Uranium in Surface Waters and Sediments Affected by Historical Mining in the Denver West 1:100,000 Quadrangle, Colorado

By Robert A. Zielinski, James K. Otton, R. Randall Schumann, and Laurie Wirt

Scientific Investigations Report 2007–5246

U.S. Department of the Interior U.S. Geological Survey

U.S. Department of the Interior

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This publication is available online at: http://pubs.usgs.gov/sir/2007/5246

Publishing support provided by: Denver Publishing Service Center, Denver, Colorado Manuscript approved for publication, October 2007 Edited by Mary Kidd Graphics and layout by Loretta Ulibarri

Suggested citation:

Zielinski, R.A., Otton, J.K., Schumann, R.R., and Wirt, L., 2008, Uranium in surface waters and sediments affected by historical mining in the Denver West 1:100,000 quadrangle, Colorado: U.S. Geological Survey Scientific Investigations Report 2007–5246, 54 p.

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Conversion Factors, Definitions, and Abbreviations

Inch/Pound to SI

Multiply	Ву	To obtain									
	Length										
inch (in.)	2.54	centimeter (cm)									
inch (in.)	25.4	millimeter (mm)									
foot (ft)	0.3048	meter (m)									
mile (mi)	1.609	kilometer (km)									
Volume											
quart (qt)	0.9464	liter (L)									
	Flow rate										
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m^3/s)									
	Mass										
ounce, avoirdupois (oz)	28.35	gram (g)									
pound, avoirdupois (lb)	0.4536	kilogram (kg)									
	Radioactivity										
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)									

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: $^{\circ}F=(1.8\times^{\circ}C)+32$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: $^{\circ}C=(^{\circ}F-32)/1.8$

Vertical coordinate information is referenced to the North American Vertical Datum of 1927 (NAVD 27).

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μ S/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L), micrograms per liter (μ g/L), picocuries per liter (pCi/L), or milliequivalents per liter (meq/L).

Additional Abbreviations Used in This Report

AA	Atomic absorption spectrometry
AR	Activity ratio
DN	Delayed neutron
dpm	Disintegrations per minute
EDX	Energy-Dispersive X-ray analysis
EDXRF	Energy-dispersive X-ray fluorescence spectrometry
eTh	Equivalent thorium
eU	Equivalent uranium
FA	Filtered-acidified
IAP	lon activity product
ICP-MS	Inductively coupled plasma-mass spectrometry
Ksp	Equilibrium solubility product
LOI	Loss on ignition
MCL	Maximum contaminant level
NURE	National uranium resource evaluation
PEC	Probable effect concentration
R	Correlation coefficient
RA	Raw-acidified
RSD	Relative standard deviation
SEM	Scanning electron microscope
SMCL	Secondary maximum contaminant level
TEC	Threshold effect concentration
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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Abstract

Geochemical sampling of 82 stream waters and 87 stream sediments within mountainous areas immediately west of Denver, Colorado, was conducted by the U.S. Geological Survey in October 1994. The primary purpose was to evaluate regionally the effects of geology and past mining on the concentration and distribution of uranium. The study area contains uranium- and thorium-rich bedrock, numerous noneconomic occurrences of uranium minerals, and several uranium deposits of variable size and production history. During the sampling period, local streams had low discharge and were more susceptible to uranium-bearing acid drainage originating from historical mines of base- and precious-metal sulfides.

Results indicated that the spatial distribution of Precambrian granites and metamorphic rocks strongly influences the concentration of uranium in stream sediments. Within-stream transport increases the dispersion of uranium- and thoriumrich mineral grains derived primarily from granitic source rocks. Dissolved uranium occurs predominantly as uranyl carbonate complexes, and concentrations ranged from less than 1 to 65 micrograms per liter. Most values were less than 5 micrograms per liter, which is less than the current drinkingwater standard of 30 micrograms per liter and much less than locally applied aquatic-life toxicity standards of several hundred micrograms per liter.

In local streams that are affected by uranium-bearing acid mine drainage, dissolved uranium is moderated by dilution and sorptive uptake by stream sediments. Sorbents include mineral alteration products and chemical precipitates of iron- and aluminum-oxyhydroxides, which form where acid drainage enters streams and is neutralized. Suspended uranium is relatively abundant in some stream segments affected by nearby acid drainage, which likely represents mobilization of these chemical precipitates. The ²³⁴U/²³⁸U activity ratio of acid drainage (0.95–1.0) is distinct from that of local surface waters (more than 1.05), and this distinctive isotopic composition may be preserved in iron-oxyhydroxide precipitates of acid drainage origin.

The study area includes a particularly large vein-type uranium deposit (Schwartzwalder mine) with past uranium

production. Stream water and sediment collected downstream from the mine's surface operations have locally anomalous concentrations of uranium. Fine-grained sediments downstream from the mine contain rare minute particles (10–20 micrometers) of uraninite, which is unstable in a stream environment and thus probably of recent origin related to mining. Additional rare particles of very fine grained (less than 5 micrometer) barite likely entered the stream as discharge from settling ponds in which barite precipitation was formerly used to scavenge dissolved radium from mine effluent.

Introduction

The Colorado Front Range immediately west of Denver includes numerous historical mining districts of base and precious metals that date back to the late 19th century (Lovering and Goddard, 1950). Uranium (U) is a commonly associated element in the vein-type sulfide ores and, at some locations, attained concentrations sufficient to support small amounts of historical uranium production, particularly in and around the Central City area (fig. 1; Sims, 1963). More substantial veintype uranium deposits were discovered after 1950 in areas closer to the mountain front and outside the former metal-mining districts (Sims and Sheridan, 1964). One of these deposits, the Schwartzwalder (fig. 1), is the largest vein-type uranium deposit in the United States and has produced approximately 20 million pounds of U₂O₆ (Preston Nieson, Cotter Corporation, oral commun., 2006). Each of the uranium mines with documented past production is associated with nearby noneconomic uranium mineral occurrences and prospects, many of which are described in a compilation by the Colorado Geological Survey (Nelson-Moore and others, 1978). The relatively large number of uranium mineral occurrences in the Colorado Front Range results from magmatic and hydrothermal redistribution of uranium that was originally derived from local bedrock of anomalous uranium content (Sims, 1963; Phair and Gottfried, 1964; Sims and Sheridan, 1964; Phair and Jenkins, 1975; Hills and others, 1982).

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Figure 1. Map of Denver West 1:100,000 quadrangle showing locations where stream-water and sediment samples were collected.

Considering the number of uranium occurrences, the presence of uranium-rich drainage in some metal mines, the proximity of some uranium occurrences to streams, and the large downstream population in metropolitan Denver, the Denver West 1:100,000 quadrangle (fig. 1) was chosen by the U.S. Geological Survey (USGS) for a detailed study of uranium mobility. The study, begun in 1994, was originally designed to include periodic geochemical sampling for uranium and other elements in streams and stream sediments within the mountainous western three-quarters of the quadrangle. The sampled area (fig. 1) included the entire drainage basin of Clear Creek, a tributary of the South Platte River and a source of drinking water for some Denver suburbs. Major metal-mining districts in the area included Central City-Idaho Springs, Lawson-Dumont, Georgetown, Empire, and Montezuma. The Schwartzwalder uranium mine and all geologically similar uranium deposits/occurrences near the mountain front were also within the sampled area. The southeast and northwest por-

tions of the quadrangle are generally devoid of metal mineralization and thus contrasted with mined and (or) mineralized areas in the rest of the quadrangle.

This report presents results of the initial phase of sampling performed during October 11–21, 1994. Chemical data for uranium and many other constituents in 82 stream-water samples, 1 sample of acid mine drainage, and 87 stream sediment samples are presented. More recent, but limited, measurements of uranium isotopes in water and observations of the mode of occurrence of uranium and thorium (Th) in sediments supplement the regional geochemical data. Dissolved concentrations of uranium and other metals are compared to current drinking-water standards and aquatic-life standards. Finally, the distributions of uranium in surface waters and sediments are compared to distributions determined in 1976 during a larger regional-scale geochemical sampling program sponsored by the U.S. Department of Energy (Smith, 1997). The combined results indicate (1) geochemical processes that control the mobility of dissolved uranium and other metals, (2) the mode of occurrence of uranium in sediments, (3) lithologic and anthropogenic controls on the spatial distribution of uranium in the Denver West 1:100,000 quadrangle, and (4) effects of uranium on water quality and aquatic life.

A change in programmatic emphasis in 1995 caused the early cancellation of this project; however, the 1994 data for dissolved uranium and other metals provide an important basis for comparison with more recent measurements of surface-water quality by other agencies or private groups. Such comparisons help to document the effects of ongoing remediation of mining effects in the Denver West quadrangle that have been undertaken since 1994. Studies of geologic and anthropogenic controls on dissolved uranium have additional relevance, considering the relatively recent establishment of a drinking-water standard for uranium of 30 micrograms per liter (µg/L) by the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 2001). In addition, recent increases in the price of uranium will lead to reopening of some uranium mines in the United States and elsewhere, and this may stimulate additional environmental sampling programs modeled after this study.

Description of the Study Area

The Denver West 1:100,000 quadrangle encompasses the area between long. 105°00' to 106°00' W. and lat. 39°30' to 40°00' N. (fig. 1). The eastern quarter of the quadrangle, not sampled in this study, is underlain by generally flat-lying sediments of the Denver Basin and includes the highly developed western suburbs of Denver and the southern suburbs of Boulder, Colorado. The remainder of the quadrangle is mountainous and rises in elevation from approximately 2,000 m at the base of the foothills west of Denver to the highest peaks of 3,500 to 4,250 m. In the western quarter of the quadrangle, the Continental Divide follows the crest of the Front Range and traverses the quadrangle in a roughly northsouth direction. The prevailing climate of the mountainous area is temperate continental with a mean annual temperature of 0 degrees Celsius (°C) and annual average precipitation of 50-60 centimeters (cm) (Bolivar and others, 1978). Most precipitation occurs as winter snows and occasional springsummer showers.

Mountainous areas of the Denver West quadrangle are underlain primarily by Precambrian igneous and

Table 1. Approximate age and average uranium and thorium content of igneous rock units in the Denver West

 1:100,000 quadrangle, Colorado.

[Ma, mega-annum; U, uranium; Th, thorium; µg/g, microgram per gram; --, no data]

Rock unit	Number of samples	Approximate age* (Ma)	U (µg/g)	Th (μg/g)	Reference				
Boulder Creek granite	151	1,700	2.7	13.4	Phair and Gottfried, 1964				
Silver Plume granite	46	1,400	5.8 ± 2.0	73±32	Hills and others, 1982				
Silver Plume granite	52	1,400	5.2	36.4	Phair and Gottfried, 1964				
Indian Creek batholith	11	1,400	6.9±2.3	55±16	Hills and others, 1982				
Pikes Peak batholith	38	1,000	5.0	25.5	Phair and Gottfried, 1964				
Apex stock	3	60	8.1±1.4	29±9.2	Phair and Jenkins, 1975				
Caribou stock	4	60	2.0±0.9	6.7 ± 2.1	Phair and Jenkins, 1975				
Empire stock	10	65	11.7 ± 4.6	46±16.8	Phair and Jenkins, 1975				
Bryan Mountain stock	14	59	7.2±11.9	35.8 ± 32.5	Phair and Jenkins, 1975				
Bostonite dikes	15	56-60	33.5 ± 36.1	103 ± 97.2	Phair and Jenkins, 1975				
Bostonite dikes	15	56-60	44	142	Phair and Gottfried, 1964				
Montezuma stock Red Mountain complex	9	39	7.3±2.6	22.2±6.7	Phair and Jenkins, 1975				
(Urad-Henderson)	372	23–28	47.0±49.8	36.2±52.6	Bright and Holland, 1973				
Crustal average			2.7	10	Taylor, 1964				
Average granite			4.8	17	Taylor, 1964				

* Ages of Tertiary igneous rocks are from Simmons and Hedge (1978) and Naeser and others (1973). Ages of Precambrian rocks are from Peterman and others (1968) and Hutchinson (1976).

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EXPLANATION



Figure 2. Generalized geologic map of Denver West 1:100,000 quadrangle showing sampling sites and approximate limits of the Colorado Mineral Belt. Modified from Tweto (1979) and Green (1992). Ma, mega-annum.

Table 2. Contrasting characteristics of vein-type uranium deposits of the Denver West 1:100,000 quadrangle, Colorado.

