, LZA1, and PVA1 (fig. 44), and west of the river include sites HFC, HCC1, SP1, SP4, DRY1, DRY5, CMG1, and RB1 (fig. 44). Aquatic-plant, aquatic-insect, and crayfish samples collected east of the Uncompahgre River from Loutsenhizer Arroyo (site LZA1 in fig. 44) contained 4.1, 26, and 12  $\mu\text{g/g}$  dry weight selenium (Butler and others, 1994, table 24). An invertebrate sample from Peach Valley Arroyo (site PVA1 in fig. 44) contained 7.1  $\mu\text{g/g}$  dry weight selenium. Lemly and Smith (1987) and Lemly (1993) recommended that 3  $\mu\text{g/g}$  dry weight selenium be used as a toxic threshold guideline for selenium transferred to consumer species of fish and wildlife through aquatic food chains. The samples from Loutsenhizer and Peach Valley Arroyos exceeded this dietary guideline.

Eight plant and algae samples collected from the western side of the Uncompahgre River had a geometric mean selenium concentration of 1.0  $\mu\text{g/g}$  dry weight (table 25), which is less than the dietary guideline. An aquatic-invertebrate sample collected from Horsefly Creek (site HFC in fig. 44) on the western side of the Uncompahgre River contained 6.1  $\mu\text{g/g}$  dry weight selenium and exceeded the 3- $\mu\text{g/g}$  dry-weight dietary guideline. A crayfish sample collected from Happy Canyon Creek (site HCC1) contained 2.1  $\mu\text{g/g}$  dry weight selenium.



**Figure 44.** Location of 1991 biota sampling sites on tributary streams in the Uncompahgre Project.

All eight fish samples collected from streams on the eastern side of the Uncompahgre River exceeded the 1984 NCBP 85th-percentile selenium concentration (table 26) of  $0.73 \mu\text{g/g}$  wet weight ( $2.92 \mu\text{g/g}$  dry weight at 75-percent moisture). Lemly (1993) advised that a whole-body selenium concentration of  $4 \mu\text{g/g}$  dry weight or greater could be of concern for the overall health and reproductive vigor of freshwater fish. All fish samples collected east of the Uncompahgre River exceeded  $4 \mu\text{g/g}$  dry

weight selenium. Two speckled dace samples collected east of the Uncompahgre River (sites DCC1 and LZA1 in fig. 44) contained 27 and  $28 \mu\text{g/g}$  dry weight selenium (table 25). A green sunfish collected from Loutsenhizer Arroyo (site LZA1) contained  $37 \mu\text{g/g}$  dry weight selenium, which is noteworthy because centrarchids (the sunfish family) seem to be especially sensitive to selenium toxicity (Cumbie and Van Horn, 1978; Lemly, 1985).

**Table 25.** Statistical summary of selenium concentrations in selected biota samples collected in 1991 in the Uncompahgre Project area

[Concentrations in micrograms per gram dry weight; N, number of samples; GM, geometric mean; GD, geometric deviation; --, no data or not computed; data for reference sites on Cedar Creek (CD4) and Roubideau Creek (RB3) were excluded]

Statistic	Aquatic plants and algae	Aquatic Invertebrates	Speckled dace	Suckers	Roundtail chub	Trout	Green sunfish
<b>UNCOMPAHGRE PROJECT—EAST OF THE UNCOMPAHGRE RIVER</b>							
N	1	3	2	5	0	0	1
GM	--	13	27.5	13.9	--	--	--
GD	--	1.9	1.0	1.4	--	--	--
MAXIMUM	4.1	26	28	22	--	--	37
MINIMUM	4.1	7.1	27	9.0	--	--	37
<b>UNCOMPAHGRE PROJECT—WEST OF THE UNCOMPAHGRE RIVER</b>							
N	8	3	3	13	1	5	0
GM	1.0	3.0	8.9	2.9	--	5.8	--
GD	2.3	1.9	1.5	1.6	--	2.3	--
MAXIMUM	2.9	6.1	13	5.9	5.9	25	--
MINIMUM	.2	2.1	5.6	1.2	5.9	3.4	--
<b>SMITH FORK AND NORTH FORK BASINS</b>							
N	3	3	3	3	1	5	0
GM	1.6	3.1	7.3	2.7	--	5.8	--
GD	1.0	1.6	1.1	1.8	--	1.5	--
MAXIMUM	1.6	4.8	7.8	3.9	6.1	9.4	--
MINIMUM	1.6	2.0	6.9	1.4	6.1	3.6	--
<b>CURRENT CREEK, ALFALFA RUN, AND TONGUE CREEK</b>							
N	3	3	2	1	2	0	0
GM	6.6	7.0	12.5	--	13.8	--	--
GD	1.7	1.4	1.1	--	1.6	--	--
MAXIMUM	12	9.4	13	12	19	--	--
MINIMUM	4.1	4.9	12	12	10	--	--

**Table 26.** Number of whole-body fish samples collected in the Uncompahgre Project area that exceeded the 1984 National Contaminant Biomonitoring Program (NCBP) 85th-percentile concentrations for seven trace constituents

[NCBP 85th-percentile concentrations in micrograms per gram wet weight; NCBP data from Schmitt and Brumbaugh (1990); east, samples from eastern side of the Uncompahgre Project; west, samples from the western side of the Uncompahgre Project; adjacent 1, samples from the Smith Fork and North Fork Basins; adjacent 2, samples from Currant Creek, Alfalfa Run, and Tongue Creek; N, number of samples; numbers in brackets are the number of exceedances expressed as a percentage of the number of samples in each group]

Trace constituent	NCBP 85th percentile	East (N=8)	West (N=29)	Adjacent 1 (N=15)	Adjacent 2 (N=8)	Crawford Reservoir (N=5)
Arsenic	0.27	0 [0]	4 [14]	1 [7]	1 [12]	1 [20]
Cadmium	.05	3 [38]	7 [24]	3 [20]	0 [0]	0 [0]
Copper	1.0	5 [62]	19 [66]	5 [33]	4 [50]	2 [20]
Lead <sup>1</sup>	.22	2 [25]	9 [31]	0 [0]	0 [0]	0 [0]
Mercury	.17	0 [0]	4 [14]	0 [0]	0 [0]	0 [0]
Selenium	.73	8 [100]	22 [76]	14 [93]	8 [100]	4 [80]
Zinc	34.2	3 [38]	5 [17]	3 [20]	3 [38]	0 [0]

<sup>1</sup>Some samples had reporting limits greater than the 1984 NCBP 85th percentile.

Twenty-two of 29 fish samples collected on the western side of the Uncompahgre Project exceeded the 1984 NCBP 85th-percentile selenium concentration (table 26). Eight of these 22 samples were collected from Dry Creek. One trout sample collected at site DRY1 from lower Dry Creek contained 25 µg/g dry weight selenium. Relatively high selenium concentrations also were in surface-water samples collected from lower Dry Creek compared to the other major streams on the western side, and these concentrations are partly attributed to the transport of water from the Uncompahgre River by the Ironstone Canal into the lower Dry Creek Basin. Two trout liver samples collected west of the Uncompahgre River (sites HCC1 and SP1 in fig. 44) contained 110 and 180 µg/g dry weight selenium. These concentrations were much greater than a guideline concentration of 12 µg/g dry weight selenium in fish livers (Lemly, 1993). Liver tissue often accumulates the greatest amount of selenium (Sager and Cofield, 1984), and concentrations in liver tissue might be useful in assessing recent exposure (Ohlendorf, 1993).

All selenium concentrations in aquatic-plant and -invertebrate samples collected in tributaries downstream from the confluence of the Uncompahgre and Gunnison Rivers (Butler and others, 1994, table 27) were less than the dietary guideline of 3 µg/g dry weight (Lemly and Smith, 1987; Lemly 1993). Ten of 13 whole-body fish samples exceeded the 1984 NCBP 85th-percentile concentration of 2.9 µg/g dry weight (at 75-percent moisture), and 9 of these samples exceeded the 4-µg/g selenium concentration of concern for reproductive problems in whole-body fish (Lemly, 1993). Highest selenium concentrations were in fish collected from Cummings Gulch (site CMG1 in fig. 44); a trout fillet contained 9.9 µg/g dry weight selenium, a whole-body speckled dace sample contained 13 µg/g dry weight selenium, and a whole-body carp sample contained 12 µg/g dry weight selenium (Butler and others, 1994, table 27).

The geometric mean selenium concentration for five sucker samples collected on the eastern side of the Uncompahgre Project was 13.9 µg/g dry weight (table 25). Two composite sucker samples from site CD4 (fig. 44), a reference site on Cedar Creek, contained 6.1 and 4.7 µg/g dry weight selenium. One composite sucker sample collected at site CD1, near the mouth of Cedar Creek, contained almost twice as much selenium (12 µg/g dry weight

selenium) as the sucker samples from site CD4 (Butler and others, 1994, table 24). The geometric mean selenium concentration for 13 sucker samples collected west of the Uncompahgre River was only 2.9 µg/g dry weight (table 25). Selenium concentrations in sucker samples from site RB3 (a reference site on Roubideau Creek) (fig. 44) contained 1.3 and 2.9 µg/g dry weight selenium. Selenium concentrations downstream at site RB1 on Roubideau Creek (fig. 44) were slightly higher than the concentrations at site RB3 at 2.2 and 4.6 µg/g dry weight. Selenium concentrations in roundtail chub samples also were similar between the sites on Roubideau Creek; the samples collected from site RB1 contained 5.9 µg/g dry weight selenium, and those collected from site RB3 contained 5.4 µg/g dry weight selenium. Two speckled dace samples collected from the eastern side of the project had selenium concentrations of 27 and 28 µg/g dry weight, whereas three speckled dace samples collected on the western side had a geometric mean of 8.9 µg/g dry weight selenium.

### Areas Adjacent to the Uncompahgre Project

Most biota samples (especially fish) collected from areas adjacent to the Uncompahgre Project also had high selenium concentrations. Data for adjacent sites (fig. 45) were collected in the Smith Fork (site SMF) and North Fork (sites NFK2 and NFK3) of the Gunnison River, plus Crawford Reservoir (site CR) (located on the Smith Fork). Data for adjacent sites also include samples collected from the Gunnison River at site GUN2 and its tributaries between the confluence with the North Fork and the confluence with the Uncompahgre River (sites CRC, AFR, and TGC in fig. 45). Geometric mean selenium concentrations for biota collected from sites adjacent to the Uncompahgre Project are listed in table 25.

Almost all whole-body fish samples from the Smith Fork, the North Fork of the Gunnison River, and Crawford Reservoir had selenium concentrations that exceeded the 1984 NCBP 85th-percentile concentration of 0.73 µg/g wet weight (table 26), and many concentrations exceeded the 4-µg/g dry-weight selenium concentration of concern for whole-body fish (Lemly, 1993). One whole-body trout sample collected from Crawford Reservoir (site CR in fig. 45) contained 18 µg/g dry weight selenium.

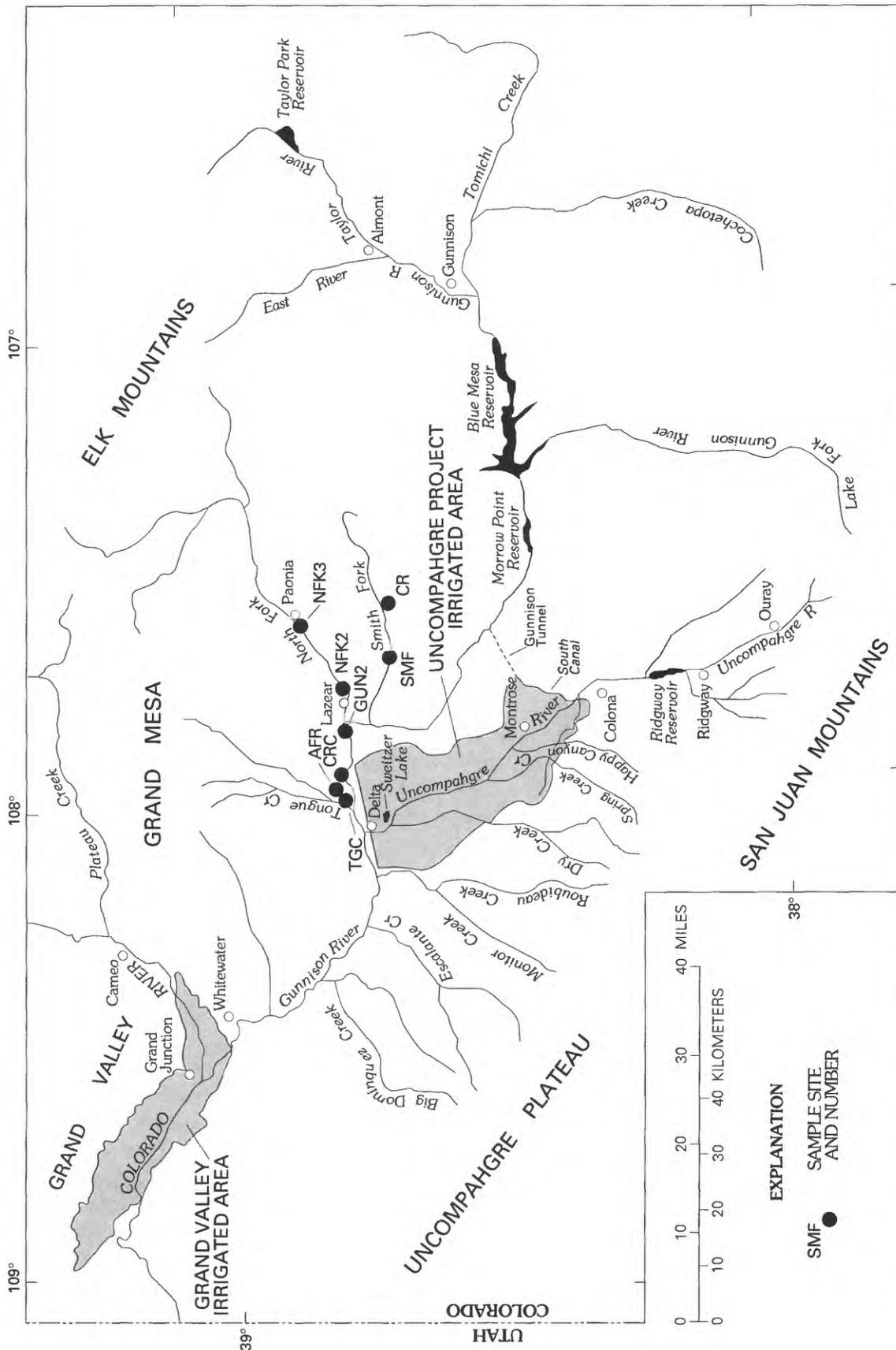


Figure 45. Location of 1991 biota sampling sites adjacent to the Uncompahgre Project.

A whole-body perch sample collected from Crawford Reservoir (site CR) contained 11  $\mu\text{g/g}$  dry weight selenium, which is slightly less than the concentration of 12  $\mu\text{g/g}$  dry weight selenium that Lemly and Smith (1987) warned could cause reproductive failure in warmwater fishes. A fillet sample taken from a yellow perch collected from Crawford Reservoir (site CR) contained 16  $\mu\text{g/g}$  dry weight selenium, which exceeded the concentration of concern of 8  $\mu\text{g/g}$  dry weight selenium for fish-fillet samples (Lemly, 1993). Although centrarchids (perch and sunfish) seem to be especially sensitive to selenium (Cumbie and Van Horn, 1978; Lemly, 1985), the yellow perch population in Crawford Reservoir is thriving with good reproduction.

Two fish-liver samples taken from a trout (site SMF in fig. 45) and a catfish (site CR) either equaled or exceeded the concentration of concern for fish livers of 12  $\mu\text{g/g}$  dry weight (Lemly, 1993). An egg sample from a trout (site SMF) contained 31  $\mu\text{g/g}$  dry weight selenium, which exceeded the concentration of concern of 10  $\mu\text{g/g}$  dry weight selenium in fish eggs (Lemly, 1993). The high selenium concentrations in biota collected from site SMF are noteworthy because selenium was not detected in the surface-water sample collected in July 1991.

Selenium concentrations in biota samples collected from the Gunnison River (site GUN2) and the three tributaries (sites CRC, AFR, and TGC in fig. 45) also were elevated (table 25). Selenium concentrations in all six dietary items (aquatic plants and invertebrates) from the three tributary sites exceeded the dietary guideline of 3  $\mu\text{g/g}$  dry weight (Lemly and Smith, 1987; Lemly, 1993). All whole-body fish samples collected from the three tributary sites exceeded the 1984 NCBP 85th-percentile concentration (table 26) and exceeded the 4- $\mu\text{g/g}$  dry-weight concentration of concern for whole-body fish (Lemly, 1993). Six whole-body fish samples collected from Currant Creek (site CRC), Alfalfa Run (site AFR), and the Gunnison River (site GUN2) (Butler and others, 1994, table 26) equaled or exceeded 12  $\mu\text{g/g}$  dry weight selenium, which is the concentration that Lemly and Smith (1987) warned might cause reproductive problems in warmwater fish. Selenium concentrations in fathead minnow whole-body samples from three sites (sites GUN2, CRC, and TGC) ranged from 7.5 to 20.4  $\mu\text{g/g}$  dry weight, exceeding known toxicity concentrations for fathead minnows. Ogle and Knight (1989) reported that a

whole-body selenium concentration of 6  $\mu\text{g/g}$  dry weight slowed growth in juvenile and adult fathead minnows. Schultz and Hermanutz (1990) reported reproductive failure in fish that had a whole-body selenium concentration of 8  $\mu\text{g/g}$  dry weight. Although the selenium concentrations in biota samples collected from Alfalfa Run (site AFR) were high, selenium was not detected in the single surface-water sample collected at site AFR in July 1991.