[Sources of information: Sims and Sheridan (1964), Wallace and Karlson (1985), Wallace and Whelan (1986), Ludwig and others (1985); NW, northwest; SE, southeast; NE, northeast; SW, southwest; <, less than; °C, degrees Celsius; ~, about; Ma, mega-annum; Zr, zirconium]

Ralston Buttes (Foothills) District Outside Colorado Mineral Belt	Central City District Inside Colorado Mineral Belt
Not closely associated with Tertiary intrusives	Closely associated with Tertiary intrusives
Minor associated sulfides	Major associated sulfides
U is the only mined commodity	U mining is minor compared to mining of veins for base and precious metals
Deposits associated with major NW-SE-trending breccia-reef faults	Deposits associated with smaller NE-SW-trending faults
Meteoric hydrothermal (<300°C)	Magmatic hydrothermal (300–500°C)
Pitchblende plus coffinite	Pitchblende only (Zr-rich)
Age, ~70 Ma	Age, 70–55 Ma
U mining history = 1953–2000	U mining history = $1871 - 1960$
U derived from deeper Precambrian metamorphic rocks	U derived from magmatically evolved magmas of high Zr content

metamorphic rocks in the age range 1,000 to more than 1,700 Ma (mega-annum) (fig. 2, table 1). The oldest rocks are shale, graywacke, and volcanic rocks that were highly deformed and metamorphosed to gneiss and schist prior to 1,700 Ma. These metasediments and metavolcanics were subsequently intruded by three different generations of Precambrian granitic rocks identified as Boulder Creek (about 1,700 Ma), Silver Plume (about 1,400 Ma) and Pikes Peak (about 1,000 Ma) granitic groups. Much smaller volumes of silicic igneous rocks were intruded as small stocks, sills, and dikes in Late Cretaceousearly Tertiary time during the Laramide orogeny. These Laramide intrusives and similar younger intrusives of middle Tertiary age are located within a northeast-trending area that crosses the west half of the Denver West quadrangle (fig. 2). This area of Tertiary intrusives and associated economic deposits of base and precious metals is part of a larger, similarly mineralized area in central Colorado termed the "Colorado Mineral Belt." In this belt, Tertiary intrusives and zones of associated mineralization were probably localized along reactivated high-angle, northeast- and northwest-trending faults and shear zones in the Precambrian basement. More detailed descriptions and summaries of the local geologic setting and mineral deposits are in Lovering and Goddard (1950), Sims (1963), Peterman and others (1968), Tweto (1975), and Hills and Houston (1979). Uranium deposits such as the Schwartzwalder are outside the Colorado Mineral Belt and are not closely associated with Tertiary intrusives but are clearly fault controlled and of Laramide age (table 2; Sims and Sheridan, 1964; Wallace and Karlson, 1985; Wallace and Whelan, 1986; Ludwig and others, 1985).

Uranium Mines and Mining History

Mines in the Denver West quadrangle with documented production of uranium ore are shown approximately located in figure 3 and identified in table 3. Production records are of questionable accuracy and completeness, particularly for the older mines (1871–1960) from Gilpin and Clear Creek Counties in and around Central City. With one exception (Kirk and Wood mine), production of uranium from metal mines in Gilpin and Clear Creek Counties is minor compared to production of uranium from single-commodity uranium mines in Jefferson County. Production from the Schwartzwalder mine (#2 in fig. 3) dwarfs that of all the other uranium mines combined. Stippled areas in figure 3 represent zones with high concentrations of noneconomic uranium prospects and uranium mineral occurrences, as identified in Colorado Geological Survey Bulletin 40 (Nelson-Moore and others, 1978).



Figure 3. Map of Denver West 1:100,000 quadrangle showing approximate locations of uranium deposits with documented historical production. Numbered mines correspond to mine descriptions in table 3. Stippled areas contain numerous uranium occurrences. Diagonal-lined area indicates approximate limits of the Colorado Mineral Belt. Modified from Sims and Sheridan (1964).

Mine/prospect	Location in figure 3	County	Production (pounds U ₃ O ₈)	Reference
Schwartzwalder	2	Jefferson	20,000,000	Preston Niesen, Cotter Corp. oral communication, May 2006
Ascension	10	Jefferson	23,431	Nelson-Moore and others, 1978
Aubrey Ladwig	12	Jefferson	9,527	Nelson-Moore and others, 1978
Grapevine	13	Jefferson	23,850	Nelson-Moore and others, 1978
Mann Ranch	15	Jefferson	15,539	Nelson-Moore and others, 1978
Mena	1	Jefferson	6,676	Nelson-Moore and others, 1978
Ohman	11	Jefferson	1,170	Nelson-Moore and others, 1978
Old Leyden	3	Jefferson	4,533	Nelson-Moore and others, 1978
Four Corners	16	Jefferson	2,667	Nelson-Moore and others, 1978
Foothills mine	14	Jefferson	113,221	Nelson-Moore and others, 1978
Carrol Group	4	Gilpin	434	Sims, 1963
Kirk and Wood (East Calhoun)	7	Gilpin	109,645	Sims, 1963
German	5	Gilpin	630	Sims, 1963
West Calhoun	8	Gilpin	90	Sims, 1963
Belcher	6	Gilpin	1,192	Sims, 1963
Bonanza	not plotted	Clear Creek	76	Nelson-Moore and others, 1978
Highlander	not plotted	Clear Creek	245	Nelson-Moore and others, 1978
Spanish Bar	not plotted	Clear Creek	196	Nelson-Moore and others, 1978
Jo Reynolds	9	Clear Creek	11,520	Sims, 1963

 Table 3.
 Uranium mines and production in the Denver West 1:100,000 quadrangle, Colorado.

Sampling

A total of 87 sites were sampled by three teams during October 11–21, 1994. This intensive sampling program provided a regional-scale snapshot of conditions presumed to be typical of early autumn, low-flow conditions in which streamflow is largely sustained by returns of ground water. Four of the sites were dry (sediment only), and two sample numbers in the available number sequence (11 and 32) were not used. Sampling sites were chosen to include successive downstream locations within the main stem of Clear Creek (12 samples), all tributaries to Clear Creek, and many other named creeks in the sampled area (fig. 1). One sample (45, fig. 1) of highly acidic (pH 3.3) drainage collected near Idaho Springs was included because it provided the only measurable discharge in a natural stream channel (Virginia Canyon) leading to Clear Creek.

Stream width was measured at each sampling site by using a tag line or steel tape. Stream cross section was estimated by recording water depth at 10 or more evenly spaced increments chosen along the tag line or tape. These same locations were the sites of vertical-integrated water sampling according to the equal-width increment method (U.S. Geological Survey, 1998). Water collected along the cross section was combined in a large polyethylene carboy kept in shallow water at streamside. Measurements of water temperature, pH, and specific conductance were performed on a subsample of the combined water. An additional 2-liter (L) subsample of the composite was collected in an acid-washed, field-rinsed polyethylene bottle that was placed in a cooler for transport to the laboratory.

Stream discharge in cubic feet per second (ft³/s) was estimated at each site by using the calculated cross-sectional area and a timed float method used to measure surface flow velocity (U.S. Geological Survey, 1969). At 25 sites, more reliable discharge estimates were available from recordings at nearby permanent stream gages operated by the USGS or the State of Colorado. Water-stage measurements at gages were converted to discharge by using established stage-discharge relations for each gage. At 12 sites on low-flow creeks, a vertical-axis current meter (Price pygmy meter) was used to more reliably measure integrated flow velocity (U.S. Geological Survey, 1969). Comparisons indicated that surface discharge estimates by the timed float method were consistently high by a factor of approximately 2±0.5 compared to the other methods, and all float measurements were corrected accordingly. High estimates of discharge by the float method result because the float was consistently placed in the fastest moving water of the stream channel and because surface discharge measured by the float method is generally greater than depth-integrated discharge.

Stream sediments were collected several meters downstream from the water samples. A composite total of 2–3 kilograms (kg) of sediment was generated by combining samples from several locations within the active channel where relatively quiet water permitted deposition of finer sediment. Preferred sampling locations were downstream from point bars and large boulders, or within pools. Sediments were collected with plastic spoons or scoops and placed in a large polyethylene bag. Excess water was decanted from the sample bag after sufficient time for the water to clarify by particle settling. Pebbles larger than 2.5-cm diameter were removed before closing the bag with a twist tie and double bagging. Sediment and water from each collection site were labeled with the site number. In the subsequent discussion of water and sediment results, the site number and sample number are used interchangeably.

Analytical Methods

Waters

Water samples were taken to USGS laboratories in Denver and split into three separate fractions: raw-acidified (RA, 125 milliliters [mL]), filtered-acidified (FA, 125 mL), and filtered-unacidified (FU, 1.5 L). Acidification was to pH<2 with high-purity nitric acid. Filtration was through cellulose acetate filter membranes of 0.45-micrometer opening, under pressure from nitrogen gas. Acidified samples (RA, FA) were submitted for analyses of major cations by atomic absorption spectrometry (AA) and of selected minor and trace elements by inductively coupled plasma-mass spectrometry (ICP-MS; Briggs and Meier, 1999). Unacidified samples (FU) were used for determination of carbonate alkalinity by Gran titration with standard acid (Stumm and Morgan, 1981) and for determination of dissolved sulfate by a turbidimetric method (Hach Company, 1992). Approximately 1 L of each remaining FU sample was submitted for determination of dissolved 226Ra by the radon emanation method (Thatcher and Janzer, 1977). Estimated accuracy and precision, expressed as relative standard deviation (RSD), was generally better than 5 percent for alkalinity and major cations and 10 percent for minor and trace elements and sulfate determinations. Radium determinations at the concentrations encountered have estimated errors of 15 to 30 percent RSD.

A group of 13 of the archived FA waters was selected in 2001 for determination of ²³⁴U/²³⁸U alpha activity ratios (AR), which are ratios of activity concentrations expressed in radioactivity units such as disintegrations per minute (dpm). Samples were chosen to represent a range of dissolved uranium concentrations and geographic locations. The 13 samples provided a basis for comparison with more recent (2002) measurements of the uranium isotope composition of some stream waters near Central City that are directly affected by acidic, uranium-rich mine drainage. Determinations of uranium isotopes were by magnetic sector ICP–MS in the single collector, rapid scan mode. Measured mass ratios of uranium isotopes have an estimated analytical precision better than 1 percent (RSD) for uranium concentrations greater than 1 μ g/L. The AR was calculated from the measured mass ratio and normalized to a similarly measured standard of known AR to correct for instrument bias.

Sediments

Upon reaching the laboratory, sediments were air dried at 40°C, then passed through a stainless steel sieve of 2-millimeter (mm) opening, and material coarser than 2 mm was discarded. Five hundred grams (g) of the sieved (<2 mm) sediment was saved for archiving, and the remainder was passed through a series of stainless steel sieves to produce the following size fractions: 2 mm to 0.18 mm (10 to 80 mesh), 0.18 mm to 0.09 mm (80 to 170 mesh), and <0.09 mm (-170 mesh). The three size fractions were weighed to determine their mass contributions to the original sediment (Asher-Bolinder, 1995). (Note: Herein the term "whole sediment" refers to sediment <2 mm, and "fine-grained sediment" refers to the sediment size fraction <0.09 mm).

Radioactivity-based activity concentrations (dpm/g) of uranium, thorium, and potassium (K) in the whole sediments were determined by gamma-ray spectrometry with a sodium iodide (NaI) detector. Samples were sealed in airtight containers for three weeks prior to counting to permit establishment of radioactive equilibrium (equal activity) between (1) ²²⁶Ra and its short-lived daughters in the ²³⁸U decay series, and (2) ²²⁸Th and its daughters in the ²³²Th decay series. Intense gamma-ray emissions of ²³⁸U daughter ²¹⁴Bi (bismuth), and ²³²Th daughter ²⁰⁸Tl (thallium) were used to determine activity concentrations. Assumed radioactive equilibrium between these daughters and their parents permitted the determination of equivalent uranium (eU) and thorium (eTh) activity concentrations and calculation of their corresponding mass equivalents as micrograms per gram ($\mu g/g$). Concentrations of potassium were obtained from direct measurement of the high-energy gamma ray of ⁴⁰K and its known specific activity (dpm/µg) and isotopic abundance. Samples were counted on the NaI detector for periods of time sufficient to generate high numbers of counts under the gamma-ray photopeaks of interest. Analytical errors based on counting statistics are less than 5 percent RSD.

The fine-grained (<0.09 mm) size fraction of each sediment was submitted for analysis of uranium and thorium content by a delayed neutron (DN) technique (Millard and Keaten, 1982) and for selected major and trace elements by energy-dispersive X-ray fluorescence spectrometry (EDXRF) (Johnson and King, 1987). Estimated accuracy and precision (RSD) of the DN method based on a 10-g sample are better than 5 percent for uranium and 15 percent for thorium. For EDXRF, the estimated RSD is better than 10 percent for most reported elements. An exception is tungsten (W), which was typically below the detection limit of approximately 20 µg/g. The few reported tungsten values above 20 $\mu g/g$ have estimated errors that become larger as they approach the detection limit.

A few samples of <0.09-mm sediment were selected for detailed examination with a scanning electron microscope (SEM) equipped with energy-dispersive X-ray analysis (SEM–EDX). Grain mounts and polished thin sections of grain mounts both were used. Observations in the backscatter electron image mode were particularly helpful for identifying minute uranium-rich particles because grains with high concentrations of elements of high atomic number appear as brighter spots on the image.

A few samples of fine-grained sediment from selected sites were mounted in epoxy resin on glass microscope slides and further processed to produce polished thin sections for petrographic observation. Some of these thin sections also provided templates for determining the microscopic distribution of uranium by fission track radiography (Zielinski and Budahn, 1998). Thin sections were covered by a thin sheet of low-uranium muscovite mica detector and irradiated in a nuclear reactor to induce fission of ²³⁵U isotope. During irradiation, fission fragments recoil from the thin section surface and produce paths of damage in the overlying mica detector. These damage paths are made optically visible as fission tracks when the detector is later recovered and chemically etched with hydrofluoric acid. Areas of high fission-track density appear as dark areas on the mica detector and can be referenced to corresponding areas of high uranium in the thin section.

Three samples of fine-grained sediment were additionally analyzed for activity concentrations of 238 U, 226 Ra, and radium (Ra) decay products 214 Pb (lead), 214 Bi, and 210 Pb by high-precision gamma-ray spectrometry using a high-purity germanium detector and multichannel analyzer (Zielinski and Budahn, 1998). Estimated precision of these determinations based on counting statistics is better than ±10 percent (RSD).

Surface Water

General Chemical Character of Filtered Surface Water

Stream waters sampled in this study are generally of circumneutral to slightly alkaline pH (6.8–8.4) (table 4). Important exceptions are the previously mentioned acid drainage (pH 3.3) of Virginia Canyon (site 45; fig. 1) and four stream samples (sites 1, 62, 65, 70; fig. 1) of pH 4.1–5.5, which are likely influenced by acid drainage from nearby mines. Excluding the Virginia Canyon sample, specific conductance ranges from 30 to 1,400 microsiemens per centimeter (μ S/cm), but most values are below 600 μ S/cm, with a median value of 140 μ S/cm. Based on the milliequivalent per liter (meq/L)

concentrations of major cations and anions, most waters are of the Ca-Mg-HCO, chemical type, but a significant subset of 22 water samples are of Ca-Na-HCO₂ or Ca-Na-SO₄ chemical type. Water chemistry variations are influenced by the diverse lithologies of bedrock units and by mineralization within the Colorado Mineral Belt (Wanty and others, 2007). Five water samples (sites 15, 18, 19, 23, 24; fig. 1) have sodium as the dominant cation, which may indicate particularly alkali-rich local bedrock compositions or anthropogenic contamination. Solution alkalinity, expressed as the concentration of bicarbonate anion (HCO₂), ranges from less than 5 to 283 milligrams per liter (mg/L), with a median value of 43 mg/L. Sulfate is the dominant anion in acidic samples and is a significant constituent in other water samples collected within or downstream from mineralized areas affected by sulfide oxidation. Other dissolved anions (chloride, fluoride, nitrate, phosphate) were not measured but are of probable low abundance based upon the close agreement (±10 percent) of calculated cationanion balances for many of the waters using only HCO₂ and SO₄ (sulfate) as anions. The more acidic waters contain excess anions over cations because unaccounted-for acid-soluble cations (aluminum, heavy metals) can become significant for the overall balance. In contrast, water samples with larger deficiencies of anions may have greater contributions from unaccounted-for chloride, nitrate, or phosphate. These latter samples tend to be located closer to developed residential areas nearer the mountain front, suggestive of some added nutrients from anthropogenic sources.

Several dissolved trace elements of potential environmental concern were analyzed along with uranium (table 4), providing a basis for comparison with uranium. Simple crossplots of element-versus-element concentrations in FA water samples indicate the extent of correlation between pairs of elements. Such plots indicate that dissolved uranium does not correlate closely with any of the other measured trace elements. The apparent positive correlation of dissolved uranium with dissolved arsenic (As) is too strongly influenced by two outlying values (samples 23 and 24; table 4) from Ralston Creek downstream from the Schwartzwalder mine (fig. 4). Likewise, the apparent correlation of uranium with molybdenum (Mo) is largely based on samples 23 and 24 and three additional samples (15, 18, 19; table 4) from the West Fork of Clear Creek (fig. 4). The West Fork includes in its drainage basin the Tertiary Red Mountain intrusive complex that hosts the Urad-Henderson molybdenum ore deposit (figs. 1, 2; Wallace and others, 1978). Unlike dissolved uranium, dissolved zinc (Zn) shows more systematic and stronger correlations (R>0.67) with other dissolved metals such as cadmium (Cd) and copper (Cu) over a range of concentrations (fig. 4). Correlation of dissolved zinc with other metals is likely influenced by similar solution chemistry of metal cations or similar origins from sulfide oxidation.



Figure 4. Plots showing apparent correlations of dissolved uranium with arsenic and with molybdenum, which are too strongly influenced by a few outlier values. For comparison, plots showing positive correlations of dissolved zinc with cadmium and with copper are based on data that are better distributed over a range of values. $\mu g/L$, micrograms per liter.

Stream Discharge and Uranium Load

Stream discharges measured in October 1994 (table 4) can be grouped into three general categories: (1) the main stem of Clear Creek (10–70 ft³/s), (2) major tributaries to Clear Creek and other major streams (10–30 ft³/s), and (3) other smaller streams (<10 ft³/s). Clear Creek and other streams with more than one downstream measurement all show increased discharge in the downstream direction, indicating progressive gains from tributary inflow and (or) ground-water seepage. The load of dissolved uranium in a stream is the amount carried at any given time and is the product of discharge and dissolved uranium concentration. Dissolved uranium concentration in the main stem of Clear Creek did not increase substantially in a downstream direction and

fell consistently in the narrow range of 1.1 to 2.5 μ g/L (table 4). In this case, downstream increases in calculated uranium load were more strongly influenced by progressive increases in discharge (table 4). In contrast, the large increase in dissolved uranium concentration in the lower reach of Ralston Creek downstream from the then (1994) inactive Schwartz-walder uranium mine (table 4) strongly influenced uranium load in Ralston Creek. At the time of sampling, the uranium load delivered by Clear Creek at Golden, Colorado (sample 54, table 4), was 0.33 kg/day, which compares to a calculated zinc load of 38 kg/day. Calculated loads of zinc in the Denver West quadrangle are more dependent on variations in concentration of dissolved zinc. Such variations are relatively large compared to uranium (table 4) and may be more influenced by local inputs from mines and mining activities.

Table 4. Selected field-measured parameters and chemical composition of surface water samples in the Denver West quadrangle, Colorado.

Sample ID	Sampling site	pН	Temp. (°C)	Sp. Cond. (µS/cm)	ft ³ /s (±10 %)	ft ³ /s method	SiO2 (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	HCO ₃ (mg/L)
94DW W01	Gamble Gulch	5.50	2.2	330	0.8	Float	23	6.9	1.9	38	10	0.11	0
94DW W02	Moon Gulch	7.20	4.0	100	0.4	Float	15	4.0	1.1	12	3.4	0.06	27
94DW W03	S. Boulder Creek at John- son mine	7.30	5.7	55	14	Gage	7.0	2.1	0.7	7.0	2.0	0.10	26
94DW W04	Mammoth Gulch	7.75	6.1	45	2.3	Pygmy	10	1.8	0.7	7.0	1.9	0.05	20
94DW W05	N. Boulder Creek at Sherwood Creek	7.55	8.9	30	22	Float	6.0	1.1	0.4	5.0	1.0	0.18	13
94DW W06	Beaver Creek	7.50	6.7	200	< 0.1		15	5.0	1.6	23	8.8	0.24	91
94DW W07	Middle Boulder Creek above Barker Res.	7.65	5.5	45	15	Gage	6.0	1.2	0.5	7.0	1.5	0.09	20
94DW W08	S. Beaver Creek at Lin- coln Hills	7.80	7.0	240	0.3	Float	12	8.0	2.4	26	8.2	0.22	111
94DW W09	S. Boulder Creek at Pine- cliff gage	7.85	8.9	65	31	Gage	8.0	2.3	0.7	8.0	2.3	0.06	28
94DW W10	Beaver Creek at Gap and Twin Spruce	7.80	11.1	220	0.1	Float	15	19	1.7	18	4.1	0.11	68
94DW W12	Coal Creek Gaging Station	7.80	10.0	1,400	< 0.1		18	200	3.2	43	16	0.27	105
94DW W13	Fall River near mouth	7.60	4.0	70	3.5	Gage	8.0	2.4	0.8	9.0	2.5	0.07	25
94DW W14	Fall River above Cum- berland	7.30	4.0	50	4.2	Float	8.0	1.9	0.7	6.0	1.9	0.16	20
94DW W15	W. Fork Clear Creek near Empire	8.00	8.0	275	22	Gage	10	33	3.4	17	3.5	0.20	59
94DW W16	Bard Creek	7.35	5.0	50	2.6	Float	8.0	1.8	0.6	6.0	2.2	0.04	27
94DW W17	Mad Creek	6.80	5.0	35	n.d.		10	1.9	0.5	5.0	1.0	< 0.01	13
94DW W18	W. Fork Clear Creek near Hoop Creek	8.30	3.0	510	6.4	Float	8.0	77	7.5	24	3.6	0.02	109
94DW W19	W. Fork Clear Creek below Henderson	7.50	3.0	250	8.0	Gage	7.0	27	2.4	21	2.5	0.04	54
94DW W20	Jim Creek	7.40	5.0	65	< 0.1		11	2.5	0.9	8.0	3.2	0.86	41
94DW W21	Fraser River at trail camp- ground	7.80	5.5	90	7.2	Gage	11	5.8	0.9	9.0	3.3	0.19	39
94DW W22	Vasquez Creek	7.30	5.5	45	5.4	Gage	11	2.9	0.5	6.0	1.2	0.02	23
94DW W23	Ralston Creek above reservoir	8.00	6.2	1,350	1.0	Float	22	180	5.8	86	38	0.03	189
94DW W24	Ralston Creek below Schwartzwalder	8.35	7.2	1,220	1.4	Float	21	150	5.4	71	31	0.02	179
94DW W26	Ralston Creek at Ralston Roost	8.00	4.5	250	0.5	Float	11	13	1.9	27	8.1	0.47	93
94DW W27	Deer Creek	7.55	5.0	100	0.2	Float	13	6.6	1.1	11	2.7	0.08	43
94DW W28	Ralston Creek at lower Golden Gate Park	7.45	6.0	220	0.5	Float	17	13	2.2	23	6.6	0.23	76
94DW W29	Ranch Creek	7.70	2.5	45	16	Gage	13	2.5	0.6	7.0	1.2	0.10	23
94DW W30	St Louis Creek	8.00	3.5	80	14	Float	10	2.2	1.1	12	2.6	0.17	45
94DW W31	Elk Creek	7.45	4.0	50	3.3	Float	20	3.3	1.3	7.0	1.5	0.43	27
94DW W35	Clear Creek below Love- land Ski area	7.70	2.5	160	4.4	Float	6.0	9.3	0.8	17	4.1	0.34	54
94DW W36	Quayle Creek	7.40	6.0	125	6.2	Float	4.0	1.3	0.6	17	4.5	<.01	50
94DW W37	Clear Creek at Baker	7.60	3.5	110	12	Float	6.0	3.2	0.6	13	3.5	0.08	45

Table 4.Selected field-measured parameters and chemical composition of surface water samples in the Denver Westquadrangle, Colorado.—Continued