### Grand Valley

Although variable, high selenium concentrations were reported in most Grand Valley biota samples (Butler and others, 1994, tables 28–30), which is not surprising because most selenium concentrations in surface-water samples often exceeded the chronic aquatic-life criterion, and many selenium concentrations in water samples exceeded the acute criterion during the nonirrigation season. Biota sampling sites on streams in the Grand Valley are shown in figure 46. Statistical summaries of selenium concentrations in aquatic plants, crayfish, and selected species of whole-body fish are listed in table 27. The summary data in table 27 does not include composite invertebrate samples nor does it include all fish species.

Three aquatic-plant samples were collected in Colorado River tributaries in the east Grand Valley, upstream from the Gunnison River confluence, and had a geometric mean selenium concentration of 4.1  $\mu\text{g/g}$  dry weight (table 27). Selenium concentrations in two of the three plant samples from sites IW and OM2 (fig. 46) exceeded the toxicity guideline of 3  $\mu\text{g/g}$  dry weight (Lemly and Smith, 1987; Lemly, 1993). The geometric mean selenium concentration for five invertebrate samples (including crayfish) collected in the east Grand Valley was 5.5  $\mu\text{g/g}$  dry weight, and concentrations in three of the five invertebrate samples from sites IW and OMD (fig. 46) exceeded the guideline of 3  $\mu\text{g/g}$  dry weight selenium. All 15 fish samples collected in the east Grand Valley tributaries contained selenium concentrations that exceeded the 1984 NCBP 85th-percentile concentration of 0.73  $\mu\text{g/g}$  wet weight (table 28) and exceeded the whole-body concentration of 4  $\mu\text{g/g}$  dry weight that could be of concern for the overall health and reproductive vigor of freshwater fish. The highest selenium concentration in a fish sample was 19  $\mu\text{g/g}$  dry weight in a red shiner collected from Lewis Wash (site LW in fig. 46).

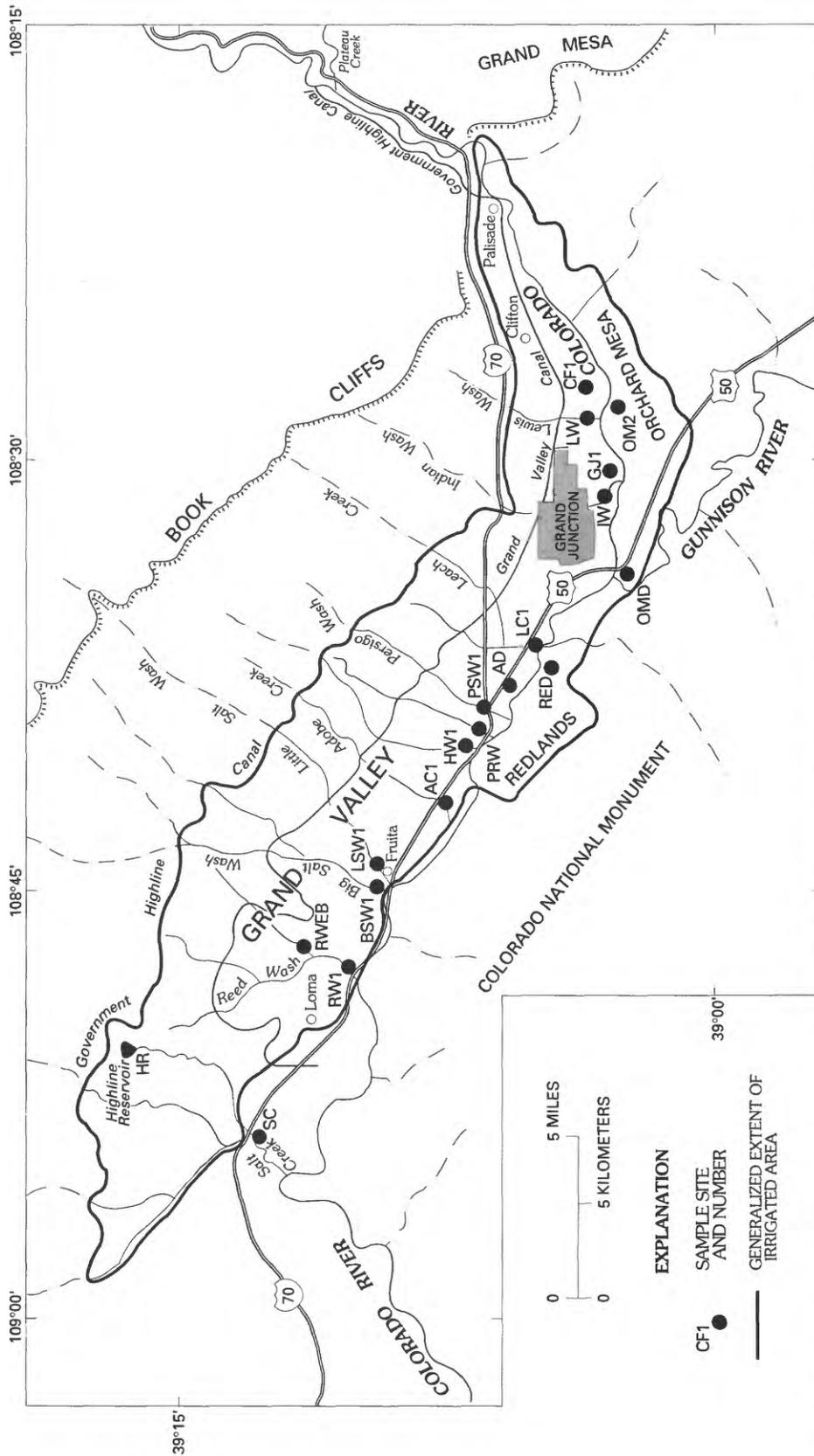


Figure 46. Location of 1991 biota sampling sites on tributary streams in the Grand Valley.

The selenium concentrations in fathead minnow whole-body samples ranged from 7.9 at site CF1 to 13 µg/g dry weight at site OMD (table 27) and exceeded known toxicity concentrations of 6 µg/g dry weight selenium for fathead minnows (Ogle and Knight, 1989; Schultz and Hermanutz, 1990).

Four aquatic-plant samples collected in the middle Grand Valley from tributaries of the Colorado River between the Gunnison River confluence and the town of Fruita (fig. 46) had a geometric mean selenium concentration of 1.8 µg/g dry weight (table 27). The selenium concentration of 7.0 µg/g dry weight from site RED (fig. 46) was the only plant sample that had a selenium concentration that exceeded the dietary guideline of 3 µg/g dry weight selenium for fish and wildlife (Lemly and Smith,

1987; Lemly 1993). A crayfish sample from Pritchard Wash at site PRW (fig. 46) containing 6.2 µg/g dry weight selenium was the only one of three invertebrate samples collected from Colorado River tributaries in the middle Grand Valley that exceeded the dietary guideline of 3 µg/g dry weight selenium. All 23 fish samples collected in tributary streams in the middle Grand Valley contained selenium concentrations that exceeded the 1984 NCBP 85th-percentile concentration of 0.73 µg/g wet weight (table 28) (Schmitt and Brumbaugh, 1990) and all but one sample exceeded the whole-body concentration of concern of 4 µg/g dry weight (Lemly and Smith, 1987; Lemly, 1993). Selenium concentrations in whole-body fathead minnows in the middle Grand Valley ranged from 8 µg/g dry weight (site LC1 in fig. 46) to 22 µg/g

**Table 27.** Statistical summary of selenium concentrations in selected biota samples collected during 1991 from the Grand Valley

[Concentrations in micrograms per gram dry weight; N, number of samples; GM, geometric mean; GD, geometric deviation; --, no data];

Statistic	Aquatic plants and algae	Crayfish	Speckled dace	Fathead minnows	Suckers	Carp	Roundtail chub	Channel catfish
<b>EAST GRAND VALLEY—UPSTREAM FROM THE GUNNISON RIVER</b>								
N	3	4	3	5	1	0	2	0
GM	4.1	4.6	7.2	10.1	--	--	6.5	--
GD	2.1	1.5	1.3	1.2	--	--	2.8	--
MAXIMUM	7.5	7.3	10	13	9.7	--	8.5	--
MINIMUM	1.8	3.0	6.1	7.9	9.7	--	4.5	--
<b>MIDDLE GRAND VALLEY—BETWEEN THE GUNNISON RIVER AND FRUITA</b>								
N	4	3	1	5	6	0	5	0
GM	1.8	4.0	--	13.2	7.8	--	7.6	--
GD	2.6	1.5	--	1.5	1.4	--	1.1	--
MAXIMUM	7.0	6.2	13	22	10	--	8.4	--
MINIMUM	.8	2.7	13	8.0	3.9	--	6.8	--
<b>WEST GRAND VALLEY—FROM FRUITA TO SALT CREEK (STREAMS)</b>								
N	0	2	3	1	10	0	4	0
GM	--	4.4	13.4	--	9.2	--	8.6	--
GD	--	1.2	1.5	--	1.7	--	1.4	--
MAXIMUM	--	5.0	19	7.3	19	--	12	--
MINIMUM	--	3.9	8.3	7.3	3.3	--	5.8	--
<b>HIGHLINE RESERVOIR</b>								
N	0	0	0	0	1	2	0	2
GM	--	--	--	--	--	9.2	--	5.5
GD	--	--	--	--	--	1.1	--	1.2
MAXIMUM	--	--	--	--	15	10	--	6.2
MINIMUM	--	--	--	--	15	8.4	--	4.9

**Table 28.** Number of whole-body fish samples collected in the Grand Valley that exceeded the 1984 National Contaminant Biomonitoring Program (NCBP) 85th-percentile concentrations for seven trace constituents

[NCBP 85th-percentile concentrations in micrograms per gram wet weight; NCBP data from Schmitt and Brumbaugh (1990); east, samples from tributary streams located upstream from the Gunnison River; middle, samples from streams located between the Gunnison River and Fruita; west, samples from streams located from Fruita to Salt Creek; all, all samples, excluding Highline Reservoir; N, number of samples; numbers in brackets are the number of exceedances expressed as a percentage of the number of samples in each group]

Trace constituent	NCBP 85th percentile	East (N=15)	Middle (N=23)	West (N=22)	All (N=60)	Highline Reservoir (N=7)
Arsenic	0.27	0 [0]	1 [4]	1 [4]	2 [3]	1 [20]
Cadmium	.05	2 [13]	2 [9]	8 [36]	12 [20]	2 [29]
Copper	1.0	9 [60]	11 [48]	11 [50]	31 [52]	3 [43]
Lead	.22	3 [20]	4 [17]	7 [32]	14 [23]	2 [29]
Mercury	.17	0 [0]	0 [0]	0 [0]	0 [0]	0 [0]
Selenium	.73	15 [100]	23 [100]	22 [100]	60 [100]	7 [100]
Zinc	34.2	11 [73]	10 [44]	5 [23]	26 [43]	2 [29]

dry weight (site PSW1) (table 27) and exceeded known toxicity concentrations to fathead minnows of 6 µg/g dry weight (Ogle and Knight, 1989; Schultz and Hermanutz, 1990).

No aquatic-plant samples were collected in the west Grand Valley from tributary streams of the Colorado River between Fruita and Salt Creek. One of two invertebrate samples (table 27), a crayfish sample containing 5 µg/g dry weight selenium from Big Salt Wash (site BSW1 in fig. 46), exceeded the dietary guideline of 3 µg/g dry weight (Lemly and Smith, 1987; Lemly, 1993). All of the 22 whole-body fish samples collected from tributaries in the west Grand Valley, plus 7 whole-body fish samples collected from Highline Reservoir (site HR in fig. 46), contained selenium concentrations that exceeded the 1984 NCBP 85th-percentile concentration (table 28) and most concentrations also exceeded the concentration of concern of 4 µg/g dry weight for whole-body fish (Lemly and Smith, 1987; Lemly 1993). The highest selenium concentrations in fish collected in the west Grand Valley were in sucker and speckled dace samples collected from Salt Creek (site SC in fig. 46), which contained 19 µg/g dry weight selenium (table 27). Egg and liver tissues were dissected from a catfish collected from Highline Reservoir; the egg sample contained 11 µg/g dry weight selenium and the liver sample contained 16 µg/g dry weight selenium (Butler and others, 1994, table 28). Lemly (1993) stated that 12 µg/g dry weight selenium in liver tissue and 10 µg/g dry weight selenium in ovary

and egg tissue are biological-effect thresholds for the health and reproductive success of freshwater anadromous fish. The selenium concentrations in the catfish tissue samples from Highline Reservoir exceeded these guidelines.

Sample sizes for each biota group were too small to use statistical analysis to compare the three areas of the Grand Valley, but there was a general increase in selenium in roundtail chubs and speckled dace samples in a downstream direction (east to west) in the Grand Valley (table 27). Only one sucker sample was collected in the east Grand Valley, and it contained 9.7 µg/g dry weight selenium. The geometric mean selenium concentration for sucker samples from the middle Grand Valley was 7.8 µg/g dry weight, and for the west Grand Valley was 9.2 µg/g dry weight (table 27). The geometric mean selenium concentration for speckled dace from the east Grand Valley was 7.2 µg/g dry weight; the concentration in the one speckled dace sample from the middle Grand Valley was 13 µg/g dry weight; and the mean concentration for speckled dace from the west Grand Valley was 13.4 µg/g dry weight. Fish samples collected from Salt Creek and Reed Wash (fig. 46), which drain much of the west part of the Grand Valley, contained consistently high selenium concentrations. The highest median selenium concentrations in surface-water samples from the Grand Valley also were for the Salt Creek and Reed Wash basins.

## Selenium Concentrations in Fish Samples from Mainstem Rivers

Beginning in March 1992, before snowmelt and irrigation began, fish samples were collected from 11 locations on the Colorado, Gunnison, and Uncompahgre Rivers (fig. 47). One of the sampling sites for the Gunnison River was on the North Fork at site NFK2 (fig. 47), the other 10 sites were on the three mainstem rivers. Sample locations were selected to include river sections that receive major selenium loading and could be subject to effects of selenium bioaccumulation. The sampling of mainstem rivers was designed to collect 10 suckers, 10 speckled dace, and 10 roundtail chubs from each of the 11 sampling sites; however, not all 3 species were present at each site. Those three fish species represent three trophic levels of species that are abundant in the study area.

For all fish species, the 112 fish collected from the Gunnison River had an arithmetic mean selenium concentration of 7.1  $\mu\text{g/g}$  dry weight, which was significantly higher than the arithmetic mean selenium concentrations for the Colorado and Uncompahgre Rivers [significance level ( $p$ ) less than or equal to 0.05]. The mean selenium concentration for 120 fish collected from the Colorado River was 4.6  $\mu\text{g/g}$  dry weight, and for 64 fish collected from the Uncompahgre River, the mean was 5.1  $\mu\text{g/g}$  dry weight. The mean selenium concentrations for fish from the Uncompahgre River and the Colorado River are not significantly different ( $p$  less than 0.05). Mean selenium concentrations for whole-body fish samples collected from each of the three river basins exceeded the concentration of concern of 4  $\mu\text{g/g}$  dry weight selenium for whole-body fish (Lemly, 1993). The mean selenium concentrations for the fish groups are shown in figure 48. Mean selenium concentrations for roundtail chubs, suckers, and speckled dace were highest for the Gunnison River (significantly greater for speckled dace;  $p$  less than 0.05). Mean selenium concentrations in those three fish-trophic groups were lowest for the Colorado River (significantly so for suckers;  $p$  less than 0.05). Of the whole-body fish samples from the Gunnison River collected in 1992, about 96 percent exceeded the 1984 NCBP 85th-percentile concentration for selenium (table 29) and about 71 percent exceeded

the selenium concentration of concern of 4  $\mu\text{g/g}$  dry weight for whole-body fish (Lemly, 1993). About 80 percent of the whole-body fish samples from the Colorado River and the Uncompahgre River exceeded the 1984 NCBP 85th percentile. Fifty-five percent of Colorado River whole-body fish samples and 64 percent of Uncompahgre River whole-body fish samples had selenium concentrations that exceeded the concentration of concern of 4  $\mu\text{g/g}$  dry weight (Lemly, 1993).

Differences in selenium concentrations among fish species were significant. Speckled dace contained significantly higher selenium concentrations than the other fish species ( $p$ -value of 0.05). When data for all sites were combined, the mean selenium concentration for 105 speckled dace was 8.3  $\mu\text{g/g}$  dry weight. The mean selenium concentration was 5.8  $\mu\text{g/g}$  dry weight in 71 roundtail chubs; 4.7  $\mu\text{g/g}$  dry weight in 10 mottled sculpins; and 3.1  $\mu\text{g/g}$  dry weight in 110 suckers. These mean selenium concentrations are all significantly different ( $p$ -value less than 0.05). Species differences accounted for almost 50 percent of the variance in the sum of squares using ANOVA ( $p$ -value equal to 0.0001).