SO4 (mg/L)	Al (µg/L)	Cr (µg/L)	Mn (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As µg/L)	Mo (µg/L)	Cd (µg/L)	Ba (µg/L)	Pb (µg/L)	La (µg/L)	U (µg/L)	Ra (pCi/L)	234U/238U Activity ratio
165	460	< 0.2	670	8.8	14	10	270	< 0.1	< 1	1.3	24	0.7	2.7	0.4		
29	8.0	< 0.2	32	0.10	0.9	1.0	2.0	< 0.1	< 1	0.02	22	< 0.1	<.1	0.1		
6.0	9.0	< 0.2	3.1	0.04	0.4	< 1	< 1	< 0.1	1.0	< 0.02	15	< 0.1	<.1	1.3		
5.0	6.0	< 0.2	3.1	0.03	0.3	< 1	< 1	< 0.1	< 1	< 0.02	11	< 0.1	<.1	< 0.05		
<5	14	0.4	7.0	0.02	< 0.2	< 1	< 1	< 0.1	< 1	< 0.02	5.7	0.4	<.1	< 0.05		
26	12	1.7	20	0.08	0.7	< 1	18	< 0.1	10	0.10	48	0.8	<.1	1.6	0.13	
<5	5.0	< 0.2	7.1	0.04	0.2	< 1	< 1	< 0.1	< 1	< 0.02	14	< 0.1	<.1	0.1		
14	23	2.5	24	0.10	0.8	< 1	< 1	0.1	< 1	< 0.02	56	< 0.1	0.2	0.8	0.14	
8.0	8.0	< 0.2	3.5	< 0.02	0.3	< 1	1.0	< 0.1	< 1	< 0.02	18	< 0.1	<1	0.9		
12	20	< 0.2	11	0.08	0.9	< 1	1.0	0.2	< 1	< 0.02	32	< 0.1	<.1	0.7		
24	23	< 0.2	390	0.40	2.1	< 1	2.0	1.2	< 1	0.04	140	0.2	0.2	1.9	0.35	
9.0	18	0.5	12	0.08	0.5	2.0	16	< 0.1	< 1	0.06	19	< 0.1	0.1	0.2		
6.0	9.0	0.6	8.0	0.07	0.2	1.0	1.0	< 0.1	< 1	< 0.02	14	< 0.1	<.1	0.2		
78	130	< 0.2	250	1.2	1.4	3.0	10	< 0.1	26	0.08	14	0.2	0.7	4.3	0.14	1.12
<5	9.0	< 0.2	6.0	0.03	0.3	< 1	21	< 0.1	< 1	0.09	18	< 0.1	<.1	0.4		
<5	14	< 0.2	1.3	< 0.02	< 0.2	< 1	15	< 0.1	< 1	0.06	8.8	0.4	0.3	0.2		
150	58	2.4	370	0.10	0.7	< 1	18	0.2	63	0.10	9.3	< 0.1	<.1	9.8	0.21	
56	10	< 0.2	53	0.04	0.7	< 1	20	< 0.1	14	0.04	9.6	< 0.1	<.1	5.2	0.15	
<5	7.0	0.9	100	0.30	0.4	< 1	1.0	< 0.1	< 1	< 0.02	33	< 0.1	<.1	0.3		
<5	58	0.9	24	0.09	0.3	<1	2.0	< 0.1	<1	< 0.02	34	0.3	<1	16	0.23	
<5	21	< 0.2	1.8	< 0.02	< 0.2	< 1	1.0	< 0.1	< 1	< 0.02	6.4	< 0.1	<.1	0.7		
600	7.0	< 0.2	15	0.20	3.0	2.0	6.0	0.8	190	0.20	85	< 0.1	<.1	65.0	0.84	
510	6.0	< 0.2	7.4	0.10	2.2	1	2.0	0.7	200	0.20	47	< 0.1	<.1	34.0	0.91	
17	20	< 0.2	120	0.20	1.1	< 1	2.0	0.2	< 1	< 0.02	32	< 0.1	0.1	3.5	0.17	
6.0	51	1.3	4.0	0.04	0.3	< 1	1.0	0.1	< 1	< 0.02	14	0.1	0.2	0.9		
29	17	< 0.2	4.6	0.05	0.7	< 1	1.0	0.1	< 1	< 0.02	32	< 0.1	<.1	1.5	0.12	
<5	15	< 0.2	2.4	< 0.02	0.2	< 1	< 1	< 0.1	< 1	< 0.02	11	< 0.1	0.1	0.1		
5.0	12	1.2	9.8	0.03	0.3	2.0	2.0	< 0.1	< 1	0.02	9.5	< 0.1	<.1	0.8		
<5	55	1.0	16	0.08	0.4	< 1	< 1	0.3	< 1	< 0.02	14	0.2	0.1	0.1		
7.0	13	< 0.2	58	0.10	0.5	1.0	6.0	< 0.1	< 1	0.02	38	0.5	0.2	1.5	0.19	
18	4.0	< 0.2	0.6	0.03	0.6	< 1	85	< 0.1	< 1	0.60	32	0.4	<.1	1.6		
9.0	6.0	< 0.2	7.5	0.04	0.3	< 1	21	< 0.1	< 1	0.20	30	0.2	0.1	1.1	0.14	

12 Uranium in Surface Waters and Sediments Affected by Historical Mining in the Denver West 1:100,000 Quadrangle, Colorado

Table 4. Selected field-measured parameters and chemical composition of surface water samples in the Denver West quadrangle, Colorado.—Continued

Sample ID	Sampling site	pН	Temp. (°C)	Sp. Cond. (µS/cm)	ft ³ /s (±10 %)	ft ³ /s method	SiO <u>2</u> (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	HCO ₃ (mg/L)
94DW W38	Clear Creek at Silver	8.00	1.5	120	15	Float	7.0	4.0	0.7	15	4.3	0.06	53
94DW W39	Clear Creek at George- town Loop	7.70	2.5	140	15	Float	5.0	4.4	0.8	17	4.9	0.09	56
94DW W40	Clear Creek above Georgetown Lake	7.90	5.5	130	25	Float	5.0	3.4	0.9	16	4.7	0.06	53
94DW W41	Clear Creek at Empire	7.60	9.0	140	29	Gage	7.0	3.9	1.1	17	5.4	0.10	54
94DW W42	Clear Creek at Lawson	7.70	8.0	200	43	Gage	6.0	15	2.0	16	4.5	0.12	58
94DW W43	Mill Creek	7.50	3.0	45	2.5	Float	10	2.0	0.7	6.0	1.7	0.04	21
94DW W44	Clear Creek above Idaho Springs	8.40	5.5	195	48	Float	6.0	14	1.9	18	4.9	0.15	58
94DW W45	Virginia Canyon	3.30	12.5	2,760	< 0.1		110	29	9.0	320	130	2.80	0
94DW W46	Clear Creek below Idaho Springs	7.40	7.5	210	64	Float	8.0	13	1.9	20	5.4	0.20	48
94DW W47	Clear Creek near junction I-70 and US 6	7.70	8.5	220	63	Gage	6.0	14	2.2	19	5.5	0.22	52
94DW W48	N. Fork Clear Creek at mouth	6.80	9.0	530	2.6	Gage	16	19	4.7	50	16	0.38	4.0
94DW W49	N. Fork Clear Creek above Missouri Creek	7.40	1.5	70	2.4	Pygmy	11	2.5	1.1	9.0	2.2	0.22	28
94DW W50	Missouri Canyon	7.55	1.5	165	0.25	Float	14	5.7	2.1	17	5.5	<.01	47
94DW W51	Eureka Gulch above Central City	6.80	8.0	440	< 0.1		16	8.4	5.4	53	16	0.05	59
94DW W52	Chase Gulch above Blackhawk	7.60	6.5	170	0.7	Float	12	3.7	2.1	19	5.8	0.18	50
94DW W53	N. Fork Clear Creek below Blackhawk	6.60	11.0	670	2.3	Pygmy	15	34	5.6	54	17	0.22	15
94DW W54	Clear Creek at Golden gage	7.50	3.5	240	71	Gage	9.0	16	2.4	21	6.3	0.23	50
94DW W55	Guy Gulch	8.20	8.5	570	< 0.1		18	21	4.2	65	22	<.01	248
94DW W56	Elk Creek	8.30	8.5	475	< 0.1		20	12	3.7	64	13	<.01	145
94DWW57	Russell Gulch at mouth	7.10	5.5	635	< 0.1		25	26	6.0	69	21	0.04	14
94DW W58	Smith Hill Gulch	7.30	6.0	265	< 0.1		18	8.6	1.8	33	10	<.01	142
94DW W59	Clear Creek below N. Fork of Clear Creek	7.80	2.5	245	64	Float	10	16	2.4	21	6.2	0.27	52
94DW W60	Keystone Gulch	7.70	2.5	100	2.5	Gage	10	2.1	0.8	13	3.0	0.05	46
94DW W61	Snake River near Key- stone Ski area	6.90	7.5	140	27	Gage	10	2.5	0.9	16	3.4	<.01	18
94DW W62	Snake River above Mon- tezuma	4.10	4.8	250	2.6	Gage	21	2.9	0.9	11	5.8	0.81	0
94DW W63	Deer Creek above Mon- tezuma	7.40	5.0	95	2.0	Gage	4.0	1.3	0.6	14	2.7	0.10	39
94DW W64	N. Fork Snake River	7.70	2.0	80	6.5	Pygmy	7.0	3.3	0.7	13	2.5	<.01	40
94DW W65	Peru Creek	5.50	3.8	140	9.7	Pygmy	10	1.8	0.7	15	3.9	0.16	0
94DW W66	Snake River above Peru Creek	7.00	5.7	150	10	Pygmy	11	2.3	0.9	19	4.6	<.01	13
94DW W67	S. Fork Clear Creek above Georgetown	8.00	8.5	95	5.0	Gage	7.0	1.7	1.4	13	4.0	<.01	53
94DW W68	Leavenworth Creek at S. Clear Creek	7.35	1.6	90	5.5	Gage	8.0	1.8	0.7	13	3.7	0.03	28
94DW W69	Geneva Creek above Grant	6.75	5.8	90	19	Gage	10	2.4	1.0	10	3.0	<.01	6.2

Table 4.Selected field-measured parameters and chemical composition of surface water samples in the Denver Westquadrangle, Colorado.—Continued

SO 4 (mg/L)	Al (µg/L)	Cr (µg/L)	Mn (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As µg/L)	Мо (µg/L)	Cd (µg/L)	Ba (µg/L)	Pb (µg/L)	La (µg/L)	U (µg/L)	Ra (pCi/L)	234U/238U Activity ratio
9.0	6.0	< 0.2	10	0.07	0.4	< 1	19	< 0.1	< 1	0.20	37	0.1	<.1	1.3	0.14	
14	4.0	1.0	19	0.07	0.6	< 1	250	0.1	< 1	0.30	38	0.5	<.1	1.3	0.16	1.06
10	9.0	< 0.2	20	0.06	0.9	< 1	180	0.1	< 1	0.20	36	0.6	<.1	1.2	0.18	
19	8.0	< 0.2	11	0.05	0.8	< 1	77	0.2	< 1	0.20	35	1.5	<.1	1.2	0.10	
43	54	< 0.2	60	0.30	0.9	2.0	36	0.2	10	0.10	25	0.6	0.2	2.5	0.14	1.10
<5	10	< 0.2	12	0.07	0.3	< 1	8.0	< 0.1	< 1	0.07	13	0.1	<.1	0.1		
40	49	< 0.2	58	0.20	1.0	2.0	53	0.2	9.0	0.20	25	0.4	0.2	2.2	0.12	
2,000	63,000	100	74,000	310	710	8,300	77,000	< 10	<100	420	20	60	390	240	0.25	0.971
56	70	< 0.2	540	1.0	2.9	11	240	0.2	7.0	1.00	24	0.3	0.6	2.2	0.14	1.09
56	87	< 0.2	460	0.80	2.4	12	150	0.2	7.0	0.70	24	0.3	0.5	2.2	0.14	
230	18	< 0.2	3,300	14	32	16	1,500	0.1	< 1	7.3	29	0.3	0.3	< 0.05	0.23	1.09
11	9.0	0.8	81	0.80	0.4	1.0	2.0	< 0.1	< 1	< 0.02	24	< 0.1	<.1	< 0.05	0.12	
33	7.0	< 0.2	3.2	0.03	0.6	1.0	2.0	< 0.1	< 1	< 0.02	35	< 0.1	<.1	0.1		
171	3.0	1.0	690	0.50	2.4	1.0	240	0.2	< 1	0.50	73	< 0.1	<.1	0.1	0.20	
37	24	< 0.2	200	0.20	2.1	3.0	690	0.2	1.0	2.2	32	0.8	0.5	0.4	0.12	1.18
275	12	< 0.2	4,300	20	36	23	1,300	0.2	< 1	6.9	20	0.1	0.3	0.1	0.19	1.05
64	78	1.2	570	1.3	4.2	10	220	0.3	6.0	0.90	27	0.4	0.4	1.9	0.14	1.10
42	6.0	5.5	6.7	0.08	1.4	< 1	2.0	0.3	1.0	0.03	83	< 0.1	<.1	5.2	0.10	
116	6.0	< 0.2	1.0	0.10	2.2	2.0	3.0	0.4	1.0	0.02	95	< 0.1	<.1	2.4	0.14	
320	50	0.3	290	0.80	20	8.0	730	0.4	< 1	3.0	20	0.1	1.3	0.5	0.28, 0.19	1.20
21	6.0	3.5	4.8	0.07	0.8	< 1	2.0	< 0.1	< 1	0.04	53	< 0.1	<.1	3.7		
66	79	< 0.2	740	1.6	4.8	13	320	0.2	7.0	1.3	31	0.4	0.6	2.4	0.13	1.10
6.0	10	< 0.2	7.5	0.03	0.4	< 1	2.0	< 0.1	< 1	< 0.02	17	< 0.1	<.1	0.8		
45	21	< 0.2	250	0.90	3.4	5.0	380	< 0.1	< 1	1.4	21	0.3	0.2	0.2		
102	4,700	< 0.2	1,000	11	21	16	520	< 0.1	< 1	2.3	27	3.2	1.8	0.7	0.33	1.15
13	11	0.2	45	0.50	1.2	1	34	0.1	1.0	0.30	15	0.6	<.1	0.6	0.13	
9.0	6.0	0.9	1.0	0.03	0.4	< 1	1.0	< 0.1	1.0	< 0.02	16	< 0.1	<.1	1.3		
68	570	< 0.2	710	2.2	5.7	63	930	< 0.1	< 1	4.1	24	4.4	2.9	0.6	0.30	
66	20	< 0.2	340	1.8	5.7	1.0	390	< 0.1	< 1	1.0	26	0.1	<.1	0.2	0.18	
8.0	6.0	< 0.2	3.4	< 0.02	0.4	< 1	2.0	< 0.1	< 1	0.04	28	< 0.1	<.1	0.8		1.08
27	25	< 0.2	21	0.07	1.5	2.0	240	< 0.1	< 1	0.70	36	1.0	<.1	0.8		
35	11	< 0.2	210	1.8	4.5	2.0	70	< 0.1	< 1	0.40	32	< 0.1	<.1	0.1		

14 Uranium in Surface Waters and Sediments Affected by Historical Mining in the Denver West 1:100,000 Quadrangle, Colorado

 Table 4.
 Selected field-measured parameters and chemical composition of surface water samples in the Denver West
 guadrangle, Colorado.—Continued

[n.d., not determined; Temp., temperature; Sp. Cond., specific conductance; °C, degree Celsius; μ S/cm, microsiemens per centimeter; ft³/s, cubic feet per second; pCi/L, picocuries per liter; mg/L, miligram per liter; μ g/L, microgram per liter; < less than; --, no data]

Sample ID	Sampling site	рН	Temp. (°C)	Sp. Cond. (µS/cm)	ft ³ /s (±10 %)	ft ³ /s method	SiO <u>2</u> (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	HCO ₃ (mg/L)
94DW W70	Geneva Creek above Duck Creek	4.65	6.6	190	7.6	Float	12	1.9	1.3	12	5.2	0.55	0
94DW W71	Duck Creek	7.40	7.7	50	1.6	Float	10	2.2	1.1	8.0	1.8	0.28	28
94DW W72	S. Fork Clear Creek above reservoir	7.35	7.6	80	6.0	Gage	5.0	1.5	1.0	10	3.5	0.17	39
94DW W73	W. Chicago Creek	7.50	4.2	55	2.8	Pygmy	12	2.5	0.9	9.0	2.1	0.20	34
94DW W74	S. Chicago Creek	7.40	4.2	45	3.7	Pygmy	10	2.1	1.0	7.0	1.5	0.05	23
94DWW75	Chicago Creek gage near Devil's Canyon	7.10	6.5	55	6.6	Gage	10	2.6	1.0	8.0	1.9	0.12	30
94DW W76	Chicago Creek at Clear Creek	7.45	7.1	65	5.3	Pygmy	11	3.0	1.1	10	2.3	0.06	31
94DW W77	Soda Creek at Idaho Springs	6.85	7.3	80	0.6	Pygmy	15	4.5	1.8	11	3.8	0.16	36
94DW W78	Beaver Brook at I-70	7.70	8.7	250	0.1	Float	16	11	2.6	35	7.3	0.19	107
94DW W79	Soda Creek above El Rancho	7.60	12.3	380	0.1	Float	19	11	1.7	57	10	<.01	194
94DW W81	Bear Creek at Morrison	7.70	5.7	160	12	Gage	7.0	13	2.0	14	2.9	0.20	50
94DW W82	Corral Creek	7.10	4.9	80	1.8	Pygmy	12	3.3	1.2	10	2.5	0.22	38
94DW W83	Bear Creek at Singing River Ranch	7.05	3.3	40	7.2	Float	11	2.2	0.7	6.0	1.2	0.14	19
94DW W84	Bear Creek at Evergreen Lake golfcourse	6.80	5.5	60	3.8	Gage	11	3.4	0.8	7.0	1.6	0.23	26
94DW W85	Cub Creek	7.30	5.6	220	0.5	Pygmy	13	16	1.6	16	4.6	0.28	60
94DW W86	N. Turkey Creek west of Hwy 285	7.70	5.0	350	0.6	Float	11	25	1.8	27	7.5	0.26	77
94DW W87	S. Turkey Creek east of Hwy 285	7.10	9.2	580	< 0.1		17	44	3.1	52	13	0.26	138
94DW W88	Turkey Creek near mouth of canyon	7.65	6.3	490	1	Float	9.0	30	2.3	31	8.8	0.23	89
94DW W89	Deer Creek at Hogback	7.70	10.3	1,100	< 0.1		21	57	4.6	86	21	<.01	283

Aqueous Geochemistry of Uranium

A plot of dissolved uranium concentration relative to pH in the sampled stream waters displays a U-shaped pattern with an apparent minimum around pH 6.5 to 7.5 (fig. 5). This pattern, defined by stream waters of generally low (<10 μ g/L) uranium concentration, is further emphasized by including previously reported data for acid mine drainage from the Denver West quadrangle (Wanty and others, 1999; Plumlee and others, 1999) and alkaline mine drainage from the Schwartz-walder uranium mine (Lammering, 1973). In oxygen-bearing surface waters of this study, uranium is oxidized to soluble U(VI) and occurs as a variety of soluble species, depending upon pH. Under acidic-oxidizing conditions, U(VI) occurs primarily as the uranyl cation (UO₂⁺²), whereas under alka-line-oxidizing conditions, U(VI) forms highly stable anionic complexes with dissolved carbonate that enhance its solubility

(Langmuir, 1978). The uranyl ion also forms a complex with dissolved phosphate at circumneutral pH (Langmuir, 1978), but very low concentrations of dissolved phosphate in most natural waters probably limit the contribution of this complex.

Speciation of dissolved U(VI) in each of the stream waters was calculated using the computer code PHREEQC (Parkhurst, 1995), utilizing the WATEQ4F thermodynamic database (Ball and Nordstrom, 1991). For these calculations, an oxidation potential (Eh) of +0.8 volt was used to simulate the oxygenated aqueous environment in flowing mountain streams. The more acidic samples contain dissolved sulfate as the major anion; thus, the calculated U(VI) species include uranyl ion (UO_2^{+2}) as well as variable amounts of uranyl sulfate complexes (fig. 6). At near-neutral to alkaline pH, which includes most of the stream samples, carbonate is the major anion, and U(VI) occurs predominantly as a variety of uranyl carbonate complexes. Increasing alkalinity favors the more

Table 4. Selected field-measured parameters and chemical composition of surface water samples in the Denver West guadrangle, Colorado.—Continued

[n.d., not determined; Temp., temperature; Sp. Cond., specific conductance; $^{\circ}$ C, degree Celsius; μ S/cm, microsiemens per centimeter; ft³/s, cubic feet per second; pCi/L, picocuries per liter; mg/L, miligram per liter; μ g/L, microgram per liter; < less than; --, no data]

SO4 (mg/L)	Al (µg/L)	Cr (µg/L)	Mn (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As µg/L)	Mo (µg/L)	Cd (µg/L)	Ba (µg/L)	Pb (µg/L)	La (µg/L)	U (µg/L)	Ra (pCi/L)	234U/238U Activity ratio
98	4,300	< 0.2	740	7.1	15	25	250	< 0.1	< 1	1.4	43	0.4	1.8	2.1	0.35	
<5	13	0.9	10	0.04	0.3	< 1	< 1	< 0.1	< 1	< 0.02	32	< 0.1	0.2	0.1		
6.0	8.0	0.9	12	0.05	0.3	< 1	1.0	< 0.1	< 1	0.10	31	< 0.1	0.1	0.6		
<5	9.0	< 0.2	4.9	0.02	0.2	< 1	< 1	< 0.1	< 1	< 0.02	19	< 0.1	0.1	0.1		
5.0	8.0	1.5	3.6	0.08	1.6	< 1	< 1	< 0.1	< 1	< 0.02	18	< 0.1	0.2	0.1		
<5	10	< 0.2	5.8	0.02	0.2	< 1	2.0	< 0.1	< 1	< 0.02	21	< 0.1	0.1	0.2		
9.0	8.0	0.7	26	0.07	0.3	< 1	30	< 0.1	< 1	0.04	21	< 0.1	<.1	0.1		
16	18	< 0.2	42	0.10	0.9	2.0	16	0.1	1.0	0.06	27	< 0.1	<.1	0.2		
9.0	9.0	2.2	16	0.06	0.9	< 1	2.0	0.2	< 1	< 0.02	48	0.1	<.1	1.1		
9.0	6.0	< 0.2	39	0.10	1.4	< 1	< 1	0.2	1.0	< 0.02	36	< 0.1	<.1	3.8	0.11	
11	17	< 0.2	4.6	0.08	0.5	1.0	2.0	0.2	< 1	< 0.02	25	0.2	0.1	0.5	0.14	
9.0	9.0	< 0.2	7.8	0.10	0.3	< 1	< 1	< 0.1	< 1	0.04	27	< 0.1	<.1	0.2	0.14	
<5	11	0.5	2.6	0.03	< 0.2	< 1	< 1	< 0.1	< 1	< 0.02	10	< 0.1	0.2	< 0.05		
7.0	14	< 0.2	9.0	0.03	0.4	< 1	1.0	< 0.1	< 1	< 0.02	14	< 0.1	0.1	0.2	0.12	
10	39	< 0.2	39	0.10	0.9	< 1	< 1	0.2	< 1	< 0.02	30	< 0.1	0.2	0.4	0.14	
8.0	22	2.1	12	0.08	0.9	< 1	< 1	0.3	2.0	< 0.02	40	< 0.1	0.1	1.7	0.14	
26	8.0	4.0	240	0.40	1.4	< 1	2.0	0.4	< 1	0.05	150	< 0.1	<.1	1.0	0.18	
11	20	< 0.2	16	0.09	1.5	< 1	1.0	0.4	1.0	< 0.02	59	< 0.1	0.1	2.0	0.24	
105	8.0	< 0.2	9.2	0.20	2.8	< 1	< 1	0.4	1.0	< 0.02	94	< 0.1	<.1	35.0	0.21	

highly charged uranyl dicarbonate $[UO_2(CO_3)_2^{-2}]$ complex, and at highest pH, the tricarbonate $[UO_2(CO_3)^{-4}]$ complex (fig. 6).

The PHREEQC computer code also permits calculation of the degree of saturation of stream waters with respect to a variety of minerals, including uranium minerals. Results for each mineral are expressed as a saturation index defined as the logarithm of the ratio of the ion activity product (IAP) divided by the equilibrium solubility product (K_{sp}). These thermodynamic-based calculations assume mineral/solution equilibria and, because reaction kinetics are not considered, are best interpreted as potentials for mineral dissolution (undersaturated condition) or mineral precipitation (oversaturated condition). Accuracy depends on the quality of the chemical analyses and the accuracy and internal consistency of the thermodynamic database. A value of zero for the saturation index indicates equilibrium saturation, positive values indicate oversaturation, and negative values undersaturation. Results for the stream waters (fig. 7) indicate consistent oversaturation with respect to iron oxides and quartz and undersaturation with gypsum, calcite, and dolomite (the latter not shown). Barite exhibits both saturation and undersaturation. All waters are highly undersaturated with the reduced U(IV) minerals uraninite (UO₂) and coffinite $[U(SiO_4)_{1-x}(OH)_{4x}]$ (not shown) and also with all U(VI) minerals in the database. U(VI) minerals that show closest approach to saturation are still many orders of magnitude undersaturated (fig. 7), and these include schoepite $[(UO_2)_4O(OH)_6.6H_2O]$, uranophane $[Ca(UO_2)_2(SiO_3)_2(OH)_25H_2O]$, and rutherfordine $[(UO_2)CO_3]$. At the low concentration of dissolved uranium in the stream waters (and most natural waters), uranium solubility is most likely limited by sorptive processes rather than uranium mineral saturation (Langmuir, 1978).



Figure 5. Plot showing dissolved uranium concentration relative to pH for surface waters and mine drainages of the Denver West quadrangle. The U.S. Environmental Protection Agency drinking-water standard of 30 micrograms per liter (μg/L) is indicated for reference.

Dissolved or Particulate Uranium

Most of the sampled waters show no analytically significant difference in uranium concentration between the rawacidified (RA) and filtered-acidified (FA) fractions (Asher-Bolinder, 1995). This indicates that amounts of suspended, particle-associated uranium are small and that uranium is either dissolved or is associated with colloidal-sized particles that pass a 0.45-micrometer filter membrane. Low amounts of suspended matter are consistent with observations during sampling that indicated clear or only faintly turbid waters (Asher-Bolinder, 1995). Two notable exceptions were relatively turbid waters from the North Fork of Clear Creek downstream from the Central City area (sites 53, 48; fig. 1), probably the result of upstream disturbances associated with construction and commercial development of Central City and Blackhawk, Colorado, that began in 1992. Bed sediments in the heavily mined North Fork watershed contain easily suspended silt, fine sand, and chemical precipitates such as iron and aluminum oxyhydroxides that derive from hydrothermally altered rock, historical mine dumps, and waste-rock piles. Based on comparisons of uranium concentrations in RA and FA fractions, greater than 80 percent of uranium in samples 53 and 48 was

associated with particles (Asher-Bolinder, 1995). Turbid waters of the North Fork of Clear Creek, therefore, provide an ongoing source of particle-associated uranium, and likely other metals (Davis and others, 1991), to the main stem of Clear Creek.

The effect of suspended particles on the budget of transported uranium and other metals in the main stem of Clear Creek is illustrated by plotting RA and FA concentrations for selected elements as a function of downstream location (fig. 8). Increased divergence of the two plotted RA- and FA-trend lines indicates locations where a given element displays increased particle association. Divergence remains high or increases downstream from the confluence with the North Fork, but particle associations appear to first become prominent farther upstream in the Idaho Springs area. Based on the relative extent of divergence of RA and FA concentrations, apparent particle affinity is greatest for iron and aluminum and decreases in the order Pb>Cu>Zn>U>Mn>Ni. Uranium falls near the bottom of this sequence, which otherwise corresponds to the order of selectivity for sorption of divalent metal cations on a variety of metal oxides (Smith, 1999). Similar plots generated for Clear Creek samples taken in October 1986 were reported by Ficklin and Smith (1994), who concluded that

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Figure 6. Plots showing relative abundance of various dissolved U(VI) species in stream waters sampled in this study. %, percent.