Selenium concentrations in whole-body fish were compared between individual sites for each of the three rivers. Mean selenium concentrations for fish representing three fish trophic groups collected from four Colorado River sites are shown in figure 49. Mean selenium concentrations for suckers collected from the Colorado River indicate a trend of increasing concentrations in a downstream direction. The mean selenium concentration for suckers from the most upstream site (COL1 in fig. 47) was significantly less than the mean selenium concentrations of suckers collected from the lower three sites (fig. 49). In contrast, speckled dace collected from site COL1 contained a higher mean selenium concentration than speckled dace from the lower three sites (fig. 49) and was significantly greater than the mean selenium concentration in speckled dace collected from site COL4. Mean selenium concentrations in roundtail chubs collected from the Colorado River sites were not significantly different ( $p$ -value of 0.05), but do have a trend of increasing concentration in a downstream direction.

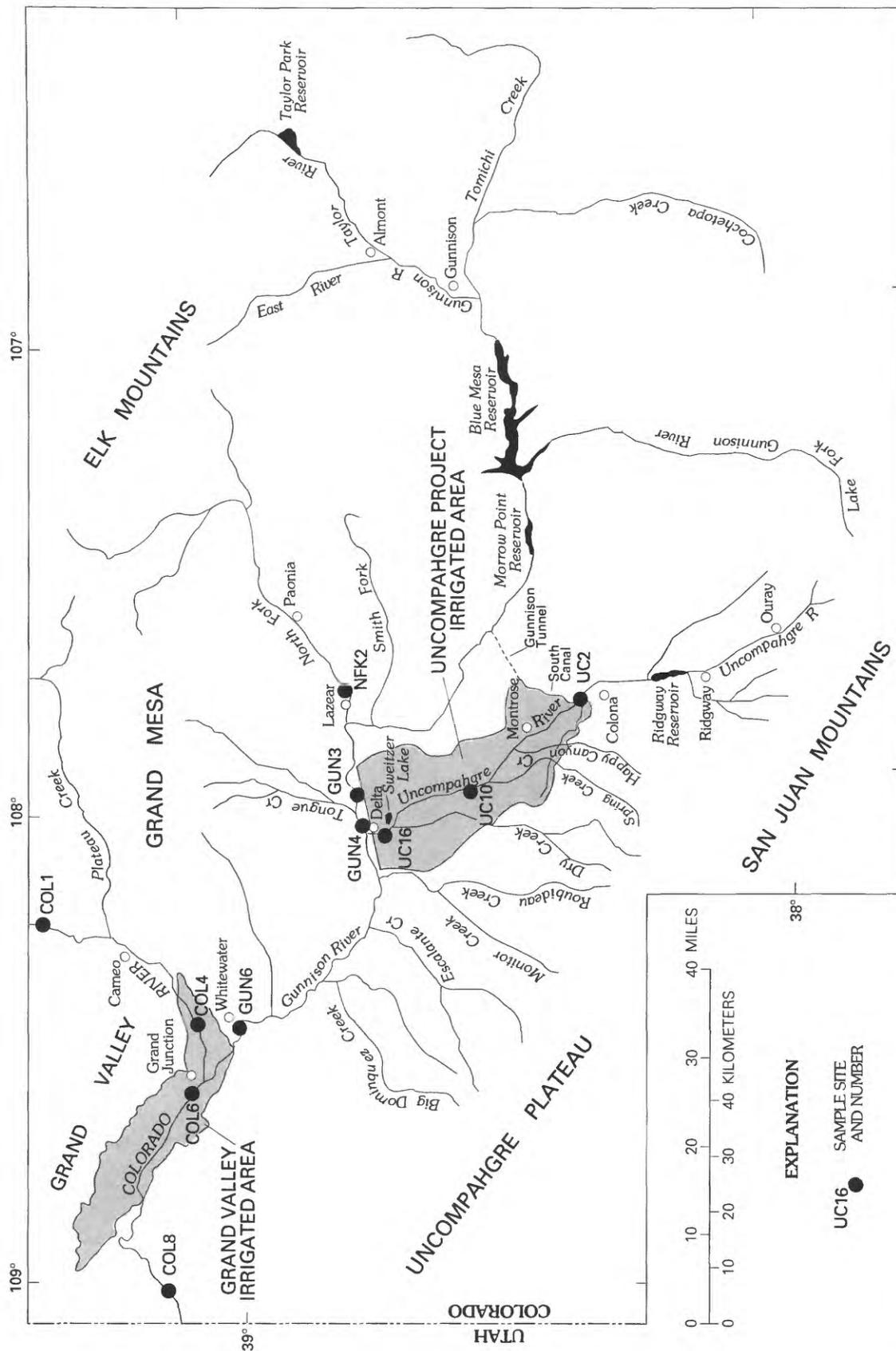
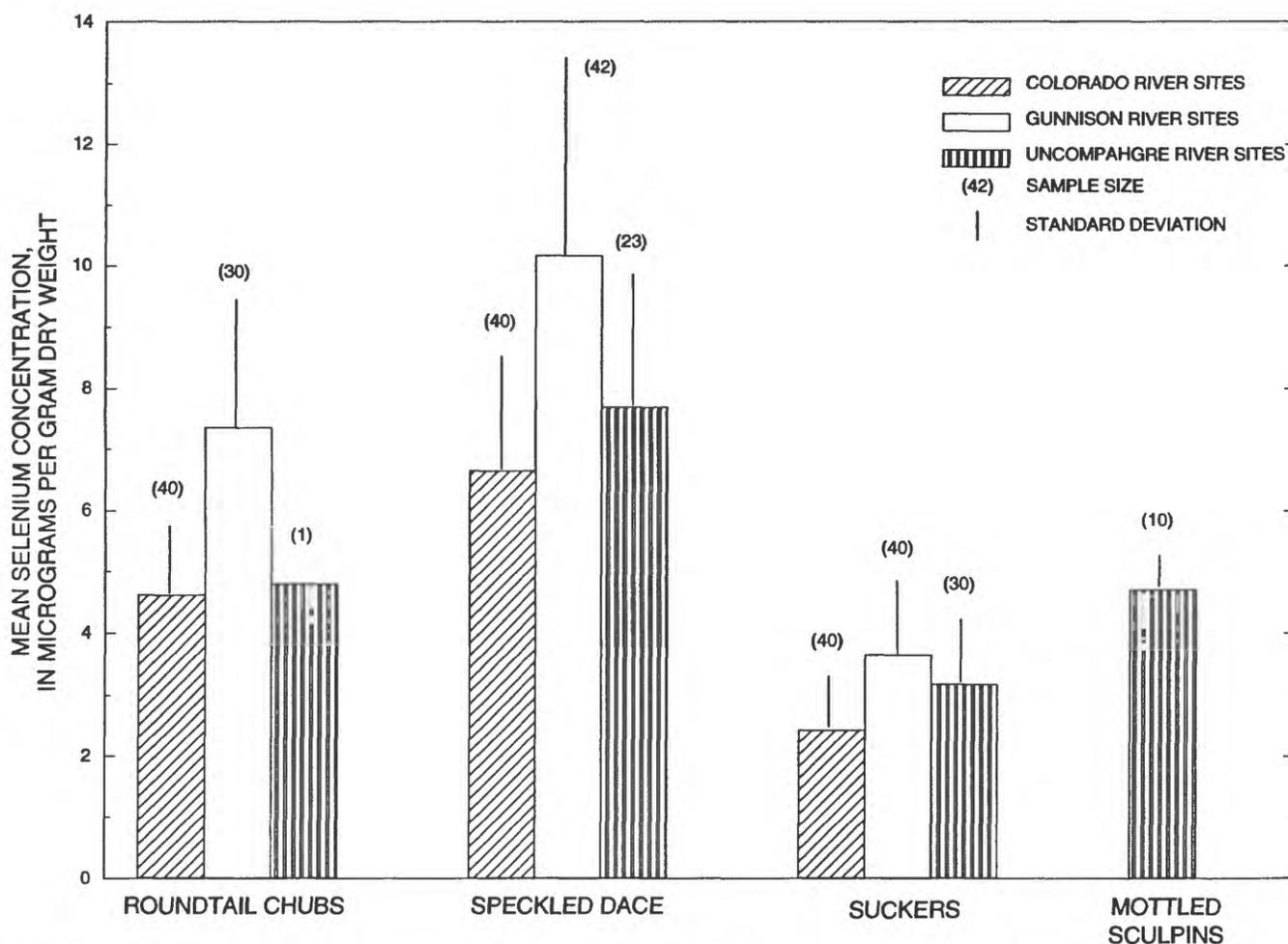


Figure 47. Location of sampling sites on major rivers where fish samples were collected in 1992.



**Figure 48.** Mean selenium concentrations in four fish-trophic groups in the Colorado, North Fork of the Gunnison, Gunnison, and Uncompahgre Rivers.

Mean selenium concentrations in fish representing three fish-trophic groups collected from four sites in the Gunnison River Basin are shown in figure 50. The mean selenium concentrations for suckers collected from the two lower Gunnison River Basin sites (sites GUN4 and GUN6 in fig. 47) were significantly higher (p-value less than 0.05) than mean selenium concentrations for suckers collected from the two upper sites (sites NFK2 and GUN3). Speckled dace collected from the outflow site for the Gunnison River Basin (site GUN6) contained a significantly higher mean selenium concentration than speckled dace from the other three sites (fig. 50). There was no significant difference among selenium concentrations in roundtail chubs for the Gunnison River Basin sites.

Mean selenium concentrations in three fish-trophic groups collected from three Uncompahgre River sites are shown in figure 51. There was not a significant difference in mean selenium concentrations among the three sites for speckled dace, although the upper site (site UC2 in fig. 47) contained the highest mean selenium concentration. The mean selenium concentration for suckers collected at the outflow site for the Uncompahgre River (site UC16) was significantly higher than the concentrations from the upper two sites (p-value less than 0.05) (fig. 51). Because only one roundtail chub sample was collected from the Uncompahgre River, comparisons among sites were not possible.

**Table 29.** Number of whole-body fish samples collected in 1992 from the Colorado, North Fork of the Gunnison, Gunnison, and Uncompahgre Rivers that exceeded the 1984 National Contaminant Biomonitoring Program (NCBP) 85th-percentile concentrations for seven trace constituents

[NCBP 85th-percentile concentrations in micrograms per gram wet weight; NCBP data from Schmitt and Brumbaugh (1990); N, number of samples; numbers in brackets are the number of exceedances expressed as a percentage of the number of samples in each group]

Trace constituent	NCBP 85th percentile	Colorado River (N=120)	North Fork of the Gunnison and Gunnison Rivers (N=112)	Uncompahgre River (N=64)
Arsenic	0.27	8 [6]	9 [8]	6 [9]
Cadmium <sup>1</sup>	.05	4 [3]	3 [3]	18 [28]
Copper	1.0	18 [15]	42 [38]	15 [23]
Lead <sup>1</sup>	.22	23 [19]	15 [13]	17 [27]
Mercury	.17	19 [16]	13 [12]	0 [0]
Selenium	.73	95 [79]	108 [96]	51 [80]
Zinc	34.2	36 [30]	28 [25]	13 [20]

<sup>1</sup> Some samples had reporting limits equal to or greater than the 1984 NCBP 85th percentile.

A paired t-test was used to test for differences between mean selenium concentrations in liver and whole-body samples from suckers. As expected from other researchers' findings (Sager and Cofield, 1984), liver samples contained significantly higher selenium concentrations than whole-body samples. However, selenium concentrations in all fish-liver samples were less than the concentration of concern of 12 µg/g dry weight (Lemly, 1993).

### Risk Assessment for Endangered Fish from Selenate and Selenite

Acute toxicity tests of the selenium species selenate ( $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ ) and selenite ( $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ ) on hatchery-raised Colorado squawfish and razorback suckers were conducted during 1993 (S.J. Hamilton, National Biological Service, written commun., 1993). The two endangered fish species are endemic to the Colorado River in and downstream from the Grand Valley. Selenate and selenite analyses were done only on five water samples from the Grand Valley; therefore, risk assessment was not done for the

Uncompahgre Project area. Three different life stages of each of the two fish species were exposed to the inorganic constituents of interest. Concentrations representing 96-hour LC50 values (lethal concentration for 50 percent of the test organism during a 96-hour test) were calculated (table 30). The toxicity data in table 30 indicate that selenite selenium is toxic to Colorado squawfish and razorback suckers at lower concentrations than selenate selenium.

One method used to estimate the hazard of chemicals to aquatic life is the margin of safety (or margin of uncertainty) between expected environmental concentrations (EEC) of a chemical and concentrations of the chemical that cause toxic effects in organisms. The 96-hour LC50 concentrations for the two endangered fish species were used to determine the biologically effective concentration (BEC). The BEC values were compared to environmental concentrations of selenate and selenite in water samples (the EEC values) collected from five drainages in the Grand Valley, which are the BEC/EEC ratios. The hazard ratios used to assess potential risk are based on dissolved selenium in the water. Although most selenium is bioaccumulated through the food chain into upper trophic levels of aquatic ecosystems (Lemly and Smith, 1987; Ohlendorf, 1989; Maier and Knight, 1994), waterborne selenium is an important indicator of bioaccumulation potential. Based on lethal effects observed in acute toxicity tests, hazard ratios (BEC/EEC) of less than 100 indicate a high potential for hazardous environmental conditions and the potential for toxicity (Cairns and others, 1978).

Hazard assessments for three life stages [0- to 98-day old (swim-up), 99- to 115-day old, and 193- to 207-day old] of Colorado squawfish and razorback suckers are summarized in table 31. The selenate concentrations in the five Grand Valley drainages could theoretically pose a moderate risk (BEC/EEC ratios between 100 and 1,000) to the swim-up life stage of the Colorado squawfish and to all tested life stages of the razorback sucker (table 31). For all three life stages of both species, selenite concentrations were in the low risk category or in the range of uncertainty (BEC/EEC ratios between 1,000 and 5,000). Adult Colorado squawfish and razorback suckers use backwater habitats in the Colorado River during spring prior to spawning.

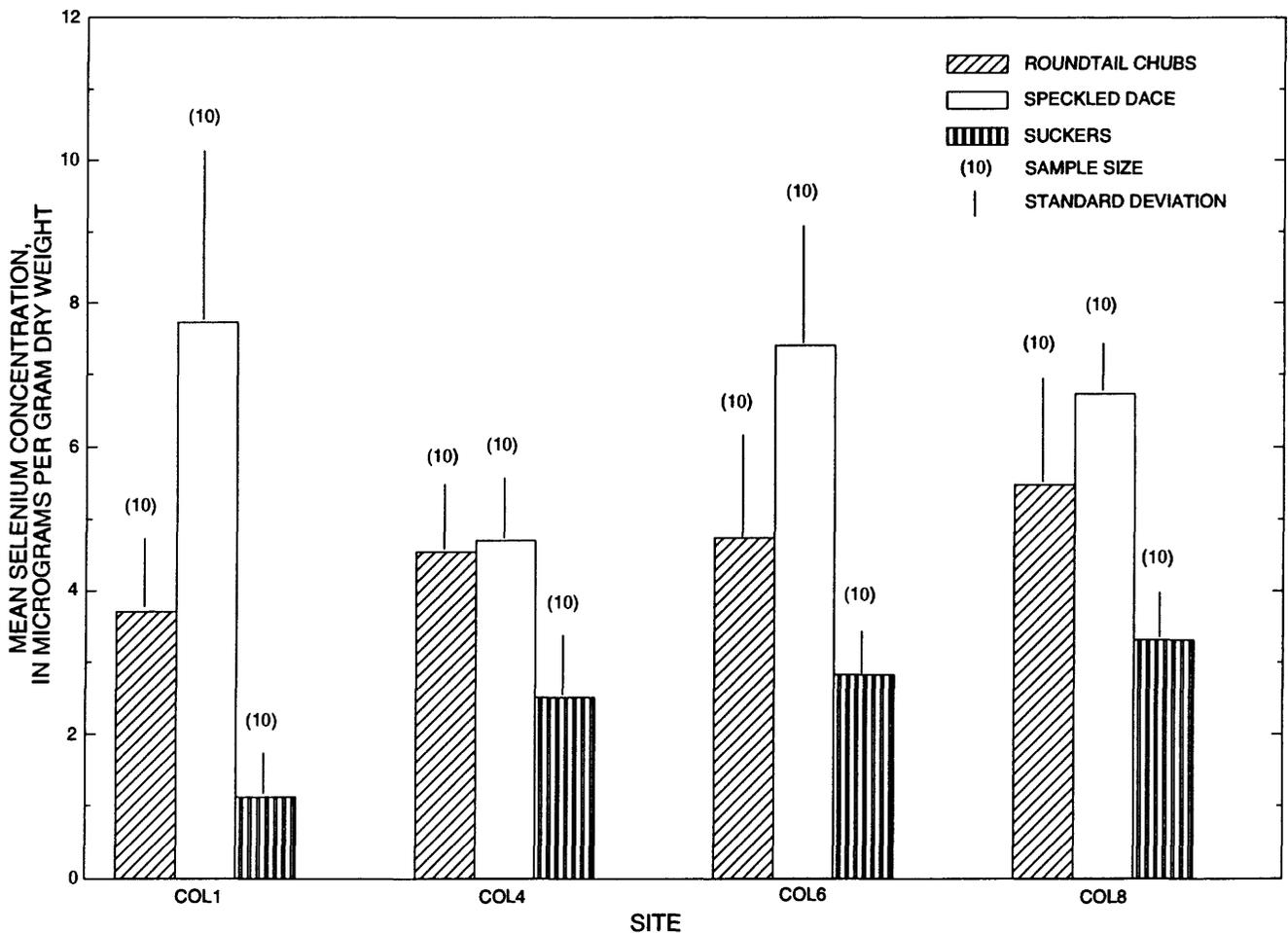


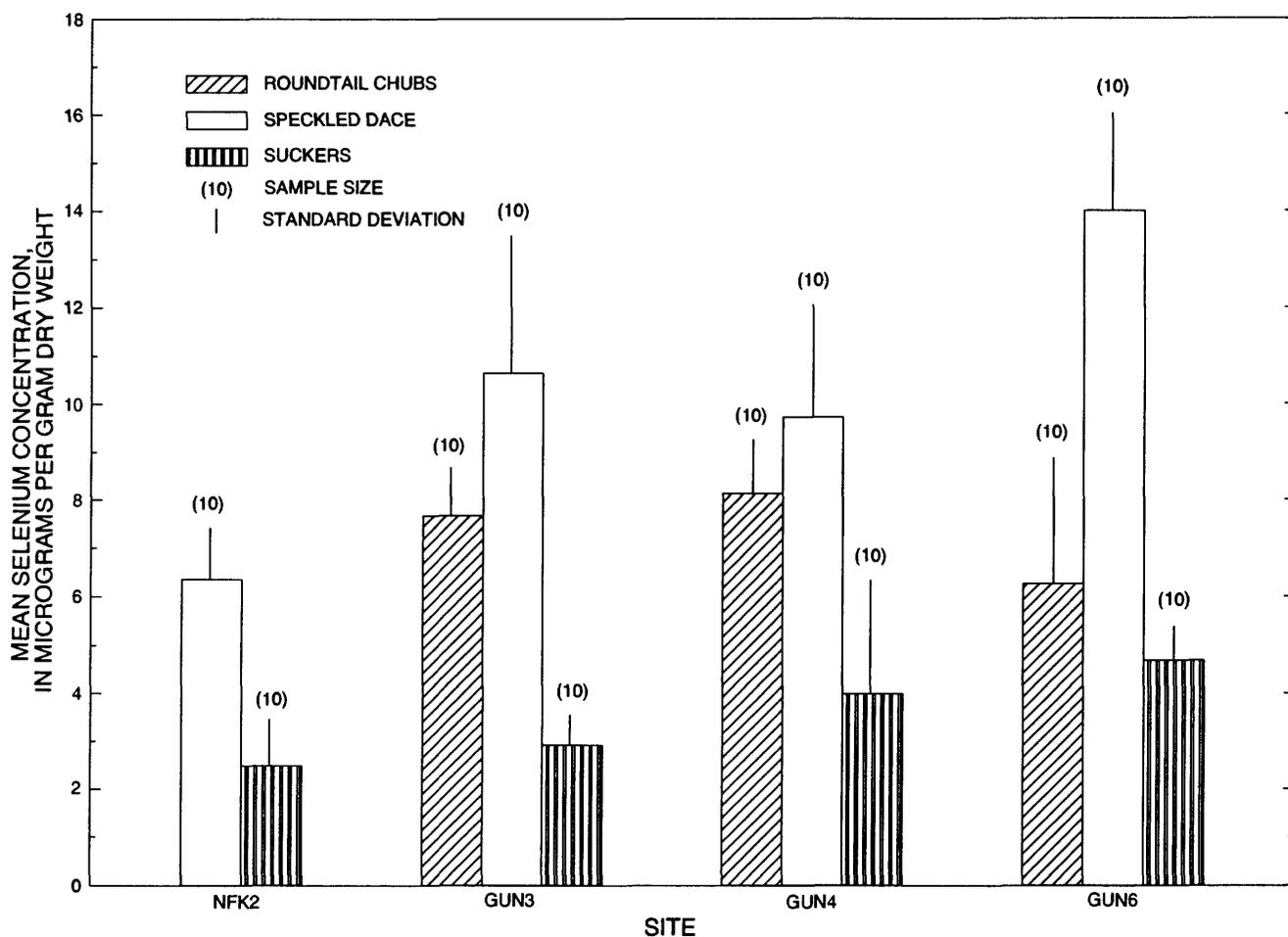
Figure 49. Mean selenium concentrations in three fish-trophic groups collected from four sites on the Colorado River. Sites are in downstream order from left to right.

## Other Trace-Constituent Concentrations in Fish Tissues and Fish Food Items in Irrigated Areas

### Uncompahgre Project Area

Other trace constituents in whole-body fish samples that exceeded the 1984 NCBP 85th-percentile concentrations are listed in table 26. Other than selenium, copper most often exceeded the 1984 NCBP 85th-percentile concentration for whole-body fish. Moore and Ramamoorthy (1984) suggested that, in unpolluted freshwater, maximum copper concentrations in fish muscle tissue seldom exceed 1 µg/g wet weight (4 µg/g dry weight at 75-percent moisture). All copper concentrations in fillet samples collected from the Uncompahgre Project area were less than this guideline concentration. Dixon and Sprague (1981)

reported that rainbow trout exposed to 30 µg/L copper for 7 to 21 days accumulated whole-body concentrations of 10 to 11 µg/g dry weight copper. This concentration range is similar to copper concentrations in some whole-body trout samples collected in the Uncompahgre Project area (sites HCC1, SP4, DRY1, and CR in figs. 44 and 45) (Butler and others, 1994). Dixon and Sprague (1981) reported that mean copper residues in trout prior to copper exposure ranged from 3.2 to 4.5 µg/g dry weight, which also are similar to copper concentrations in some whole-body trout samples collected in the Uncompahgre Project area. Dixon and Sprague (1981) reported that rainbow trout were able to acclimate to copper, which significantly altered their lethal tolerance. Moore and Ramamoorthy (1984) indicated that copper concentrations of 10 to 100 µg/g dry weight in aquatic plants and 5 to



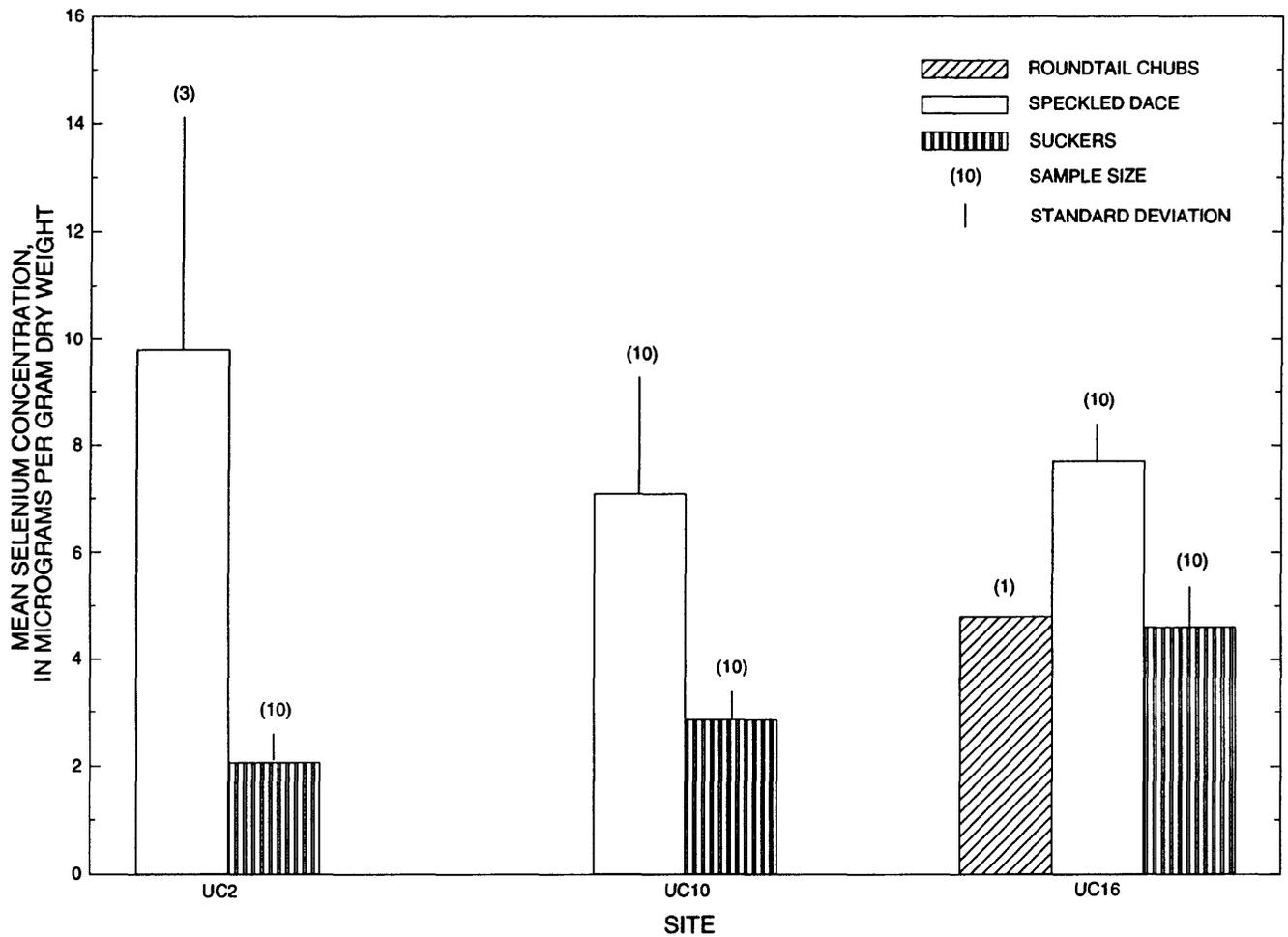
**Figure 50.** Mean selenium concentrations in three fish-trophic groups collected from four sites in the Gunnison River Basin. Sites are in downstream order from left to right.

200 µg/g dry weight in aquatic invertebrates were indicative of copper-polluted freshwater systems. Aquatic-plant and -invertebrate samples collected from the Uncompahgre Project area contained copper concentrations in these ranges.

About 20 percent of the cadmium concentrations in whole-body fish collected within and adjacent to the Uncompahgre Project exceeded the NCBP 85th percentile (table 26). Cadmium concentrations were less than the 2-µg/g wet-weight concentration that Moore and Ramamoorthy (1984) indicated was evidence of probable contamination and less than the 5-µg/g wet-weight concentration that Eisler (1985) reported was a possible toxic cadmium concentration for fish.

Concentrations of arsenic, lead, and mercury in a few whole-body fish samples exceeded 1984 NCBP 85th percentiles (table 26). Moore and Ramamoorthy

(1984) indicated that, in unpolluted or mildly contaminated water, arsenic concentrations in whole-body fish should not exceed the range of less than 0.1 to 0.4 µg/g wet weight. Fish samples from Dry Creek (site DRY1 in fig. 44) (0.55 µg/g wet weight), Roubideau Creek (site RB1) (0.63 µg/g wet weight), and Crawford Reservoir (site CR in fig. 45) (2.54 µg/g wet weight) exceeded this guideline. Diminished growth and survival have been reported for bluegills when arsenic residues in muscle tissue exceeded 11.3 µg/g wet weight in immature fish or 5 µg/g wet weight in the adults (Natural Resources Council of Canada, 1978). A whole-body yellow perch sample collected from Crawford Reservoir (site CR) had an arsenic concentration (2.54 µg/g wet weight) that was comparable to the toxic arsenic concentrations in adult bluegill muscle. Lead concentrations in whole-body fish exceeded the 1984 NCBP



**Figure 51.** Mean selenium concentrations in three fish-trophic groups collected from three sites on the Uncompahgre River. Sites are in downstream order from left to right.

85th percentile for two samples collected east of the Uncompahgre River and nine samples collected west of the Uncompahgre River (table 26). Highest lead concentrations were in two bluehead sucker samples collected from Dry Creek and Roubideau Creek (sites DRY1 and RB1 in fig. 44). Four whole-body fish samples collected from tributaries west of the Uncompahgre River contained mercury concentrations that exceeded the 1984 NCBP 85th percentile of 0.1 µg/g wet weight (table 26) and exceeded the dietary guideline of 0.1 µg/g wet weight for the protection of sensitive consumer bird species (Eisler, 1987a). The highest mercury concentration of 0.34 µg/g wet weight was in a speckled dace sample from Spring Creek (site SP4 in fig. 44).

**Table 30.** Concentrations of selenate and selenite selenium causing acute toxicity to Colorado squawfish and razorback suckers

[96-hour LC50 concentration is the lethal concentration for 50 percent of the test organisms during a 96-hour exposure; data from Hamilton (1993)]

Life stage (age, in days)	96-hour LC50 concentrations, in micrograms per liter			
	Colorado squawfish		Razorback sucker	
	Selenate	Selenite	Selenate	Selenite
Less than 99 (swim-up)	67,000	14,000	48,000	15,000
99 to 115	297,000	36,000	35,000	9,200
193 to 207	320,000	31,000	26,000	16,000

**Table 31.** Hazard assessment of selenate and selenite selenium in water samples collected in March 1992 from five streams in the Grand Valley to three life stages of Colorado squawfish and razorback suckers

[Selenate and selenite data from R.F. Fujii (U.S. Geological Survey, written commun., 1992); µg/L, micrograms per liter; hazard assessment is equal to BEC/EEC, where BEC is the biologically effective concentration and EEC is the estimated environmental concentration of a contaminant; a hazard assessment greater than 5,000 is low risk, 1,000 to 5,000 is uncertain risk, 100 to 1,000 is moderate risk, and less than 100 is high risk (Cairns and others, 1978); --, no risk assessment because contaminant concentration was 0 microgram per liter]

Stream	Selenate selenium				Selenite selenium			
	Water concentration (µg/L)	BEC/EEC for the three life stages			Water concentration (µg/L)	BEC/EEC for the three life stages		
		Less than 99 days old (swim-up)	99 to 115 days old	193 to 207 days old		Less than 99 days old (swim-up)	99 to 115 days old	193 to 207 days old
<b>COLORADO SQUAWFISH</b>								
Salt Creek	71.7	934	4,142	4,463	1.1	12,727	32,727	28,182
Reed Wash	126.2	531	2,353	2,536	0	--	--	--
Adobe Creek	72.5	924	4,097	4,414	2.3	6,087	15,652	13,478
Leach Creek	83.4	803	3,561	3,837	2.2	6,364	16,364	14,091
Indian Wash	82.8	809	3,587	3,865	3.3	4,242	10,909	9,394
<b>RAZORBACK SUCKER</b>								
Salt Creek	71.7	670	488	363	1.1	13,636	8,364	14,546
Reed Wash	126.2	380	277	206	0	--	--	--
Adobe Creek	72.5	662	483	359	2.3	6,522	4,000	6,957
Leach Creek	83.4	576	420	312	2.2	6,818	4,182	7,273
Indian Wash	82.8	580	423	314	3.3	4,546	2,788	4,849

About 22 percent of the zinc concentrations in whole-body fish samples collected in the Uncompahgre Project area exceeded the 1984 NCBP 85th-percentile concentration (table 26). Schmitt and Brumbaugh (1990) reported that the mean zinc concentration in common carp (63.4 µg/g wet weight) was significantly higher than the mean for all other species combined. The highest zinc concentrations in fish collected from the Uncompahgre Project area were in carp from sites NFK2, CMG1, and RB1 (figs. 44 and 45), and these concentrations (Butler and others, 1994, tables 25 and 27) were comparable to the geometric mean concentrations in carp reported by Schmitt and Brumbaugh (1990).

Some samples collected from tributaries west of the Uncompahgre River had concentrations that exceeded NCBP 85th percentiles for each of the seven trace constituents. In other streams in the Uncompahgre River Basin, these exceedances could be attributed to pollution from mining activities. However, no mining is occurring on the Uncompahgre Plateau upstream from the irrigated areas, which is the source of the natural runoff in tributary streams

on the western side of the project. The trace constituents probably were introduced in the irrigation water diverted from the Uncompahgre River, which may be affected by runoff from previous mining activities.

### Grand Valley

As in the Uncompahgre Project area, copper was the trace constituent other than selenium that most often exceeded the 1984 NCBP 85th-percentile concentration for whole-body fish from the Grand Valley (table 28). Highest copper concentrations were 3.0 µg/g wet weight (11.1 µg/g dry weight) in a red shiner sample collected from Lewis Wash (site LW in fig. 46) and 3.0 µg/g wet weight (10.2 µg/g dry weight) in the speckled dace sample from Salt Creek (site SC) (Butler and others, 1994, tables 28 and 30). These concentrations are within the range of copper concentrations in rainbow trout after exposure to 30 µg/L copper for 7 to 21 days (Dixon and Sprague, 1981). Most copper concentrations in whole-body fish collected from the Grand Valley were

comparable to the pre-exposure concentrations of 3.2 to 4.5  $\mu\text{g/g}$  dry weight reported by Dixon and Sprague (1981).

Only two arsenic concentrations in whole-body fish from streams exceeded the 1984 NCBP 85th-percentile concentration; 0.32  $\mu\text{g/g}$  wet weight in a bluehead sucker from Leach Creek (site LC1 in fig. 46) and 0.32  $\mu\text{g/g}$  wet weight in a bluehead sucker sample from Salt Creek (site SC) (Butler and others, 1994, tables 29 and 30). All cadmium concentrations were less than the 2- $\mu\text{g/g}$  wet-weight concentration in whole-body vertebrates that Moore and Ramamoorthy (1984) suggested was evidence of probable cadmium contamination.