Figure 7. Plot showing degree of saturation of stream waters with respect to a variety of minerals, including uranium minerals. Most waters are undersaturated with respect to most minerals, as indicated by plotted positions below the equilibrium saturation reference line. IAP, ion activity product; K_{sp}, equilibrium saturation product.

iron-rich acid mine drainage from the Argo Tunnel in Idaho Springs provided a local source of dissolved metals to Clear Creek. The Argo Tunnel was constructed in the late 1890s to transport ores and mine drainage from deep mines below Central City to a mill at Idaho Springs (Stewart, 1994). Argo Tunnel drainage was still flowing in 1994, but a facility to intercept and treat this drainage was completed in 1998 (Colorado Department of Public Health and Environment, 2005).

Dissolved uranium and other metals in acid drainage entering Clear Creek are likely sorbed by iron-rich precipitates, such as iron-oxyhydroxides that form when the ironrich acid drainage is neutralized, oxidized, and diluted by Clear Creek water (Smith, 1999). Uptake of uranium by iron oxyhydroxide is well documented both in field and in laboratory studies and should be particularly efficient in waters of circumneutral pH and low dissolved carbonate concentration (Hsi and Langmuir, 1985; Van der Weijden and others, 1985; Ho and Miller, 1986). Uranium is sorbed on surfaces of iron oxyhydroxide as a stable inner-sphere complex that changes in character in response to changes in pH or to the carbonate concentration of coexisting solution (Waite and others, 1994; Ulrich and others, 2006). Depending on the stability of these surface complexes, uranium may not be as readily desorbed as previously assumed. Fine-grained precipitates of iron oxyhydroxide are easily suspended and contribute to the downstream transport of uranium and other metals in Clear Creek.

Figure 8 also indicates that in 1994 the concentration of dissolved zinc spiked at a location near the town of Silver Plume, upstream from Georgetown. This zinc-specific spike was also identified in 1986 by Ficklin and Smith (1994) and may indicate input of iron-poor, but zinc-rich, acid drainage from the Burleigh Tunnel (Plumlee and others, 1999; Colorado Department of Public Health and Environment, 2005).

Spatial Distribution of Dissolved Uranium

Locations of streams with highest dissolved uranium concentrations can be represented on a geochemical "dot map" of the Denver West quadrangle in which sampling sites are identified by dots that are sized to indicate particular ranges of uranium concentrations (fig. 9*A*). The highest dissolved uranium concentration (240 μ g/L) was in the single reference sample of acid mine drainage collected near Idaho Springs (site 45; fig. 1, table 4). For the samples of stream water, some of the higher dissolved uranium concentrations were in samples 23 (65 μ g/L) and 24 (34 μ g/L) located downstream from the Schwartzwalder uranium mine, and samples 18 (9.8 μ g/L) and 19 (5.2 μ g/L) along the West Fork of Clear Creek, downstream from the Urad–Henderson molybdenum mine (fig. 1, fig. 9*A*)

Bedrock in the historically mined areas of Central City and Idaho Springs, near the center of the Denver West quadrangle (fig. 1), can be highly altered and includes some uraniumrich varieties such as Tertiary quartz bostonite porphyry (Sims, 1963). Unremarkable concentrations of dissolved uranium in these areas (fig. 9A, table 4) indicate relatively insoluble hosts of uranium in the bedrock and (or) an insignificant contribution of uranium-rich acid mine drainage to the inventory of dissolved uranium in local streams. If acid drainage enters a stream, dissolved uranium is diminished by dilution or by sorption onto precipitates of iron and aluminum oxyhydroxide that form when pH is neutralized (Wanty and others, 1999).

For comparison, a similar dot map of uranium concentration in streams can be constructed using data from the National Uranium Resource Evaluation (NURE) program (Smith, 1997; fig. 9B). Waters and sediments in the Denver West quadrangle, including portions of the quadrangle that lie east of the mountain front, were sampled for this program during August-October 1976 (Bolivar and others, 1978). Dissolved uranium concentrations in the easternmost portions tend to be higher on average than the rest of the quadrangle, as indicated in figure 9B. In fact, the NURE program indicated that surface waters in the high plains of eastern Colorado contain higher average dissolved uranium than surface waters in most other quadrangles that were sampled in the Western United States (Shannon, 1979). The proposed mechanism for generating soluble uranium in this area of the High Plains is natural weathering or irrigation-enhanced leaching of uranium-bearing Upper Cretaceous marine shales (Boberg and Runnells, 1971; Zielinski and others, 1995).

For mountainous areas of the Denver West quadrangle, the NURE data provide more extensive coverage that confirms and expands upon the observations of the present study. For example, the NURE data confirm relatively high dissolved uranium (5–10 μ g/L) in the West Fork of Clear Creek. Ongoing surface remediation at the Urad mine in 1976 could have contributed dissolved uranium and other metals at that time. Streams near Central City and Idaho Springs are again shown to contain unremarkable concentrations of dissolved uranium. Unfortunately, NURE sampling did not include samples of Ralston Creek downstream from the Schwartzwalder uranium mine.



Figure 8. Plots showing abundance of various dissolved elements as a function of sampling-site location along the main stem of Clear Creek. The two curves in each plot illustrate concentration differences between raw-acidified and filtered-acidified samples. μg/L, micrograms per liter.



Figure 8. Plots showing abundance of various dissolved elements as a function of sampling-site location along the main stem of Clear Creek. The two curves in each plot illustrate concentration differences between raw-acidified and filtered-acidified samples. µg/L, micrograms per liter.—Continued

The coverage of the NURE data better emphasizes lithologic control of dissolved uranium. The dot map portrays a tendency for dissolved uranium to be relatively high in west-central portions of the quadrangle underlain by the 1,400-Ma Silver Plume batholith (fig. 2). Hills and others (1982) identified the Silver Plume batholith and its surrounding contact zone as an area favorable for uranium mineralization. Favorability was based on observations of the degree of fracturing and weathering, the relatively high radioelement content, and the relatively high Th/U ratio, the latter indicating possible preferential leaching of uranium.

The NURE data indicate that in 1976 dissolved uranium was relatively high $(1-5 \ \mu g/L)$ in streams draining mineralized but largely unmined areas in the southwestern portion of the quadrangle. Much lower dissolved uranium concentrations

(less than 1 μ g/L) observed in the same area in 1994 could be influenced by attempts to remediate acid drainage in the area (Limerick and others, 2005) but more likely are influenced by dilution from rainfall. Rainfall adds variability to the measured stream concentrations, which can complicate comparisons within or between data sets. Mountainous areas in particular are subject to localized and sometimes intense rain showers.

Figure 9. Geochemical "dot maps" indicating distribution of dissolved uranium in stream waters of the Denver West quadrangle. Dot size increases with increasing ranges of uranium concentration. Samples collected in 1994 during this study (*A*) are compared with a 1976 sampling under the NURE program (*B*). μg/L, micrograms per liter.





Uranium Isotopes

Measured ²³⁴U/²³⁸U activity ratios (AR) for 12 surface streams sampled in this study range from 1.05 to 1.20 (table 4). Values greater than 1.0 are common in surface waters and result from preferential leaching and decay-induced recoil of ²³⁴U during slow weathering of uranium-bearing rocks and minerals (Osmond and Cowart, 1976). In contrast, the sample of acid mine drainage containing 240 µg/L (sample 45, table 4) has an AR of 0.971. In this case, relatively aggressive leaching of the host rock by acid drainage generates dissolved uranium with an isotopic composition that more closely mimics that of the host rock. Data from Leavenworth and Russell Gulches near Central City indicate that acid mine drainage, with pH<4.0 and variable dissolved uranium concentration, has AR values between 0.95 and 1.0 (fig. 10). These limited results indicate that dissolved uranium derived from acid drainage is isotopically distinct from uranium derived during natural weathering processes. Quantification of mixing relations is hindered by the rapid sorption of acid-derived uranium by precipitates of iron and aluminum oxyhydroxides. However, these precipitates should retain the distinctive uranium isotopic composition of acid drainage and are potentially traceable if they can be physically concentrated or selectively extracted from sediments. Future research is needed to determine whether uranium isotopes can be used to quantify mixtures of natural uranium and acid drainage-derived uranium

in oxyhydroxide precipitates. Such investigations would be modeled after previous studies that successfully quantified sedimentary lead components using the lead isotopic composition of sediment extracts (Church and others, 1999, and references therein).

Comparison of Stream-Water Concentrations with Water-Quality Standards

Excluding the acid-drainage sample (45, table 4), only three of the remaining 81 stream waters (samples 23, 24, 89; table 4) exceeded the current U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) of 30 µg/L for uranium in drinking water (U.S. Environmental Protection Agency, 2001; fig. 11). Only one of these three waters (sample 23; 65 µg/L) slightly exceeded the Colorado standard for drinking water of 60 µg/L in effect in 1994 (Colorado Department of Public Health and Environment, 2006). Only five stream waters clearly contain more than 5 µg/L uranium, which is proposed to be a highly conservative no-effect concentration for protection of freshwater invertebrates (Sheppard and others, 2005). Dissolved uranium is much less toxic to freshwater fish, which show no effects at concentrations as high as several hundred micrograms per liter of uranium in waters of low hardness (Sheppard and others, 2005). The USEPA has not established aquatic-life toxicity standards for uranium, but a current hardness-dependent standard applied in



Figure 10. Plot of ²³⁴U/²³⁸U activity ratio (AR) compared to dissolved uranium concentration for selected stream waters of this study (solid dots). AR values of streams are high (greater than 1.0) compared to AR values of acid mine drainage in Leavenworth Gulch and Russell Gulch near Central City, Colorado (open symbols). Representative error bars for AR values are shown for reference.



Figure 11. Box and whisker plots showing concentration distributions of selected elements in stream waters of this study. Unlabeled double-arrows indicate U.S. Environmental Protection Agency aquatic-life toxicity standards that are appropriate for conditions of average carbonate hardness in these waters (about 50 milligrams per liter) and an assumed chronic exposure level. Labeled double-arrows are included for reference and are USEPA drinking-water standards that fall within the plotted concentration ranges. Values shown as circles are outliers from the normal population distribution for each element. MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; µg/L, micrograms per liter.

Colorado is permissive of 700 μ g/L uranium at 50 mg/L hardness and assumed chronic exposure (Colorado Department of Public Health and Environment, 2006).

The USEPA has published recommended aquatic-life toxicity standards for other dissolved metals that, in some cases (for example, copper and zinc), are considerably lower than their respective drinking-water standards (U.S. Environmental Protection Agency, 2006a). In addition, the toxicity of some dissolved metals is dependent upon water hardness (as CaCO₃). Increasing hardness allows aquatic organisms to tolerate higher concentrations of dissolved metals because free metal ions (including UO_2^{+2}) bind with carbonate or compete with Ca⁺² for uptake and thus become less available to the organisms (Kelly, 1999). Water-quality standards for aquatic life (U.S. Environmental Protection Agency, 2006a) or drinking-water standards (U.S. Environmental Protection Agency, 2006b) that fall within the range of most of the measured dissolved concentrations are indicated in figure 11. In cases where water hardness is a mitigating factor, the average carbonate hardness of 47 mg/L for waters in the Denver West quadrangle was used to calculate aquatic-life toxicity standards under a chronic exposure scenario. Dissolved copper, cadmium, and zinc commonly exceed aquatic-life standards, and dissolved manganese commonly exceeds a secondary maximum contaminant level (SMCL) for drinking water (fig. 11). Contamination of the main stem, West Fork, and North Fork of Clear Creek with dissolved metals was well documented prior to this study, with dissolved copper and zinc posing the most consistent threat to aquatic life in these streams (Colorado Water Quality Control Division, 1989). In some stream segments within highly mineralized watersheds, high natural background values of dissolved metals may preclude attaining the generally applied water-quality standards (Colorado Department of Public Health and Environment, 2006).

Stream Sediments

General Summary

Uranium concentration in whole sediment (<2 mm) determined by gamma-ray spectrometry, ranges from 1.6 to 25.6 μ g/g (table 5) and averages 4.7 μ g/g. This average falls between an estimated value for average granite of 4.8 μ g/g and an estimated crustal average of 2.7 μ g/g (Taylor, 1964; table 1). This finding is consistent with the mixed provenance of the sediments that includes relatively uranium-rich granitic rocks and a variety of metamorphic rocks, the latter derived from sedimentary and volcanic precursors that in composite likely approximate average crustal composition. Uranium and thorium correlate strongly (R=0.66, two highest uranium samples omitted), and their correlation is explained by their similar actinide element chemistry and similar behavior during magma generation and evolution. Thorium concentrations show a proportionately larger range of values, 5.0 to

131 µg/g (average=20.6 µg/g), probably influenced by contributions from 1,400-Ma granites of exceptionally high average thorium content and Th/U ratio (table 1). Potassium contents range from 1.2 to 4.2 weight percent (average = 2.9) and show generally good agreement with corresponding values determined by X-ray fluorescence on finely ground and homogenized subsamples (table 5).