Fourteen whole-body fish samples collected from Grand Valley tributaries and two samples collected from Highline Reservoir (site HR in fig. 46) contained lead concentrations that exceeded the 1984 NCBP 85th-percentile concentration (table 28). All mercury concentrations in Grand Valley fish were less than the 1984 NCBP 85th-percentile concentration (table 28).

Zinc concentrations in fish from the Grand Valley were comparable to the concentrations in fish collected in the Uncompahgre Project area. Highest zinc concentrations in Grand Valley fish (Butler and others, 1994, tables 28–30) were in a red shiner sample collected from Lewis Wash (site LW in fig. 46) in the east Grand Valley and in a speckled dace sample collected from Salt Creek (site SC) in the west Grand Valley.

### **Other Trace-Constituent Concentrations in Fish Tissues and Fish Food Items from Mainstem Rivers**

In addition to selenium, copper and zinc had the greatest number of exceedances of the 1984 NCBP 85th-percentile concentrations (Schmitt and Brumbaugh, 1990) for whole-body fish collected from the three major river basins (table 29). Samples from North Fork of the Gunnison and the Gunnison River had a higher proportion of copper exceedances (38 percent) than samples from the Uncompahgre River (23 percent) and the Colorado River (15 percent). All of the fish samples from the Uncompahgre and Colorado Rivers that exceeded the 1984 NCBP 85th percentile for copper contained

between 1 and 2.5  $\mu\text{g/g}$  wet weight (Butler and others, 1994, tables 36 and 37). However, 13 of the Gunnison River fish samples had copper concentrations that exceeded 2.5  $\mu\text{g/g}$  wet weight and ranged from 2.68 to 86.2  $\mu\text{g/g}$  wet weight. The copper concentrations in Gunnison River fish samples indicated considerable exposure to a copper-contaminated environment (Dixon and Sprague, 1981; Moore and Ramamoorthy, 1984).

Exceedances of the 1984 NCBP 85th percentile for arsenic were fairly evenly distributed among the three major river basins (table 29). According to Moore and Ramamoorthy (1984), arsenic concentrations of less than 0.1 to 0.4  $\mu\text{g/g}$  wet weight were indicative of fish from environments uncontaminated by arsenic. Eight samples from the Gunnison River and two samples from the Uncompahgre River exceeded the guideline concentration of 0.4  $\mu\text{g/g}$  wet weight. Fish samples collected from the Uncompahgre River contained the highest proportion of concentrations that exceeded the NCBP 85th percentiles for cadmium and lead (table 29). All cadmium concentrations were less than the guideline concentration of 2  $\mu\text{g/g}$  wet weight that Moore and Ramamoorthy (1984) indicated was evidence of probable cadmium contamination. The highest lead concentrations were in two flannelmouth sucker samples collected from the Gunnison River in Delta (site GUN4 in fig. 47), at 4.0 and 6.6  $\mu\text{g/g}$  dry weight (Butler and others, 1994, table 35). Several samples had reporting limits for lead greater than the 1984 NCBP 85th percentile; therefore, the actual number of exceedances is not known.

Mercury concentrations in about 16 percent of Colorado River fish samples and about 12 percent of Gunnison River fish samples exceeded the 1984 NCBP 85th-percentile concentration (table 29). None of the Uncompahgre River fish samples contained mercury concentrations that exceeded the 1984 NCBP 85th percentile. All mercury concentrations in fish from the Colorado and Gunnison Rivers that exceeded the 1984 NCBP 85th percentile also exceeded the 0.1- $\mu\text{g/g}$  wet-weight concentration that is recommended for the protection of sensitive consumer bird species (Eisler, 1987a), but were less than the whole-body concentration of 5  $\mu\text{g/g}$  wet weight for the protection of brook trout (Armstrong, 1979).

Fish from the Colorado River had the highest proportion of concentrations that exceeded the NCBP 85th percentile for zinc (30 percent), followed by the Gunnison River (25 percent) and the Uncompahgre River (20 percent) (table 29). Schmitt and Brumbaugh (1990) reported high variability in zinc concentrations among fish species. Of all fish collected from mainstem rivers during this study, speckled dace often had the greatest proportion of zinc concentrations that exceeded the NCBP 85th percentile.

### Risk Assessment for Endangered Fish from Four Trace Constituents

Acute toxicity tests for boron, uranium, vanadium, and zinc were conducted (Hamilton, 1993) on three different life stages of Colorado squawfish and razorback suckers by methods similar to that described for selenium. Lethal concentrations (LC50's) for each of the three life stages of Colorado squawfish and razorback suckers are listed in table 32. As was done for selenium, the 96-hour LC50 concentrations for the two endangered fish species (BEC) were compared to actual concentrations of boron, uranium, vanadium, and zinc in water samples (EEC) collected from five Grand Valley drainages. Hazard assessments (the BEC/EEC ratios) for each life stage of the two endangered fish species were calculated for the four trace constituents. Maximum water concentrations of the four trace constituents (Butler and others, 1994, table 5) were used to determine the BEC/EEC ratio so that the maximum hazard could be estimated. Hazard assessments for the three life stages of each endangered fish species are listed in table 33 for boron and uranium and in table 34 for vanadium and zinc.

Most of the hazard estimates for boron, vanadium, and zinc (tables 33 and 34) are in the moderate range of risk; the BEC/EEC ratio usually was between 100 and 1,000. Of most concern are zinc concentrations in Adobe Creek, Leach Creek, and Indian Wash, which were in the high-risk category for the swim-up life stage of Colorado squawfish. Most of the hazard ratios for uranium (table 33) were greater than 1,000, but less than 5,000, which is in the range of uncertain risk.

**Table 32.** Concentrations of boron, uranium, vanadium, and zinc causing acute toxicity to Colorado squawfish and razorback suckers

[96-hour LC50 concentration is the lethal concentration for 50 percent of the test organisms during a 96-hour exposure; >, greater than; data from Hamilton (1993)]

Life stage (age, in days)	96-hour LC50 concentration, in micrograms per liter			
	Boron	Uranium	Vanadium	Zinc
<b>COLORADO SQUAWFISH</b>				
Less than 99 (swim-up)	279,000	46,000	7,800	1,700
99 to 115	>100,000	46,000	3,800	4,200
193 to 207	511,000	46,000	4,200	12,000
<b>RAZORBACK SUCKERS</b>				
Less than 99 (swim-up)	254,000	46,000	8,700	4,000
99 to 115	279,000	46,000	4,000	6,400
193 to 207	>100,000	46,000	3,200	15,000

### Organic Contaminants in Fish Tissues

Four fish samples collected in the Uncompahgre Project area and two fish samples collected in the Grand Valley area were analyzed for organochlorine pesticides and polychlorinated biphenyls (PCB's) (Butler and others, 1994, table 38). One flannelmouth sucker sample collected from Dry Creek (site DRY1 in fig. 44) contained concentrations of p,p'-DDE (0.63 µg/g wet weight), p,p'-DDD (0.08 µg/g wet weight), p,p'-DDT (0.14 µg/g wet weight), dieldrin (0.09 µg/g wet weight), and toxaphene (0.82 µg/g wet weight) that exceeded the 1984 NCBP geometric mean concentrations for these compounds (table 35) (Schmitt and others, 1990). A white sucker sample collected from Roubideau Creek (fig. 44) also contained a p,p'-DDE concentration (0.41 µg/g wet weight) that was higher than the 1984 NCBP geometric mean concentration. The organic compound p,p'-DDE is the most persistent degradation product of the parent compound p,p'-DDT. DDT was banned in the United States in 1972. Schmitt and others (1990) reported that the percentage of total DDT that consists of DDE has increased steadily from 48 percent in 1970 to 73 percent in 1984.

**Table 33.** Hazard assessment of boron and uranium in water samples collected from five streams in the Grand Valley to three life stages of Colorado squawfish and razorback suckers

[µg/L, micrograms per liter; hazard assessment is equal to BEC/EEC, where BEC is the biologically effective concentration and EEC is the estimated environmental concentration of a contaminant; a hazard assessment greater than 5,000 is low risk, 1,000 to 5,000 is uncertain risk, 100 to 1,000 is moderate risk, and less than 100 is high risk; >, greater than]

Stream	Boron				Uranium			
	Maximum water concentration (µg/L)	BEC/EEC for the three life stages			Maximum water concentration (µg/L)	BEC/EEC for the three life stages		
		Less than 99 days old (swim-up)	99 to 115 days old	193 to 207 days old		Less than 99 days old (swim-up)	99 to 115 days old	193 to 207 days old
<b>COLORADO SQUAWFISH</b>								
Salt Creek	330	846	>303	1,549	23	2,000	2,000	2,000
Reed Wash	380	734	>263	1,345	35	1,314	1,314	1,314
Adobe Creek	330	846	>303	1,549	17	2,706	2,706	2,706
Leach Creek	370	754	>270	1,381	20	2,300	2,300	2,300
Indian Wash	600	465	>167	852	48	958	958	958
<b>RAZORBACK SUCKER</b>								
Salt Creek	330	770	846	>303	23	2,000	2,000	2,000
Reed Wash	380	668	734	>263	35	1,314	1,314	1,314
Adobe Creek	330	770	846	>303	17	2,706	2,706	2,706
Leach Creek	370	687	754	>270	20	2,300	2,300	2,300
Indian Wash	600	423	465	>167	48	958	958	958

**Table 34.** Hazard assessment of vanadium and zinc in water samples collected from five streams in the Grand Valley to three life stages of Colorado squawfish and razorback suckers

[µg/L, micrograms per liter; hazard assessment is equal to BEC/EEC, where BEC is the biologically effective concentration and EEC is the estimated environmental concentration of a contaminant; a hazard assessment greater than 5,000 is low risk, 1,000 to 5,000 is uncertain risk, 100 to 1,000 is moderate risk, and less than 100 is high risk]

Stream	Vanadium				Zinc			
	Maximum water concentration (µg/L)	BEC/EEC for the three life stages			Maximum water concentration (µg/L)	BEC/EEC for the three life stages		
		Less than 99 days old (swim-up)	99 to 115 days old	193 to 207 days old		Less than 99 days old (swim-up)	99 to 115 days old	193 to 207 days old
<b>COLORADO SQUAWFISH</b>								
Salt Creek	5	1,560	760	840	10	170	420	1,200
Reed Wash	5	1,560	760	840	10	170	420	1,200
Adobe Creek	5	1,560	760	840	20	85	210	600
Leach Creek	4	1,950	950	1,050	30	57	140	400
Indian Wash	9	867	422	467	20	85	210	600
<b>RAZORBACK SUCKER</b>								
Salt Creek	5	1,740	800	640	10	400	640	1,500
Reed Wash	5	1,740	800	640	10	400	640	1,500
Adobe Creek	5	1,740	800	640	20	200	320	750
Leach Creek	4	2,180	1,000	800	30	133	213	500
Indian Wash	9	967	444	356	20	200	320	750

**Table 35.** Geometric mean and maximum concentrations of the 1984 National Contaminant Biomonitoring Program (NCBP) for selected organochlorine pesticides and polychlorinated biphenyls (PCB's)

[Concentrations in micrograms per gram wet weight; NCBP data from Schmitt and others (1990)]

Compound	NCBP geometric mean concentration	NCBP maximum concentration
p,p'-DDE	0.19	4.74
p,p'-DDD	.06	2.55
p,p'-DDT	.03	1.79
Total DDT	.26	9.08
Heptachlor	.01	.29
Dieldrin	.04	1.39
Toxaphene	.14	8.2
cis-Chlordane	.03	.66
trans-Chlordane	.02	.35
cis-Nonachlor	.02	.45
trans-Nonachlor	.03	1.0
Oxychlordane	.01	.29
Total PCB's	.39	6.7

The toxaphene concentration of 0.82 µg/g wet weight in the flannelmouth sucker from Dry Creek (site DRY1) was almost six times greater than the 1984 NCBP geometric mean concentration (table 35). Mayer and Mehrle (1977) reported that toxaphene residues in excess of 0.4 to 0.6 µg/g wet weight might be hazardous to fish health, and Eisler and Jacknow (1985) indicated that such concentrations indicate possible environmental contamination. The toxaphene concentration of 0.82 µg/g wet weight exceeded these two guidelines. However, the toxaphene concentration was less than the U.S. Food and Drug Administration's action level of 5.0 µg/g wet weight in fish that is considered hazardous for human consumption (U.S. Environmental Protection Agency, 1980).

Bile samples were collected from fish and analyzed to provide an indication of polycyclic aromatic hydrocarbon (PAH) exposure. Bile is a sensitive indicator for assessing the exposure of fish to PAH's (McDonald and others, 1991). High concentrations of PAH metabolites in bile indicated actual exposure, and high concentrations of PAH's in sediment indicated a potential for exposure (Johnston and Baumann, 1989).

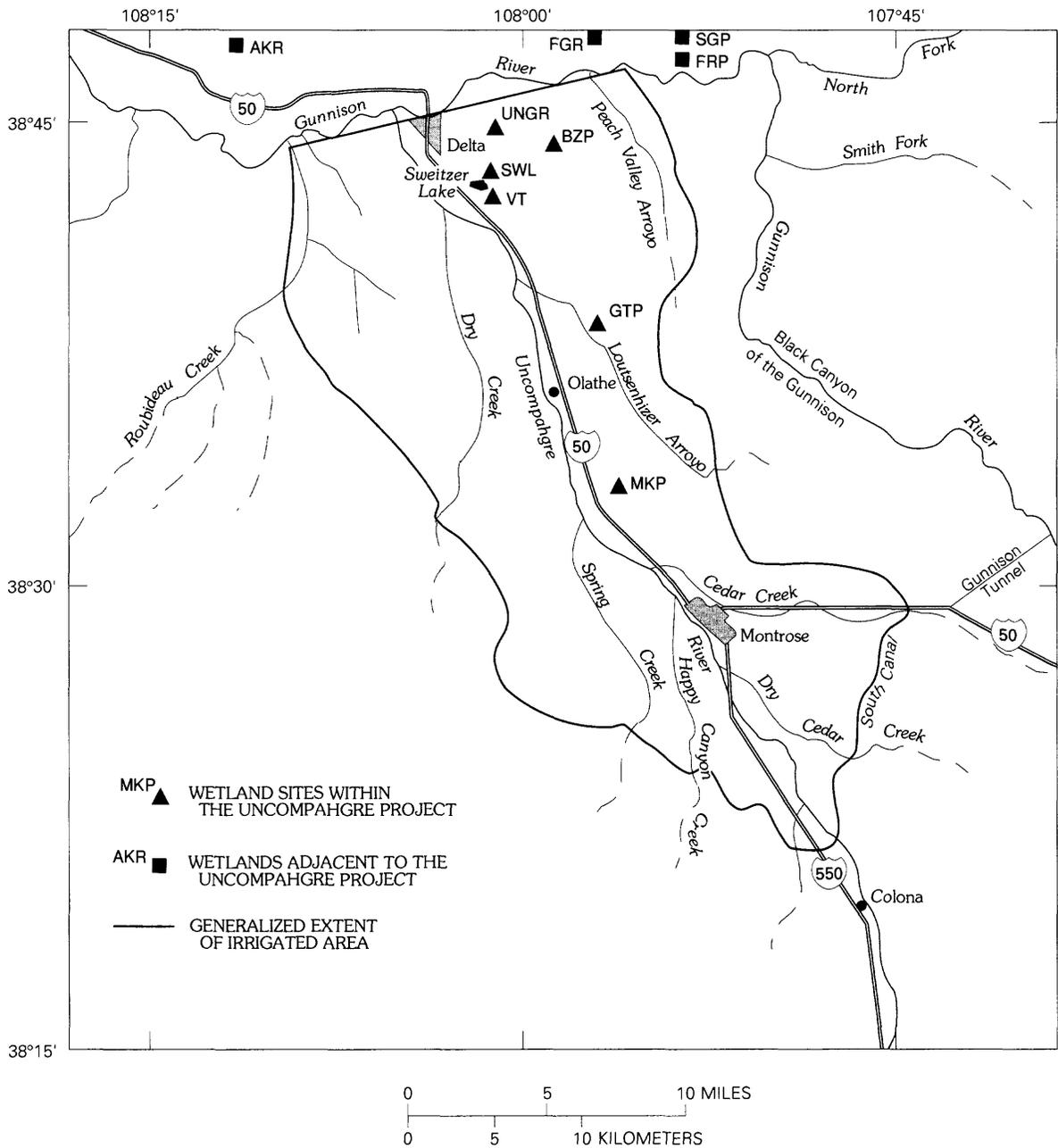
Ten fish-bile samples collected from stream and river sites in and adjacent to the Uncompahgre Project, plus one fish-bile sample collected from Crawford Reservoir, were analyzed for 24 PAH's. Two fish-bile samples collected from streams in the Grand Valley area and one fish-bile sample from Highline Reservoir also were analyzed for PAH's. All PAH data are listed in table 39 in Butler and others (1994). One of the compounds included in the PAH analysis was a-benzopyrene, a known carcinogen (Eisler, 1987b). Eisler (1987b) reported that selenium can be an effective inhibitor of PAH-induced tumor development. Eisler (1987b) also reported that no criteria or standards have been established for PAH's by any regulatory agency for the protection of sensitive species of aquatic organisms or wildlife. The highest concentrations of PAH's, including a-benzopyrene, in fish bile collected for this study were in a white sucker sample collected from the North Fork of the Gunnison River near Paonia (site NFK3 in fig. 45).

## Selenium Concentrations in Migratory Birds and Their Food Items

### Uncompahgre Project Area Wetlands

Migratory birds were sampled from wetlands during 1991 and 1992. Wetlands were geographically divided into those in the irrigated area of the Uncompahgre Project and those adjacent to the Uncompahgre Project (fig. 52). Sites in the Uncompahgre Project are: Markley Pond (site MKP), Grets Pond (site GTP), Vo-Tech marsh (site VT), Sweitzer Lake (site SWL), Brozina Pond (site BZP), and a drainage at G Road (site UNGR) (fig. 52). The wetland sites adjacent to the Uncompahgre Project are: Ferrier Pond (site FRP), Fruitgrowers Reservoir (site FGR), St. George Pond (site SGP), and Alkali Reservoir (site AKR) (fig. 52).

Selenium concentrations in aquatic-plant and algae samples collected from the Uncompahgre Project area wetlands ranged from 4.2 µg/g dry weight at site GTP (fig. 52) to 12 µg/g dry weight at site BZP (Butler and others, 1994, table 32). Fathead minnows had selenium concentrations that ranged from 36 µg/g dry weight at site GTP to 59 µg/g dry weight at site BZP. An aquatic-invertebrate sample collected from site MKP contained 32 µg/g dry weight selenium. These selenium concentrations greatly exceeded 3 µg/g dry weight, a dietary selenium



**Figure 52.** Location of sampling sites at wetlands in the Uncompahgre Project area.

concentration of concern for protection of fish and bird species (Lemly and Smith, 1987; Lemly 1993). The selenium concentrations in fathead minnows greatly exceeded the concentrations reported in laboratory studies in which fathead minnows showed adverse effects, especially reproductive failure (Ogle and Knight, 1989; Schultz and Hermanutz, 1990).

Selenium concentrations in bird-liver and -egg samples (table 36) exceeded normal concentrations in some samples and were in the range of potentially

toxic concentrations in other samples. Skorupa and Ohlendorf (1991) considered normal selenium concentrations for bird eggs to average less than or equal to 3 µg/g dry weight and stated that there was a high risk of adverse biological effects occurring with a population mean of greater than or equal to 20 µg/g dry weight selenium in bird eggs. Skorupa and Ohlendorf (1991) also advised that a population mean selenium concentration between 3 and 20 µg/g dry weight in bird eggs needed

further field studies of reproductive performance to assess biological risk. The geometric mean selenium concentration for eggs for all bird species collected within the Uncompahgre Project was 14.7 µg/g dry weight (geometric deviation 1.8) (table 36). The geometric mean selenium concentration in five avocet eggs collected from Brozina Pond (site BZP) was 41.9 µg/g dry weight (geometric deviation 1.1). Selenium concentrations of that magnitude were associated with a 5-percent incidence of teratogenic effects (J.P. Skorupa and others, U.S. Fish and Wildlife Service, written commun., 1993). A liver from an immature avocet from site BZP contained 98 µg/g dry weight selenium, greatly exceeding 30 µg/g dry weight selenium, a concentration associated with a high risk of adverse biological effects (J.P. Skorupa and others, U.S. Fish and Wildlife Service, written commun., 1993). Geometric mean selenium concentrations in coot, killdeer, and blackbird egg samples collected in the Uncompahgre Project were in the range of concern of 3 to 20 µg/g dry weight (Skorupa and Ohlendorf, 1991).

As in samples collected from wetlands located in the irrigated area of the Uncompahgre Project, selenium concentrations in bird-livers and -egg samples from wetlands adjacent to the project (table 36) exceeded normal concentrations in some samples and were in the range of adverse health effects and reproductive failure in other samples. St. George Pond (site SGP in fig. 52) and Ferrier Pond (site FRP) contained some of the highest selenium concentrations in biota samples collected for this study. One aquatic-plant sample collected from Ferrier Pond contained 68 µg/g dry weight selenium (Butler and others, 1994, table 33), which is more than 20 times greater than the recommended dietary guideline of 3 µg/g dry weight selenium for the protection of fish and wildlife resources (Lemly and Smith, 1987; Lemly, 1993). Two fathead minnow samples collected at site SGP contained 72 and 110 µg/g dry weight selenium (table 36), which not only greatly exceeded the dietary guideline for protection of birds, but also were much greater than the range of 6 to 8 µg/g dry weight associated with adverse health effects and reproductive failure in fathead minnows (Ogle and Knight, 1989; Schultz and Hermanutz, 1990).

**Table 36.** Statistical summary of selenium concentrations in selected bird-food and bird-tissue samples collected during 1991–92 from wetlands in the Uncompahgre Project, wetlands adjacent to the Uncompahgre Project, and wetlands in the Grand Valley

[Concentrations in micrograms per gram dry weight; N, number of samples; GM, geometric mean; GD, geometric deviation; --, no data]

Statistic	Bird-food samples					Bird-tissue samples			
	Aquatic plants	Aquatic invertebrates	Fathead minnows	Green sunfish	Carp	Whole body	Liver	Breast	Egg
<b>WITHIN THE UNCOMPAHGRE PROJECT</b>									
N	5	1	4	1	0	33	1	0	34
GM	7.3	--	48.7	--	--	13.7	--	--	14.7
GD	1.6	--	1.2	--	--	1.7	--	--	1.8
MAXIMUM	12	32	59	55	--	39	98	--	47.6
MINIMUM	4.2	32	36	55	--	4.2	98	--	7.0
<b>ADJACENT TO THE UNCOMPAHGRE PROJECT</b>									
N	2	0	2	0	2	13	14	5	25
GM	23.7	--	91.2	--	14.6	18.3	30.3	20.4	13.4
GD	4.4	--	1.3	--	1.1	1.5	1.5	1.9	1.6
MAXIMUM	68	--	110	--	15	43	59	47	24
MINIMUM	8.3	--	72	--	14	10	17	10	4.1
<b>GRAND VALLEY</b>									
N	0	0	0	0	0	10	11	0	20
GM	--	--	--	--	--	10.0	23.9	--	6.7
GD	--	--	--	--	--	1.9	1.5	--	1.5
MAXIMUM	--	--	--	--	--	18	37	--	17
MINIMUM	--	--	--	--	--	2.3	10	--	3.9

The geometric mean selenium concentration for 25 bird eggs (all species) collected from wetlands adjacent to the Uncompahgre Project was 13.4  $\mu\text{g/g}$  dry weight (geometric deviation 1.6) (table 36). Geometric mean selenium concentrations in coot, yellow-headed blackbird, and grebe eggs collected in adjacent wetlands also were in the range of concern of 3 to 20  $\mu\text{g/g}$  dry weight (Skorupa and Ohlendorf, 1991).

### Grand Valley Wetlands

Bird samples were collected from six Grand Valley wetland sites: Romig Pond (site RMP), Reid Pond (site RDP), Thompson Pond (site TMP), Mack Wash (site MWP), Reed Wash (site RWEB), and 19 and M Roads (site 19M) (fig. 53). The geometric mean selenium concentration for 20 egg samples of all bird species collected in Grand Valley wetlands was 6.7  $\mu\text{g/g}$  dry weight (geometric deviation 1.5) (table 36), which is one-half of the geometric mean selenium concentrations for eggs collected from the Uncompahgre Project area, but the mean is in the range of concern. The geometric mean selenium concentration in three avocet eggs from Thompson Pond (site TMP) was 5.9  $\mu\text{g/g}$  dry weight (geometric deviation 1.2), which was considerably lower than the geometric mean selenium concentration for avocet eggs from the Uncompahgre Project area (from site BZP). The geometric mean selenium concentrations for red-winged blackbird eggs of 7.3  $\mu\text{g/g}$  dry weight (geometric deviation 1.4) and for mallard eggs of 6.6  $\mu\text{g/g}$  dry weight (geometric deviation 1.6) were in the range of concern (3 to 20  $\mu\text{g/g}$  dry weight) that would need further field reproductive studies to determine the biological risk (Skorupa and Ohlendorf, 1991). The geometric mean selenium concentration for seven mallard liver samples collected from Grand Valley wetlands was 23.4  $\mu\text{g/g}$  dry weight (geometric deviation 1.5), also in the range of selenium concentrations in bird livers that would need additional investigation to assess biological risk.

### Other Trace-Constituent Concentrations in Birds and Their Food Items

Mercury concentrations in aquatic-plant, aquatic-invertebrate, and fathead minnow samples collected within the irrigated area of the

Uncompahgre Project at Markley Pond (site MKP), Grets Pond (site GTP), and Brozina Pond (BZP) (fig. 52) were less than the 0.1- $\mu\text{g/g}$  wet-weight concentration that Eisler (1987a) recommended for the protection of sensitive consumer bird species. Mercury concentrations in all bird eggs collected from the Uncompahgre Project area and in the Grand Valley were less than the 0.9- $\mu\text{g/g}$  wet-weight concentration associated with adverse behavioral effects in mallards (Heinz, 1979). The highest mercury concentration in a bird-egg sample was 1.7  $\mu\text{g/g}$  dry weight in a pied-billed grebe egg collected from Fruitgrowers Reservoir (site FGR in fig. 52).

Mercury concentrations in bird-liver samples collected from the Uncompahgre Project area and the Grand Valley were less than the 20- $\mu\text{g/g}$  wet-weight concentration in bird soft tissues that Finley and others (1979) considered to be hazardous to bird health. The highest mercury concentration in a bird-liver sample was in a pied-billed grebe liver from Ferrier Pond (site FRP) that had a concentration of 15.6  $\mu\text{g/g}$  dry weight (4.0  $\mu\text{g/g}$  wet weight). Two western grebe samples collected adjacent to the Uncompahgre Project from Fruitgrowers Reservoir (site FGR) had mercury concentrations of 6.6  $\mu\text{g/g}$  dry weight (2.0  $\mu\text{g/g}$  wet weight) and 1.98  $\mu\text{g/g}$  dry weight (0.49  $\mu\text{g/g}$  wet weight) (Butler and others, 1994, table 33). Eisler (1987a) reported that mercury concentrations in birds were highest in species that eat fish or other birds. Eisler (1987a) also reported that mercury concentrations greater than 1.0 mg/kg ( $\mu\text{g/g}$ ) fresh weight in any bird sample often were associated with proximity to human use of mercury and that the effect of mercury residues in birds is not fully understood.

Arsenic concentrations in all bird-liver samples collected from the Uncompahgre Project area and from the Grand Valley were less than the range 2- to 10- $\mu\text{g/g}$  wet-weight concentration that Eisler (1988) indicated as being elevated. Boron concentrations in aquatic-plant samples collected from Markley Pond (site MKP) and Grets Pond (site GTP in fig. 52) were less than the 30- $\mu\text{g/g}$  wet-weight concentration known to adversely affect waterfowl growth (Eisler, 1988). Most bird tissue samples collected from the Uncompahgre Project area and from the Grand Valley contained boron concentrations that were less than the analytical reporting limits.

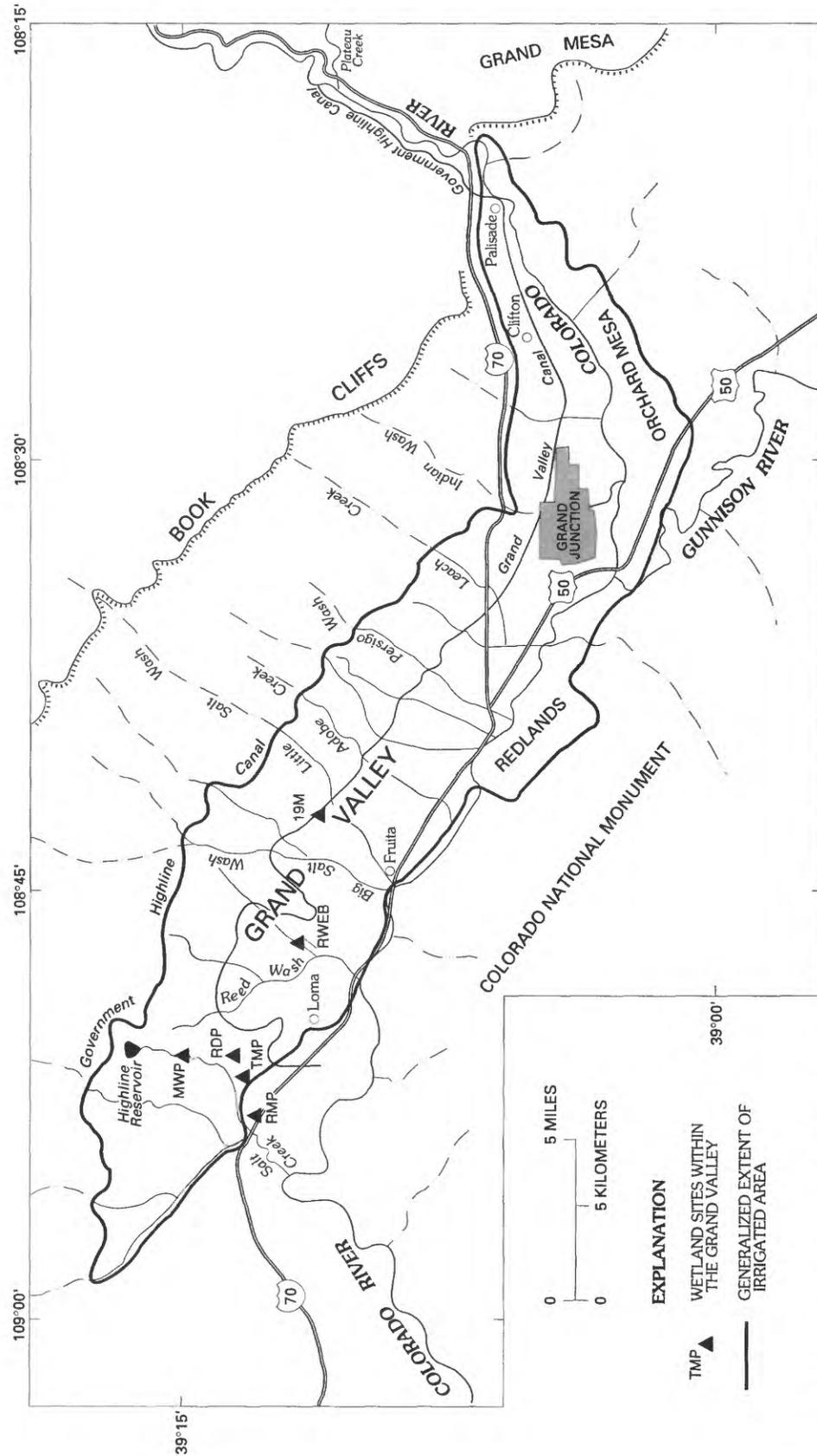


Figure 53. Location of sampling sites at wetlands in the Grand Valley.

Cadmium concentrations in all bird samples collected from the Uncompahgre Project area and from the Grand Valley were less than the 2- $\mu\text{g/g}$  wet-weight concentration for whole-body vertebrates, or the 10- $\mu\text{g/g}$  wet-weight concentration for bird livers that Eisler (1985) reported was evidence of probable cadmium contamination. Eisler (1986) reported that chromium concentrations greater than 4  $\mu\text{g/g}$  dry weight in organs and tissues of fish and wildlife are indicative of chromium contamination. For samples collected in the Uncompahgre Project, the chromium concentrations of 6.3  $\mu\text{g/g}$  dry weight in a snipe egg from Markley Pond (site MKP in fig. 52) and 4.8  $\mu\text{g/g}$  dry weight in a Wilson's phalarope whole-body sample from Brozina Pond (site BZP) exceeded the guideline for chromium. Chromium concentrations in whole-body killdeer samples collected at Sweitzer Lake (site SWL) ranged from 3.6 to 3.9  $\mu\text{g/g}$  dry weight and were slightly less than the guideline for chromium contamination. Adjacent to the Uncompahgre Project, a chromium concentration of 4.1  $\mu\text{g/g}$  dry weight in a yellow-headed blackbird whole-body sample exceeded the guideline of 4  $\mu\text{g/g}$  dry weight. In the Grand Valley, a widgeon liver sample from Reid Pond (site RDP in fig. 53) had a chromium concentration of 19.6  $\mu\text{g/g}$  dry weight.

## Incubation Studies of Bird Eggs

During 1991, an attempt was made to monitor nest success at a few wetland sites in the Uncompahgre Project area and in the Grand Valley. The monitoring had limited success because, at many sites, eggs in ground nests were eaten by predators before the eggs reached full term. Additionally, nests could not be visited on a daily basis, and, because of rapid dispersal of the young, visual inspection of hatchlings for external deformities or to document hatching success was almost impossible. Because of these problems, eggs were brought from the field into the laboratory and incubated for the 1992 bird study.

Bird eggs were collected from 10 sites in the Uncompahgre Project area and from 6 sites in the Grand Valley. Bird eggs were either candled or, if several eggs were collected from the same nest, one egg was cracked open and a hatching date projected. The egg contents were saved in an acid-cleansed jar and, depending on the species, either kept separate or composited with other egg contents from the same nest for trace-constituent analysis.

Species collected and incubated included yellow-headed and red-winged blackbirds, American coots, cinnamon teal, mallards, killdeer, American avocets, and common snipe. Because of equipment limitations, all eggs collected were placed in the same incubator. Temperature and humidity were kept constant throughout the incubation period, and the eggs were automatically turned twice a day.

Hatching success for all eggs placed in the incubator was 68 percent. Hatching success for eggs incubated from the Uncompahgre Project area was 78 percent and for eggs incubated from the Grand Valley was 42 percent. Because of the large number of variables that can affect hatching success, these percentages are not necessarily representative of the overall hatching success in the study area.