The fine-grained size fractions (<0.09 mm) of stream sediments generally have higher concentrations of uranium and other elements and show greater chemical variability (table 6). Greater contrasts in concentration, particularly for trace elements in sediments, can facilitate identification of sediment provenance and sources of mineralization or contamination. One reason that trace elements such as uranium, thorium, and heavy metals (copper, lead, zinc) tend to be enriched in finer sized fractions is because they are concentrated in detrital minerals of small size, such as zircon (ZrSiO₄), monazite [(La, Ce, Th) PO₄], and metal sulfides, respectively.

Positive correlations between some trace elements in sediments are influenced by co-substitution in specific host minerals. For example, thorium in the sediments correlates most strongly with lanthanum (La, R=0.89) and cerium (Ce, R=0.90), which are highly enriched in detrital monazite. Zirconium (Zr) correlates strongly with yttrium (Y, R=0.82), which, along with heavy rare earth elements, is readily incorporated in zircon. Uranium is also enriched in zircon, but the relatively weak correlation with zirconium (R=0.44) indicates that zircon abundance alone is not as strong a determinant of uranium concentration in sediments. There is strong correlation between lead and zinc (R=0.74), as these heavy metals are concentrated in the distinct sulfide minerals, galena and sphalerite, that are present in mineralized zones near some sampling sites.

Histograms of trace-element concentrations in sediments tend to show the expected log-normal distribution for geochemical data. If a small subset of sediments is highly enriched in a particular element, then the histogram takes on more of a bimodal distribution. Bimodal distribution may not be highly obvious on a histogram plot but is also indicated as a discontinuity of slope on a plot of cumulative frequency relative to log concentration (fig. 12). The inflection point of slope is tentatively identified as the threshold concentration for identifying anomalously concentrated samples. Cumulative frequency plots for copper, lead, and zinc in the fine-grained sediments show marked inflection points at 60 μ g/g, 100 μ g/g, and 300 μ g/g, respectively. Fine-grained fractions of sediments containing concentrations above these thresholds may be more highly enriched in heavy metals derived from nearby ineralized areas or mines. In contrast, the cumulative frequency plot for uranium shows no obvious inflection point, which indicates that no significant subset of sediments containing anomalously high uranium was sampled. The few sediment samples of highest uranium content could be explained as outliers within a typical log-normal distribution of geochemical data.



Figure 12. Plots of log concentration relative to percent cumulative frequency for selected elements in fine-grained (less than 0.09 millimeter) stream sediments. Inflection of slope occurs at a concentration value (threshold value) that may indicate a lower bound to a distinct subset of more concentrated values within the distribution. μ g/g, micrograms per gram.

Sediment Composition Variations Within the Main Stem of Clear Creek

Downstream variations of sediment composition in the <0.09-mm fraction, within the main stem of Clear Creek, are a function of the relative contribution of rock fragments and mineral grains derived from contrasting lithologies (granitic, metamorphic) and from specific sources of sulfide mineralization. Upstream sediments, derived primarily from granitic rocks in the western half of the Denver West quadrangle, tend to be richer in alkali elements such as potassium and rubidium, and in incompatible trace elements such as uranium and thorium, that are enriched in granites through processes of magmatic differentiation (fig. 13). In contrast, downstream sediments, derived primarily from metamorphic rocks in the central portion of the quadrangle, tend to be richer in alkalineearth elements (calcium, strontium) and mafic elements (iron, titanium). Heavy metals, such as copper, lead, and zinc, should follow iron by this reasoning but are also subject to concentration spikes caused by local sources of sulfide minerals from

mineralized areas or former mines. In addition, chemical precipitates of iron and aluminum oxyhydroxides may provide an additional, relatively mobile host of some trace elements in the streambed sediments (Miller and others, 1999; Schemel and others, 2007).

Concentration spikes for zinc in fine-grained sediment (<0.09 mm) of the main stem of Clear Creek are particularly noticeable downstream from its confluence with the West Fork near Empire and also in the vicinity of Idaho Springs (fig. 13). Lead also shows a marked spike in concentration downstream from the confluence with the West Fork. Iron, titanium, and copper (not shown) show a marked spike in concentration downstream from Idaho Springs. The greatest thorium concentrations are observed in sediments within an upstream reach of Clear Creek that traverses the thorium-rich Silver Plume batholith (fig. 13), likely indicating input of thorium-rich rock fragments and detrital monazite. High concentrations of thorium in fine-grained sediments are in sediments at Idaho Springs, approximately 15 km downstream from the nearest outcrop of the Silver Plume batholith. Uranium concentrations

26 Uranium in Surface Waters and Sediments Affected by Historical Mining in the Denver West 1:100,000 Quadrangle, Colorado

Table 5. Radiometric and chemical data for whole sediment (less than 2 millimeter) from the Denver West 1:100,000 quadrangle, Colorado.

[eU, equivalent uranium concentration; eTh, equivalent thorium concentration; wt%, weight percent; $\mu g/g$, micrograms per gram; <, less than; DUP., duplicate; --, no data]

		Gam	ma-ray spe	ctrometry				X-ray fluores				
Sample ID	Sampling site	K (wt%)	eU (µg/g)	eTh (µg/g)	K (wt%)	Ca (wt%)	Ti (wt%)	Ba (µg/g)	Ce (µg/g)			
94DW S01	Gamble Gulch	3.2	2.5	15.2								
94DW S02	Moon Gulch	2.7	5.7	62.9								
94DW S03	S. Boulder Creek at Johnson mine	2.9	3.7	19.3								
94DW S04	Mammoth Gulch	2.8	3.7	23.2								
94DW S05	N. Boulder Creek at Sherwood Creek	3.3	2.5	15.5								
94DW S06	Beaver Creek	3.4	8.2	131								
94DW S07	Middle Boulder Creek above Barker Res.	3.1	3.0	25.0								
94DW S08	S. Beaver Creek at Lincoln Hills	2.7	2.2	10.8								
94DW S09	S. Boulder Creek at Pinecliff gage	2.9	3.1	16.2								
94DW S10	Beaver Creek at Gap and Twin Spruce	3.1	3.3	15.4								
94DS-10 (DUP.)		3.1	3.9	24.0								
94DW S12	Coal Creek Gaging Station	3.9	1.7	7.7								
94DW S13	Fall River near mouth	2.5	5.0	27.9								
94DW S14	Fall River above Cumberland	2.9	3.7	19.4								
94DW S15	W. Fork Clear Creek near Empire	3.5	9.5	35.4								
94DW S16	Bard Creek	3.2	7.4	39.4								
94DW S17	Mad Creek	3.7	5.5	22.1								
94DW S18	W. Fork Clear Creek near Hoop Creek	4.2	12.7	39.5								
94DW S19	W. Fork Clear Creek below Henderson	4.1	9.5	58.8								
94DW S20	Jim Creek	2.7	5.5	17.2								
94DW S21	Fraser River at trail campground	3.5	6.0	20.0								
94DW S22	Vasquez Creek	3.3	2.3	13.1								
94DW S23	Ralston Creek above reservoir	2.8	14.1	11.1								
94DW S24	Ralston Creek below Schwartzwalder	2.6	25.6	15.5								
94DW S25	Ralston Creek trib. above reservoir	2.2	7.2	11.1								
94DW S26	Ralston Creek at Ralston Roost	2.6	7.0	32.4								
94DW S26 (DUP.)		2.6	5.1	23.6								
94DW S27	Deer Creek	3.6	4.5	16.4								
94DW S28	Ralston Creek at lower Golden Gate Park	3.2	4.6	22.7								
94DW S29	Ranch Creek	3.5	3.2	15.5								
94DW S30	St Louis Creek	2.8	3.4	13.9								
94DW S31	Elk Creek	2.6	2.8	17.9								
94DW S33	Tucker Gulch at Golden Gate Canyon	1.2	2.2	5.0								
94DW S34	Crawford Gulch	2.8	6.4	25.0								
94DW \$35	Clear Creek below Loveland Ski area	3.2	3.7	23.1	3.50	0.67	0.26	609	105			
94DW S36	Quayle Creek	3.6	4.3	47.3								
94DW S37	Clear Creek at Baker	3.4	3.1	23.8	3.59	0.59	0.25	641	97			
94DW S38	Clear Creek at Silver Plume	3.2	3.7	24.7	3.54	0.39	0.17	527	98			
94DW S39	Clear Creek at Georgetown Loop	3.1	3.9	30.0	2.95	0.47	0.21	598	103			
94DW S40	Clear Creek above Georgetown Lake	3.2	4.0	29.6	3.26	0.71	0.35	682	99			
94DW S41	Clear Creek at Empire	3.1	4.4	30.2	3.26	0.72	0.37	810	116			
94DW S42	Clear Creek at Lawson	3.4	5.3	23.8	3.51	0.66	0.20	663	85			

Table 5. Radiometric and chemical data for whole sediment (less than 2 millimeter) from the Denver West 1:100,000 quadrangle, Colorado.—Continued

[eU, equivalent uranium concentration; eTh, equivalent thorium concentration; wt%, weight percent; µg/g, micrograms per gram; <, lo	ess than; DUP.,
duplicate;, no data]	

X-ray fluorescence												
Cu (µg/g)	La (µg/g)	Nb (µg/g)	Pb (µg/g)	Rb (µg/g)	Sr (µg/g)	W (µg/g)	Ү (µg/g)	Zn (μg/g)	Zr (µg/g)			
<14	45	9	39	152	133	<20	13	68	123			
<14	41	5	32	151	143	<20	13	114	142			
<14	36	7	12	146	109	<20	19	69	106			
38	40	8	101	140	126	<20	14	467	123			
28	50	10	100	158	174	<20	16	689	171			
65	47	9	193	137	191	<20	20	1,790	160			
22	35	6	54	148	145	<20	9	437	121			

Table 5. Radiometric and chemical data for whole sediment (less than 2 millimeter) from the Denver West 1:100,000 quadrangle, Colorado.—Continued

 $[eU, equivalent uranium concentration; eTh, equivalent thorium concentration; wt\%, weight percent; \mu g/g, micrograms per gram; <, less than; DUP,, duplicate; --, no data]$

		Gam	ma-ray spec	ctrometry				X-ray fluo	rescence
Sample ID	Sampling site	K (wt%)	eU (µg/g)	eTh (µg/g)	K (wt%)	Ca (wt%)	Ti (wt%)	Ba (µg/g)	Ce (µg/g)
94DW S43	Mill Creek	2.8	3.5	15.3					
94DW S43(DUP.)		2.8	3.4	16.0					
94DW S44	Clear Creek above Idaho Springs	3.3	7.7	34.4	3.11	0.77	0.30	761	119
94DW S45	Virginia Canyon	2.5	5.0	13.3					
94DW S46	Clear Creek below Idaho Springs	2.6	4.9	16.1	2.70	0.96	0.37	669	80
94DW S47	Clear Creek near junct I-70 and US 6	2.5	4.1	16.8	2.61	0.93	0.33	547	87
94DW S48	N. Fork Clear Creek at mouth	2.7	4.3	12.9					
94DW S49	N. Fork Clear Creek above Missouri Creek	2.9	4.6	23.8					
94DW S50	Missouri Canyon	2.4	2.8	10.4					
94DW S50(DUP.)		2.4	2.4	8.6					
94DW S51	Eureka Gulch above Central City	2.2	4.2	12.3					
94DW S52	Chase Gulch above Blackhawk	2.2	5.0	23.4					
94DW S53	N. Fork Clear Creek below Blackhawk	2.4	3.8	12.5					
94DW S54	Clear Creek at Golden gage	2.4	4.4	20.2	2.96	0.93	0.36	588	54
94DW S55	Guy Gulch	1.9	3.0	11.2					
94DW S56	Elk Creek	1.4	2.0	6.8					
94DW S57	Russell Gulch at mouth	2.2	3.6	10.6					
94DW S57(DUP.)		2.2	4.3	14.4					
94DW S58	Smith Hill Gulch	1.8	3.6	10.1					
94DW S59	Clear Creek below N. fork of Clear Creek	2.9	5.5	16.8	3.97	0.81	0.64	767	64
94DW S60	Keystone Gulch	2.2	3.0	11.7					
94DW S61	Snake River near Keystone Ski area	3.3	4.6	17.4					
94DW S62	Snake River above Montezuma	2.5	4.7	17.4					
94DW S63	Deer Creek above Montezuma	2.0	5.6	14.1					
94DW S64	N. Fork Snake River	3.3	5.0	23.5					
94DW S65	Peru Creek	3.1	5.1	18.8					
94DW S66	Snake River above Peru Creek	2.5	4.7	12.7					
94DW S67	S. Fork Clear Creek above Georgetown	2.3	2.5	14.2					
94DW S68	Leavenworth Creek at S. Clear Creek	2.8	4.2	17.2					
94DW S69	Geneva Creek above Grant	3.2	4.3	12.1					
94DW S70	Geneva Creek above Duck Creek	2.8	4.7	15.0					
94DW S71	Duck Creek	3.3	9.1	59.7					
94DW S72	S. Fork Clear Creek above reservoir	2.6	8.7	22.7					
94DW S73	W. Chicago Creek	2.8	3.0	10.0					
94DW S74	S. Chicago Creek	2.6	1.6	5.3					
94DW S75	Chicago Creek gage near Devil's Canyon	2.9	4.2	15.2					
94DW S75(DUP.)		3.0	3.4	9.6					
94DW S76	Chicago Creek at Clear Creek	2.7	3.3	11.1					
94DW S77	Soda Creek at Idaho Springs	2.6	4.6	15.0					
94DW S78	Beaver Brook at I-70	2.3	2.3	9.2					
94DW S79	Soda Creek above El Rancho	1.6	5.7	34.1					
94DW S80	Kerr Gulch	2.1	3.8	17.5					