The primary reason for collecting and incubating eggs was to inspect visually each hatchling for any obvious deformities. Sixty-five eggs were incubated during the study period, and only one bird, a red-winged blackbird from Mack Wash Pond (site MWP), had any visual deformities. This bird had fused toes on his left foot, which possibly could be attributed to selenium toxicity (Ohlendorf and others, 1988) or to improper incubator temperature for that species (Stromberg, 1975). The whole-body selenium concentration in that bird was 8  $\mu\text{g/g}$  dry weight, which is slightly higher than the geometric mean of 7.3  $\mu\text{g/g}$  dry weight for all red-winged blackbirds collected at Mack Wash Pond, but is in the range of selenium concentrations (3 to 20  $\mu\text{g/g}$  dry weight) that indicates further field reproductive studies are needed to determine biological risk (Skorupa and Ohlendorf, 1991).

## Field Observations at Wetland Sites

General field observations were conducted at each of the wetland sites on each visit. These observations included recording the number and species of birds observed at each of the wetland sites. Most of the ponds in the study areas were used extensively during spring and fall migrations. Wetland use during the nesting season was limited by the pond size. Waterfowl that used the ponds displayed aggressive behavior, tending to be territorial because of the limited amount of suitable nesting habitat.

At two sites in the Uncompahgre Project area, Ferrier Pond and Markley Pond (sites FRP and MKP in fig. 52), a detailed study of the hatching success of yellow-headed blackbirds was conducted in 1992. Initially, American coots were going to be included in the hatching success study; however, they rarely nested successfully.

On May 20, 1992, 118 active yellow-headed blackbird nests were located at Ferrier Pond. On May 23, 1992, the observers returned to Ferrier Pond and marked 25 full clutch (four-egg) nests from random locations around the pond for continued observation. On June 2, 1992, 10 days after first marking the nests, each nest was revisited, and the eggs in 23 of 25 nests had hatched. One nest had been destroyed, and one nest still contained four eggs. Each of the young, which varied in age from 1 to 12 days, were inspected in the field for any deformities or abnormalities. No deformities were found on any yellow-headed blackbirds from Ferrier Pond. After inspection, each prefledgling was returned to its nest. The site was revisited on June 8, 1992, and once again, each nest was visited and data recorded. There were many fledglings scattered throughout the cattails. The birds had fledged completely from 10 of the nests. Three nests had three prefledglings still in the nest. Six fledglings were collected for trace-constituent analysis, including one full-term prefledgling found dead in the nest. These birds were analyzed as whole-body samples. The birds were prepared for analysis by removing all feathers, legs, and beak. Selenium concentrations in these six birds ranged from 10  $\mu\text{g/g}$  dry weight in one live bird to 43  $\mu\text{g/g}$  dry weight in the prefledgling found dead in its nest. The appearance of the dead prefledgling indicated it was very near fledging. The bird showed no external abnormalities or deformities, but had a selenium concentration almost three times higher than the geometric mean of 16.1  $\mu\text{g/g}$  dry weight selenium (geometric deviation 1.6) for the other five live fledglings collected from this site.

Of the 25 yellow-headed blackbird nests monitored at Ferrier Pond, one contained addled eggs. Two young were fledged from this nest, but two unhatched eggs remained. These two eggs were collected and analyzed. The selenium concentration of the contents of these two eggs was 13  $\mu\text{g/g}$  dry weight, which is the same as the geometric mean selenium concentration of 13  $\mu\text{g/g}$  dry weight for the other three egg samples (consisting of two eggs each) collected from this site. This selenium concentration

was in the range of concern of 3 to 20  $\mu\text{g/g}$  dry weight that, according to Skorupa and Ohlendorf (1991), would need further field studies to assess biological risk.

Adult coots commonly were seen at Ferrier Pond. On June 2, 1992, 12 coots were seen on the pond. Over the period of the detailed bird-monitoring study (May 20, 1992, to July 6, 1992), four coot nests were located on the pond. Egg samples were collected from three of the nests. The geometric mean selenium concentration of the three samples of coot eggs was 18.6  $\mu\text{g/g}$  dry weight (geometric deviation 1.1), which was in the range of concern (Skorupa and Ohlendorf, 1991). From two of the coot nests from which eggs were collected and selenium concentrations determined, six eggs were incubated to full term. No external deformities were detected in these hatchlings. The geometric mean selenium concentration for the combined two samples of coot hatchlings was 19.8  $\mu\text{g/g}$  dry weight (geometric deviation 1.2). No young coots were observed during 1992 on Ferrier Pond, even though coots were successfully hatched in the laboratory.

A study similar to the one conducted at Ferrier Pond also was conducted at Markley Pond (site MKP in fig. 52) from May to July 1992. This pond receives surface runoff from agricultural lands above the pond and from shallow ground water discharging from Mancos Shale. Markley Pond was chosen because several hunters who leased this pond noticed dead birds on or near the pond and attributed mortality to causes other than hunting-induced injuries.

On May 19, 1992, a prefledgling mallard was found dead in a slough that flows into Markley Pond. This prefledgling had recently died and appeared normal with no visible trauma, deformities, or abnormalities. This sample contained a whole-body selenium concentration of 26  $\mu\text{g/g}$  dry weight. A second fresh prefledgling mallard was found dead in this same general area on May 27, 1992. This bird, much like the first bird, had no visible signs of trauma, deformities, or abnormalities and was found floating among the cattails. This sample contained a whole-body selenium concentration of 27  $\mu\text{g/g}$  dry weight.

Red-winged blackbirds also were studied during 1992 at Markley Pond. However, most red-winged blackbird nests were not directly associated with the pond and were in remote wetland areas adjoining the pond. Selenium concentrations in red-winged blackbird eggs and whole-body prefledglings ranged from 7.1 to 19  $\mu\text{g/g}$  dry weight. The geometric mean

selenium concentration was 13.0 µg/g dry weight (geometric deviation 1.4) for three egg samples and 10.6 µg/g dry weight (geometric deviation 1.6) for the five pre fledglings sampled.

On May 27, 1992, 35 active yellow-headed blackbird nests were found scattered throughout the cattails on the south and west sides of Markley Pond. Twenty nests were flagged using the same method that was used at Ferrier Pond. Eight nests were located that had full clutches of four eggs, and all other nests had zero to three eggs. On June 2, 1992, most of the nests that previously had zero to three eggs had full clutches of four eggs. Four of the nests had new hatchlings. By June 9, 1992, all marked nests had been pulled down, and eggs and young eaten by raccoons.

On June 24, 1992, 10 coots were observed on Markley Pond, and 8 coot nests were located. Coot eggs were collected from four of the nests, and the contents analyzed for trace constituents. The geometric mean selenium concentration of the four egg samples was 24.4 µg/g dry weight (geometric deviation 1.5), which exceeded the concentration range of 3 to 20 µg/g dry weight associated with biological risk (Skorupa and Ohlendorf, 1991). Two dead coot hatchlings were found in close proximity to the nest where one of the egg samples was collected. This egg sample contained a selenium concentration of 30.3 µg/g dry weight. The combined whole-body sample of the two dead coot hatchlings had a selenium concentration of 19 µg/g dry weight.

Two additional coot egg samples were brought back to the laboratory on June 24, 1992, and placed in the incubator. One of the two coot eggs was cheeping at the time it was picked up, so was assumed to be in a later stage of development. Both eggs were opened on June 29, 1992, because they had not yet hatched, and both embryos were dead. The two embryos had reached full term and appeared normal with no external deformities. The selenium concentration of the two embryos (combined into one sample) was 39 µg/g dry weight.

During subsequent visits, no pre fledgling coots were observed on the pond. Adult coots were seen, but only one of the eight nests discovered on June 24, 1992, was found on a subsequent visit on July 6. This nest contained three eggs, the same number of eggs as when discovered on June 24. In addition, no other pre fledgling waterfowl were seen or collected from Markley Pond.

## Water and Bottom-Sediment Bioassays

After reviewing the selenium concentrations in water from the 1991 sampling, five sampling sites on washes in the Grand Valley were selected to conduct toxicity tests. The five streams sampled had some of the highest selenium concentrations in the Grand Valley. The streams were Salt Creek (site SC), Reed Wash (site RW1), Adobe Creek (site AC1), Leach Creek (site LC1), and Indian Wash (site IW) (fig. 46). Water and bottom-sediment samples were collected for bioassays in March 1992 and sent to the U.S. Environmental Protection Agency in Denver, Colo., for analysis. Chronic tests on larval fathead minnows and daphnia (*Ceriodaphnia dubia*) were conducted according to methods described by Weber and others (1989) and according to guidelines by the U.S. Environmental Protection Agency National Pollutant Discharge Elimination System (NPDES) Whole Effluent Toxics Control Program of December 1990. Daphnia and 3-day-old fathead minnows were exposed to the water samples using dilutions that included five selenium concentrations (a control, 12.5 percent, 25 percent, 50 percent, and 100 percent of the original sample concentration). Samples from Leach Creek and Indian Wash did not have tests at the 12.5-percent concentration because of limited sample quantity. Bottom-sediment samples were sent to Technology Applications, Inc., in Cincinnati, Ohio, for testing with amphipods (*Hyallela azteca*) and fathead minnow embryos.

### Water Bioassays

Water bioassays using *Ceriodaphnia* exposed to water samples from the five test sites indicated no significant differences between the number of young produced in control solutions and in test solutions. There were no significant differences in the fathead minnow growth in controls compared to the test solutions from Salt Creek, Reed Wash, Adobe Creek, and Indian Wash. However, growth and survival of fathead minnows in bioassays using water from Leach Creek indicated potential chronic toxicity. When survival of fathead minnows was analyzed, the lowest observed effect concentration (LOEC) for Leach Creek water was 100 percent (the undiluted concentration) and the no-observed effect concentration (NOEC) was 50-percent

concentration. When growth was analyzed, the LOEC was 50-percent concentration and the NOEC was 25-percent concentration.

The U.S. Environmental Protection Agency (1987) reported that freshwater aquatic organisms would not be adversely affected if the 4-day average selenium concentration in the water did not exceed 5 µg/L more than once every 3 years on the average, and if the 1-hour average concentration did not exceed 20 µg/L more than once every 3 years. All total-selenium concentrations in water samples in the five sites greatly exceeded these guideline concentrations (Butler and others, 1994, table 5). Although Reed Wash had the largest selenium concentration for the samples collected in March 1992 at the five sites (table 20), toxicity was reported only for the Leach Creek water sample. The presence of one or more contaminants, such as other trace constituents, salts, or pesticides, in addition to selenium, might have been responsible for the harmful environment in the Leach Creek sample.

#### **Bottom-Sediment Bioassays**

Two different bioassays were conducted on bottom-sediment samples. The first test was a 7-day growth and survival test using *Hyallela*. The only samples that had results different from the control were from Reed Wash and Adobe Creek. The sample from Reed Wash had a survival rate of 59 percent, and the sample from Adobe Creek had a survival rate of 43 percent. All other samples had a survival rate of greater than 70 percent. None of the mean dry weights (the value used to indicate growth) of *Hyallela* that were cultured on bottom-sediments samples were statistically different from the mean dry weights of *Hyallela* from the control samples.

The second test on bottom-sediment samples was a fathead minnow embryo-larval test, which was a first attempt at a new bottom-sediment exposure method using embryos. A volume of 25-mL of bottom sediment from each of the five tributaries was placed in a container and covered by 100 mL of distilled water. The 24- to 48-hour-old embryos were placed on top of the bottom sediment. Hatch rate and survival rate for the control embryos and larvae were greater than 90 percent. All embryos exposed to the bottom sediments from the five streams were dead in less than 24 hours. The cause or causes of the fathead minnow embryo deaths are unknown.

Bottom-sediment samples from Salt Creek, Reed Wash, Adobe Creek, Leach Creek, and Indian Wash had total-selenium concentrations of 1.9, 6.3, 3.9, 5.6, and 16 µg/g (or mg/kg). Lemly and Smith (1987) indicated that a selenium concentration greater than or equal to 4 mg/kg was of concern to fish and birds because of possibilities of reproductive failure or mortality due to food-chain bioconcentration. Selenium concentrations in Reed Wash, Leach Creek, and Indian Wash exceeded this guideline. As in the water samples, other contaminants (including high salinity), as well as selenium, could be causing toxic effects in bottom sediments.

### **BIOACCUMULATION OF SELENIUM**

Bioaccumulation is the uptake by aquatic organisms of chemicals from water directly or through consumption of food containing the chemicals. Numerous publications have addressed the subject of selenium bioaccumulation, including Lemly and Smith (1987), Ohlendorf (1989), Ohlendorf and others (1993), and Maier and Knight (1994). Selenium is bioaccumulated by aquatic organisms through two mechanisms: bioconcentration and biomagnification. Bioconcentration is the direct uptake of dissolved selenium across respiratory and epithelial membranes by passive or active processes. Biomagnification is the process in which higher trophic-level organisms accumulate selenium by ingesting and assimilating organo-selenium compounds synthesized by lower food-chain organisms (Maier and Knight, 1994). Biomagnification is the major pathway of selenium accumulation for higher trophic-level biota.

Data summarizing the bioaccumulation of selenium in the Uncompahgre Project area and in the Grand Valley are listed in table 37. Geometric mean selenium concentrations are listed in table 37 for water, bottom sediment, and several groups of biota. Because bird samples were collected only at wetlands, only water, bottom-sediment, and other biological samples collected at wetland sites were used to describe bioaccumulation in the study area. Selenium concentrations are expressed in micrograms per liter for water and micrograms per kilogram for bottom sediment and biota; both units are equivalent to parts per billion.

**Table 37.** Geometric mean selenium concentrations in water, bottom-sediment, and biota samples from wetlands in the Uncompahgre Project, wetlands adjacent to the Uncompahgre Project, and wetlands in the Grand Valley

[Water concentrations in micrograms per liter; bottom-sediment and biota concentrations in micrograms per kilogram (both units are equivalent to parts per billion); number in brackets is the number of samples; --, no data]

Sample matrix	Uncompahgre Project	Adjacent to the Uncompahgre Project	Grand Valley
Water	4.7 [5]	10 [1]	7.4 [4]
Bottom sediment	27,400 [2]	-- [0]	17,700 [2]
Aquatic plants	7,300 [5]	23,700 [2]	-- [0]
Aquatic invertebrates	32,000 [1]	-- [0]	-- [0]
Fish, whole body	49,900 [5]	33,700 [4]	13,000 [2]
Bird, whole body	13,700 [33]	18,300 [13]	10,000 [10]
Bird liver	98,000 [1]	30,300 [14]	23,900 [11]
Bird breast	-- [0]	20,400 [5]	-- [0]
Bird egg	14,700 [34]	13,400 [25]	6,700 [20]

At wetlands adjacent to the Uncompahgre Project, the selenium concentration of the single water sample was 10 µg/L, and, in whole-body fish samples, the geometric mean concentration was 33,700 µg/kg (table 37). These concentrations indicated a bioaccumulation factor of 3,370 (33,700 divided by 10) between fish and water. At wetlands in the Uncompahgre Project, the geometric mean selenium concentrations were 4.7 µg/L for water and 49,900 µg/kg for whole-body fish, indicating a bioaccumulation factor of 10,600. For wetlands in the Grand Valley, geometric mean selenium concentrations were 7.4 µg/L for water and 13,000 µg/kg for whole-body fish (table 37), indicating a bioaccumulation factor of 1,800. Lemly and Smith (1987) reported that, where selenium in water has been concentrated from 100 to more than 30,000 times, fish were affected by chronic toxicity.

Bioaccumulation factors between bottom sediment and all biota matrices and among the successive biota trophic levels were much smaller than the bioaccumulation factors between water and bottom sediment and between water and biota. These data indicate that bottom sediment had accumulated selenium at ratios similar to biological tissues. The bioaccumulation factors among biota trophic levels are similar to the factors of 2 to 6 between successive trophic levels of a food chain reported by Lemly and Smith (1987, p. 9).

The three areas were quite similar regarding bioaccumulation factors, indicating that the relative rates of selenium accumulation between sample matrices are similar in the Uncompahgre Project area and in the Grand Valley, although selenium concentrations were somewhat variable among the areas. The highest bioaccumulation factor for selenium was about 20,900 between water and bird-liver concentrations for the irrigated area of the Uncompahgre Project.

## IMPLICATIONS FOR HUMAN HEALTH

Selenium is a necessary nutritional component for humans in quantities from 50 to 200 µg/d, depending on sex, age, and weight (National Academy of Sciences, 1983). However, too much intake of selenium can result in selenosis and can be detrimental to human health (Beath, 1962; Lo and Sandi, 1980; Shamberger, 1981; Levander, 1984; Combs and Combs, 1986).

Sweitzer Lake (site SWL in fig. 52), located near Delta in the Uncompahgre Project, was posted in 1977 by the Colorado Department of Health advising the public not to eat fish caught from the lake. Selenium concentrations in catfish-fillet samples collected in 1988–89 averaged 28 µg/g dry weight selenium (about 5.9 µg/g wet weight) (Butler and others, 1991), or about 167 µg of selenium per ounce of fillet. The National Academy of Sciences (1980) considered an upper limit of 200 µg/d selenium to be safe for human intake. Levander (1984) suggested 500 µg/d selenium to be the safe upper limit for humans.

The highest selenium concentrations in fish-fillet and bird-breast samples collected for the detailed study from the Uncompahgre Project area and from the Grand Valley are listed in table 38. The quantity of each sample that an adult human could safely consume without exceeding 200 µg/d selenium was computed and is listed in table 38. The consumption limits do not account for selenium consumed in other food sources. Amounts of fillet or breast meat that could safely be consumed on a daily basis were quite small and ranged from 0.68 oz of mallard breast taken from Ferrier Pond to 3.7 oz of coot breast taken from Fruitgrowers Reservoir and to 3.7 oz of catfish fillet taken from Highline Reservoir in the Grand Valley. Ferrier Pond and Fruitgrowers Reservoir (sites FRP and FGR in fig. 52) are located near irrigated areas adjacent to the Uncompahgre Project, but are not in

the irrigated area served by the project. Highline Reservoir (fig. 53) is in the upper Mack Wash Basin, and most of the inflow into the reservoir is irrigation water from the Government Highline Canal. Apparently, selenium accumulates in fish and birds in the study area to levels that indicate human consumption of such items need to be limited if eaten on a daily basis. It is unlikely that residents eat fish and game birds on a daily basis; therefore, selenium toxicity probably is not a major issue regarding human health in the Uncompahgre Project area and in the Grand Valley.

**Table 38.** Selenium concentrations in fish-fillet and bird-breast samples from the Uncompahgre Project area and the Grand Valley, and the quantity of each sample that could be consumed without exceeding the maximum recommended daily quantity for an adult human

[Selenium concentrations in micrograms per gram wet weight; recommended daily consumption limit for selenium is 200 micrograms (National Academy of Sciences, 1980); daily consumption limit is the quantity of the food item, in ounces per day, that would need to be consumed to equal the daily consumption limit of 200 micrograms]

Type of sample	Sampling location	Selenium concentration	Daily consumption limit
Yellow perch fillet	Crawford Reservoir	3.1	2.3
Brown trout fillet	Cummings Gulch	2.6	2.7
Channel catfish fillet	Highline Reservoir	1.9	3.7
Largemouth bass fillet	Highline Reservoir	2.2	3.2
Mallard breast	Ferrier Pond	7.4	.95
Mallard breast	Ferrier Pond	5.6	1.3
Mallard breast	Ferrier Pond	10.3	.68
Coot breast	Fruitgrowers Reservoir	1.9	3.7
Coot breast	Fruitgrowers Reservoir	2.2	3.2

## SUMMARY

The U.S. Department of the Interior began a program in 1985 to determine the effects of irrigation drainage on water quality and on fish and wildlife resources in the Western United States. This report describes results of a study done in 1991–93 of irrigation drainage associated with the Uncompahgre Project area and the Grand Valley in west-central Colorado. The focus of the report is on the sources,

distribution, movement, and fate of selenium in the hydrologic and biologic system. The information collected for the study is for use in identifying potentially serious water-quality problems related to irrigation drainage and to provide scientific understanding needed to develop alternatives to mitigate or resolve the problems.

In irrigated areas of the Uncompahgre Project, residual soils and alluvium primarily derived from Mancos Shale contained the highest concentrations of total and water-extractable selenium. Geometric mean selenium concentrations for soils derived from the Mancos Shale were 10 to 13 times greater than the geometric mean for soils in the Western United States. Selenium concentrations in 128 alfalfa samples ranged from less than 0.3 to 9.5  $\mu\text{g/g}$  dry weight, and only 5 samples had concentrations that exceeded the recommended dietary limit of 4  $\mu\text{g/g}$  for consumption by livestock. These results indicate that irrigation practices might be mobilizing and redistributing selenium in the Uncompahgre Project.

In the Uncompahgre Project area and in the Grand Valley, distribution and concentrations of dissolved selenium in ground water differ according to the hydrogeologic setting. The highest concentrations of dissolved selenium (maximum 1,300  $\mu\text{g/L}$ ) were in water from wells completed in alluvium overlying Mancos Shale. The lowest concentrations of dissolved selenium were in water from wells completed in terrace deposits on the western side of the Uncompahgre Valley and in water from wells completed in Mancos Shale residuum. Dissolved-selenium concentrations in ground water of the study area generally were higher during summer when irrigation water was applied than during winter. Selenium concentrations decreased in winter when irrigation ceased and reducing geochemical conditions tended to remove selenium from solution. Dissolved-selenium concentrations were low where the platinum-electrode potential was low and the hydrogeologic system was more reducing. Selenium in the Uncompahgre Project and in the Grand Valley could be mobilized by oxidation of reduced selenium, desorption of selenium from aquifer sediments, ion exchange, and by dissolution of selenium. Dissolved solids and dissolved selenium are positively correlated in water from wells completed in alluvium, possibly because of desorption and ion-exchange processes, but dissolved solids and selenium are negatively correlated in water from wells completed in shale

residuum. The application of irrigation water and perhaps nitrate fertilizers on alluvium and shale residuum in the study area mobilizes selenium by desorption, ion exchange, or oxidation into more mobile chemical forms where the selenium is transported by ground water to streams and irrigation drains tributary to the Gunnison, Uncompahgre, and Colorado Rivers.

Median selenium concentrations in the Gunnison and Colorado Rivers upstream from the Uncompahgre Project area and the Grand Valley were less than or equal to 1 µg/L. Downstream from the irrigated areas, the median selenium concentrations (1975–92) were 7 µg/L for the Gunnison River at Whitewater (about 10 mi from the confluence with the Colorado River) and 5 µg/L for the Colorado River near the Colorado-Utah State line. About 64 percent of the samples from the Gunnison River and almost 50 percent of the samples from the Colorado River exceeded the U.S. Environmental Protection Agency's aquatic-life criterion of 5 µg/L. There apparently was a significant decreasing trend in selenium concentrations in the Colorado River near the Colorado-Utah State line during 1975–92. The Uncompahgre Project and the Grand Valley may account for as much as 75 percent of the selenium load in the Colorado River near the State line.

The highest selenium concentrations in surface-water samples were collected in areas primarily irrigated on Mancos Shale. The selenium concentrations exceeded 5 µg/L in almost all surface-water samples collected during the nonirrigation season (November through March) from the eastern side of the Uncompahgre Project and from the Grand Valley. For nonirrigation-season samples, the median selenium concentration was 105 µg/L for the eastern side of the Uncompahgre Project and 50 µg/L for the Grand Valley. The largest selenium concentrations in surface water in the Uncompahgre Project were in the Loutsenhizer Arroyo Basin and in the area between the Garnet Canal and Peach Valley Arroyo. In the Grand Valley, the highest selenium concentrations were in parts of the Salt Creek, Reed Wash, and Leach Creek Basins. The maximum selenium concentrations in surface-water samples collected in 1991–93 were 600 µg/L in the Uncompahgre Project area and 380 µg/L in the Grand Valley. Selenium concentrations generally were lower on the western side of the Uncompahgre Project and in the Redlands and Orchard Mesa areas in the Grand Valley because these

areas primarily are irrigated on soils derived from terrace deposits that contain less shale detritus than soils in Mancos Shale areas.

The eastern side of the Uncompahgre Project is the primary source of selenium loading from the Uncompahgre Project. Loutsenhizer Arroyo and Cedar Creek, on the eastern side of the project, and Dry Creek, on the western side of the project, discharged the largest selenium loads to the Uncompahgre River. The highest mean selenium load from a tributary stream was 14.0 lb/d in Loutsenhizer Arroyo. Much of the selenium load measured during 1991–92 in west-side tributaries, such as Dry Creek and Roubideau Creek, probably was transported into these basins in the irrigation water and winter water by the Ironstone Canal. The Uncompahgre Project also contributes substantial selenium loads to the Gunnison River between Peach Valley Arroyo and the Uncompahgre River.

The largest selenium loads from the Grand Valley were in Salt Creek, Reed Wash, Big Salt Wash, and Leach Creek, which drain large areas of irrigated land in the western one-half of the valley. The highest selenium load from the Grand Valley during 1991–92 was 12.8 lb/d in Reed Wash. Generally, selenium loads were less than 0.2 lb/d in washes and ditches in the Redlands area, the area east of Grand Junction, and on Orchard Mesa. In some Grand Valley streams, such as Reed Wash, selenium loads were considerably larger during the irrigation season than the nonirrigation season.

Irrigation drainage from the Uncompahgre Project and from the Grand Valley is a major source of dissolved solids in the Upper Colorado River Basin. Median dissolved-solids concentrations for nonirrigation-season samples were 1,160 mg/L for the western side of the Uncompahgre Project, 4,110 mg/L for the eastern side of the Uncompahgre Project, and 3,600 mg/L for the Grand Valley. There are positive correlations between selenium and dissolved-solids loads for tributary streams in the study area. For 15 basins in the Grand Valley, the correlation coefficient was 0.91 between selenium yield and dissolved-solids yield. Salinity-control projects that were designed to decrease dissolved-solids loads from irrigated areas also could have decreased selenium loading.

Much of the gain in dissolved solids in irrigation-drain water in the study area was from gains of calcium, sodium, magnesium, and sulfate

ions. An analysis of chloride and selenium data indicated that selenium concentrations in irrigation drainage in the Grand Valley were 5 to 100 times greater than the selenium concentrations predicted from evaporative concentration of the irrigation source water. Based on ratios of sulfate to selenium, selenium was most readily mobilized in the Loutsenhizer Arroyo Basin; in the area between the Garnet Canal and Peach Valley Arroyo; and in the Salt Creek, Reed Wash, Leach Creek, and Indian Wash Basins. Low selenium concentrations and higher sulfate to selenium ratios for pond-water samples might be indicative of removal of selenium by chemical and biological processes in ponds. Some of the highest selenium concentrations in surface water were associated with high nitrite-plus-nitrate concentrations, and there are significant correlations of selenium to nitrite-plus-nitrate concentrations in surface-water samples from the study area.

Many concentrations of other potentially toxic trace constituents in surface water were equal to or less than analytical reporting limits and did not exceed aquatic-life criteria. The highest uranium concentrations in surface water in each area were in samples from reference sites; the maximum uranium concentration was 83 µg/L for Big Salt Wash upstream from the Government Highline Canal in the Grand Valley. A one-time sampling for 26 organophosphate and carbamate insecticides in the Grand Valley indicated that concentrations of most compounds were at or less than reporting limits.

Selenium concentrations in bottom-sediment samples from eight streams and four ponds exceeded the base-line concentration of 1.4 µg/g for soils in the Western United States, and most of the concentrations exceeded the level of concern of 4 µg/g for fish and wildlife. The maximum selenium concentration in bottom-sediment samples was 47 µg/g. Ponds and wetlands probably are sinks for selenium in the study area. Soluble and adsorbed selenium accounted for less than 10 percent of the total selenium in seven of eight bottom-sediment samples from streams.

Biota collected from the eastern side of the Uncompahgre Project generally had higher selenium concentrations than biota from the western side. Selenium concentrations in some aquatic-plant and aquatic-invertebrate samples exceeded 3 µg/g dry weight, a dietary guideline for fish and wildlife. Most whole-body fish samples from the Uncompahgre Project and adjacent areas

had selenium concentrations that exceeded the 1984 NCBP 85th percentile (0.73 µg/g wet weight). The NCBP 85th percentile is used for comparative purposes and does not necessarily indicate a hazard to fish. A trout sample from Crawford Reservoir had a selenium concentration of 18 µg/g dry weight.

Selenium concentrations in some aquatic plants and aquatic invertebrates from the Grand Valley exceeded the dietary guideline (3 µg/g dry weight) for protection of fish and wildlife. All selenium concentrations in whole-body fish samples collected from tributary streams and washes in the Grand Valley exceeded the 1984 NCBP 85th percentile. Egg and liver samples from catfish from Highline Reservoir and Salt Creek had selenium concentrations that exceeded levels of concern for reproductive success of freshwater anadromous fish. There was a general trend of increasing selenium concentrations in roundtail chubs and speckled dace in a downstream (east to west) direction for tributary streams in the Grand Valley.

The mean selenium concentration of 7.1 µg/g dry weight for fish samples collected in 1992 from the Gunnison River Basin (one site was on the North Fork) was significantly higher (probability 0.05) than the mean concentrations for fish from the Uncompahgre River (5.1 µg/g dry weight) and from the Colorado River (4.6 µg/g dry weight). Selenium concentrations in about 71 percent of the fish samples from the Gunnison and North Fork of the Gunnison Rivers, about 64 percent of the fish samples from the Uncompahgre River, and about 55 percent of the fish samples from the Colorado River exceeded a guideline of 4 µg/g dry weight for selenium in whole-body fish. Speckled dace contained significantly (probability 0.05) higher selenium concentrations than roundtail chubs, mottled sculpin, or suckers. Mean selenium concentrations in suckers from the Gunnison River at Delta and Whitewater were significantly higher than the mean concentrations in suckers from the Gunnison River at Austin and the North Fork near Lazear. Suckers from the Colorado River collected upstream from the Grand Valley had significantly (probability 0.05) less selenium than suckers collected in and downstream from the Grand Valley.

Using selenate and selenite data for five streams in the Grand Valley to calculate risk factors for endangered fish, selenate concentrations would pose a theoretical moderate risk to the swim-up life stage (0 to 98 days old) of endangered Colorado squawfish

and to all three of the tested life stages of endangered razorback suckers. Because selenite concentrations were much smaller than selenate concentrations, selenite would be a lower risk to the endangered fish than selenate.

Except for selenium, copper concentrations in whole-body fish from the study area most often exceeded the 1984 NCBP 85th percentile. Some copper concentrations in aquatic plants and invertebrates from the Uncompahgre Project area and in fish from the Gunnison River were indicative of copper contamination. Relatively few concentrations of arsenic, cadmium, lead, mercury, and zinc in whole-body fish exceeded the 1984 NCBP 85th-percentile concentrations. About 16 percent of the fish from the Colorado River exceeded the 1984 NCBP 85th percentile for mercury. Risk assessments for Colorado squawfish and razorback suckers to boron, vanadium, and zinc for five tributary streams in the Grand Valley most often were in the moderate risk category. Zinc concentrations in Adobe Creek, Leach Creek, and Indian Wash were in the high-risk category for the swim-up stage of Colorado squawfish.

An anomalously high toxaphene concentration of 0.82  $\mu\text{g/g}$  wet weight was reported for a flannel-mouth sucker from Dry Creek in the Uncompahgre Project. The highest concentrations of several polycyclic aromatic hydrocarbons (PAH) were in a white sucker collected from the North Fork of the Gunnison River near Paonia.

Selenium concentrations in food items of migratory birds in the Uncompahgre Project area greatly exceeded a recommended guideline of 3  $\mu\text{g/g}$  dry weight for protection of consumer wildlife. Fathead minnows from ponds had very high concentrations, including 59  $\mu\text{g/g}$  dry weight in a sample from Brozina Pond (located in the Uncompahgre Project) and 72 and 110  $\mu\text{g/g}$  dry weight in two samples from St. George Pond (located outside the project north of the Gunnison River). Selenium concentrations in bird eggs and livers in the Uncompahgre Project area exceeded normal concentrations, and some samples had concentrations in the high-risk category for adverse biological effects. The geometric mean selenium concentration of 41.9  $\mu\text{g/g}$  dry weight for five avocet eggs from Brozina Pond was similar to selenium concentrations associated with a 5-percent incidence of teratogenic effects. The geometric mean selenium concentration of 6.7  $\mu\text{g/g}$  dry weight for bird eggs from the Grand Valley was about one-half the mean concentration

for eggs from the Uncompahgre Project area. The selenium concentrations in bird eggs and livers from the Grand Valley were in the range of uncertainty regarding biological risk. Concentrations of other trace constituents in biota from wetlands generally were less than adverse-effect levels or were in normal concentration ranges.

Bird eggs were collected in 1992 and incubated in a laboratory, and of the 65 eggs incubated, only one had any visual deformities. Of the 25 yellow-headed blackbird nests monitored at Ferrier Pond (east of the Uncompahgre Project) in 1992, one pre fledgling bird was found dead, and that bird had 43  $\mu\text{g/g}$  dry weight of selenium. Two dead pre fledgling mallards (selenium concentrations of 26 and 27  $\mu\text{g/g}$  dry weight) found at Markley Pond on the eastern side of the Uncompahgre Project did not have abnormalities or deformities. Also from Markley Pond, two dead coot hatchlings had a selenium concentration of 19  $\mu\text{g/g}$  dry weight (combined sample), and two coot eggs incubated at the laboratory that had dead embryos when opened (never hatched) had a selenium concentration of 39  $\mu\text{g/g}$  dry weight (combined sample).

Chronic toxicity water tests on *Ceriodaphnia* and fathead minnow larvae using irrigation drainage from five Grand Valley streams indicated no significant difference between control solutions and test solutions, except for chronic toxicity to fathead minnows for the water sample from Leach Creek. A growth and survival test using *Hyallela* on bottom-sediment samples indicated no significant difference between test sediment and control sediment.

The highest bioaccumulation factors of selenium in the study area were from water to biota. For samples collected at wetlands in the Uncompahgre Project irrigated area, the bioaccumulation factor between water and fish was about 10,600. The highest bioaccumulation factor was about 20,900 from water to bird livers collected in the Uncompahgre Project. Bioaccumulation of selenium between bottom sediment and biota and in biota trophic levels were much smaller than between water and biota.

Selenium accumulates in fish and birds in the study area to levels that would limit human consumption if eaten on a daily basis. Because it is unlikely that residents eat fish and birds taken in the study area on a daily basis, selenium probably is not a human health concern in the study area.

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