Table 5. Radiometric and chemical data for whole sediment (less than 2 millimeter) from the Denver West 1:100,000 quadrangle, Colorado.—Continued

[eU, equivalent uranium concentration; eTh, equivalent thorium cor	ncentration; wt%,	weight percent; µg/g,	micrograms per gram;	<, less than; DUP.,
duplicate;, no data]				

X-ray fluorescence											
Cu (µg/g)	La (µg/g)	Nb (µg/g)	Pb (µg/g)	Rb (µg/g)	Sr (µg/g)	W (µg/g)	Ү (µg/g)	Zn (µg/g)	Zr (µg/g)		
52	47	8	79	161	190	<20	31	1,240	180		
80	35	7	153	118	176	<20	24	408	152		
64	40	5	70	88	159	<20	15	453	128		
82	13	8	79	93	170	<20	19	642	101		
175	24	9	122	101	141	<20	16	764	98		
								-			
			-		-						

 Table 5.
 Radiometric and chemical data for whole sediment (less than 2 millimeter) from the Denver West 1:100,000 quadrangle,

 Colorado.—Continued
 Colorado.—Continued

[eU, equivalent uranium concentration; eTh, equivalent thorium concentration; wt%, weight percent; $\mu g/g$, micrograms per gram; <, less than; DUP,, duplicate; --, no data]

		Gamma-ray spectrometry					X-ray fluorescence		
Sample ID	Sampling site	K (wt%)	eU (μg/g)	eTh (µg/g)	K (wt%)	Ca (wt%)	Ti (wt%)	Ba (µg/g)	Ce (µg/g)
94DW S81	Bear Creek at Morrison	3.0	2.8	15.4					
94DW S81(DUP.)		3.0	2.9	13.6					
94DW S82	Corral Creek	2.9	9.7	25.0					
94DW S83	Bear Creek at Singing River Ranch	3.4	2.6	10.6					
94DW S84	Bear Creek at Evergreen Lake golfcourse	3.0	3.8	14.1					
94DW S84(DUP.)		3.2	4.5	15.3					
94DW S85	Cub Creek	3.7	2.9	17.3					
94DW S86	N. Turkey Creek west of Hwy 285	3.7	3.1	18.3					
94DW S87	S. Turkey Creek east of Hwy 285	3.5	2.8	11.5					
94DW S88	Turkey Creek near mouth of canyon	2.9	3.5	16.7					
94DW S89	Deer Creek at Hogback	3.1	2.7	9.8					

in fine-grained sediments of the main stem tend to increase in the downstream direction, at least to Idaho Springs (fig. 13). Analogous to thorium, this increase may record the transport and cumulative downstream storage of relatively uranium-rich particles derived from upstream sources.

Spatial Distribution of Uranium in Sediments

The spatial distribution of uranium in fine-grained stream sediments of the Denver West quadrangle is illustrated by the results of this study (fig. 14*A*) and by a comparable sampling in 1976 under the NURE program (fig. 14*B*). In general, the highest concentrations of uranium in stream sediments are in the western one-third of the quadrangle, particularly in areas underlain by the 1,400-Ma Silver Plume batholith and its contact zone (fig. 2). The middle one-third of the quadrangle, underlain primarily by Precambrian metamorphic rocks and other granites, tends to have lower uranium concentration in sediments, despite the additional overprint of extensive mining activity. The lowest uranium concentrations are in stream sediments in the eastern one-third of the quadrangle, east of the mountain front, in areas underlain by Tertiary and Cretaceous sedimentary rocks.

NURE data indicate that despite relatively low uranium concentrations in easternmost sediments, dissolved uranium concentrations in stream waters east of the mountain front are relatively high (fig. 9*B*). As discussed previously, this mobile uranium is likely derived from organic-rich, variably weathered Cretaceous marine shale. In areas of the Colorado Front Range composed of weathered Precambrian crystalline rocks, much of the easily mobilized uranium may be long removed from the near surface, producing low dissolved uranium in surface waters. Remaining uranium and thorium in weathered

rock are more strongly associated with relatively insoluble mineral hosts such as zircon and monazite. Small, insoluble zircon and monazite grains that enter streams do not contribute dissolved uranium, are subject only to physical transport and may be carried considerable distances downstream from their point of origin. Such minerals are relatively dense and may preferentially concentrate in quiet backwater areas of stream channels. Irregular distribution of heavy minerals in streambeds can contribute to sampling error, made evident when composites of stream sediments are collected in duplicate and analyzed for uranium and thorium (compare samples 84 and 84DUP. in table 6). Additional variability between the two data sets results from the collection of different size fractions of fine-grained sediments: <0.09 mm (-170 mesh) in this study, and <0.15 mm (-100 mesh) in 1976.

Sediments from Ralston Creek downstream from the Schwartzwalder uranium mine (sites 23, 24; fig. 1) were sampled only in 1994. Uranium concentrations of 28.6 and 38.1 μ g/g (table 6) are not anomalously elevated compared to other Denver West sediment samples but are higher than samples from farther upstream (sites 26, 28; fig. 1) and from the surrounding vicinity (fig. 14, table 6). Fine-grained sediments from the West Fork of Clear Creek (sites 18, 19; fig. 1) have some of the highest uranium concentrations reported $(>40 \mu g/g, table 6)$. Sediments in the West Fork are derived from the Silver Plume batholith and from surface exposures of the Red Mountain intrusive complex that hosts the Urad-Henderson molybdenum deposit (fig. 1). Chemical data from surface exposures and deep mine workings indicate that the Red Mountain intrusive complex contains highly variable and locally elevated concentrations of uranium that can exceed 50 µg/g (Bright and Holland, 1973; table 1).

Table 5. Radiometric and chemical data for whole sediment (less than 2 millimeter) from the Denver West 1:100,000 quadrangle,

 Colorado.—Continued

	X-ray fluorescence											
Cu (µg/g)	La (µg/g)	Nb (µg/g)	Pb (µg/g)	Rb (µg/g)	Sr (µg/g)	W (µg/g)	Ү (µg/g)	Zn (µg/g)	Zr (µg/g)			

[eU, equivalent uranium concentration; eTh, equivalent thorium concentration; wt%, weight percent; μg/g, micrograms per gram; <, less than; DUP,, duplicate; --, no data]

Sediment Concentrations and Sediment Quality Guidelines for Ecotoxicity

Site-specific and sample-specific toxicity measurements that use reference aquatic organisms in a field or laboratory setting were beyond the scope of this study. In the absence of such measurements, sediment toxicity can be estimated based on the concentration of metals in whole sediment. Such predictions are, however, subject to large errors caused by uncertainty in the specific metal hosts and their solubility, and by variability in pore-water chemistry that can affect bioavailability. In addition, false positives for toxicity can arise if standards based on concentrations in whole sediment are erroneously applied to concentrations determined in finer grained, more metal-rich sediment fractions.

In a recent paper, MacDonald and others (2000) compiled various sources of sediment-quality guidelines for heavy metals, developed consensus benchmarks defined as threshold effect concentration (TEC) and a higher probable effect concentration (PEC) and then tested the predictability and reliability of these benchmarks by using various field-collected sediments. The PECs were approximately 150 µg/g for copper and lead, and approximately 450 µg/g for zinc. Whole sediment samples collected from various sites in the main stem of Clear Creek (table 5) locally exceed the PEC for lead and zinc. Concentrations in finer grained fractions of the sediments (table 6) are not directly comparable to PEC values derived for whole sediments, but some concentrations of copper, lead, and zinc exceed the PEC values by several times. Possibly toxic concentrations of lead and zinc in stream sediments associated with mining were reported for sites in and near the Denver West quadrangle by Deacon and Driver (1999). Similar attempts to develop toxic effect levels for uranium in stream

sediments were discussed by Sheppard and others (2005), who suggested a threshold value for toxic effects of 100 μ g/g in dry bulk sediments. Based on this criterion, uranium concentrations in Denver West sediments (tables 5, 6) are not toxic to aquatic organisms.

Fission-Track Radiography of Stream Sediments

The major rock-forming minerals generally contain low concentrations (<5 µg/g) of uranium (Wedepohl, 1969), but the minerals are sufficiently abundant to account for much of the inventory of uranium in rocks. Fission-track radiographs are particularly useful for identifying minor, but relatively uranium-rich, primary minerals such as zircon and uraniumbearing alteration products such as secondary iron oxides that are enriched by sorptive uptake of soluble uranium. Examples of these uranium-bearing trace phases and uranium-bearing organic matter are in the fine-grained sediments (fig. 15) and decrease in relative importance as uranium hosts in the order zircon > iron oxides > organic matter. Secondary iron oxides in the sediments generally occur as coatings on hosts of ironbearing primary minerals and are highly variable in uranium concentration (fig. 15A). This variability is expected, considering variations in their origin, oxide form, crystallinity, and history of exposure to uranium-bearing solutions.

One radiograph (fig. 15*E*) of sediment collected from the North Fork of Clear Creek near its mouth (sample 48, fig. 1) showed particularly pervasive association of uranium and secondary iron oxide coatings. These are fine-grained sediments transported downstream from the mining areas of Central City, and some of the iron oxides probably originated as alteration products and chemical precipitates related to hydrothermal mineralization and acid drainage. Secondary



Figure 13. Plots showing concentrations of selected elements in fine-grained (less than 0.09 millimeter) sediments as a function of sampling-site location within the main stem of Clear Creek.



Figure 13. Plots showing concentrations of selected elements in fine-grained (less than 0.09 millimeter) sediments as a function of sampling-site location within the main stem of Clear Creek.—Continued

Table 6. Location and chemical composition of fine-grained stream sediment (less than 0.09 millimeter) from the Denver West

 1:100,000 quadrangle, Colorado.
 1

[lat., latitude; long., longitude; DUP, duplicate field sample; n.d., not determined; LOI, loss on ignition; NAD27, North American datum, 1927; wt%, weight percent; $\mu g/g$, micrograms per gram; <, less than. Analyses by X-ray fluorescence and delayed neutron analysis (U and Th only)]

Sample ID	Sampling site	NAD27 Decimal lat.	NAD27 Decimal long.	LOI (%)	Fe ₂ 0 ₃ (wt %)	K (wt %)	Ca (wt %)	Ti (wt %)	Rb (µg/g)	Sr (µg/g)	Y (µg/g)
94DW S01	Gamble Gulch	39.907	105.501	8.0	7.9	2.69	0.72	0.53	155	184	56
94DW S02	Moon Gulch	39.914	105.510	12.5	8.3	2.18	0.91	0.51	123	195	68
94DW S03	S. Boulder Creek at Johnson mine	39.914	105.531	2.5	6.4	2.09	2.00	0.47	75	210	55
94DW S04	Mammoth Gulch	39.902	105.611	9.0	9.4	2.20	1.20	0.47	113	234	121
94DW S05	N. Boulder Creek at Sherwood Creek	39.989	105.490	6.0	6.5	2.57	1.74	0.64	116	369	83
94DW S06	Beaver Creek	39.964	105.528	7.5	7.6	2.83	1.20	0.56	126	255	82
94DW S07	Midddle Boulder Creek above Barker Res.	39.962	105.504	8.7	n.d.	2.27	1.66	0.58	108	393	70
94DW S08	S. Beaver Creek at Lincoln Hills	39.925	105.455	7.6	5.5	2.60	1.66	0.66	146	334	54
94DW S09	S. Boulder Creek at Pinecliff gage	39.931	105.424	8.0	8.4	2.30	1.54	0.51	120	259	85
94DW S10	Beaver Creek at Gap and Twin Spruce	39.899	105.344	6.0	5.3	2.80	1.08	0.40	154	203	44
94DS-10(DUP.)				5.0	5.0	2.82	1.13	0.40	145	206	54
94DW S12	Coal Creek Gaging Station	39.878	105.277	7.4	n.d.	2.76	1.33	0.38	136	250	61
94DW S13	Fall River near mouth	39.756	105.556	3.5	8.4	2.27	1.60	0.47	106	198	108
94DW S14	Fall River above Cumberland	39.798	105.624	8.1	n.d.	2.61	1.04	0.42	143	195	57
94DW S15	W. Fork Clear Creek near Empire	39.759	105.660	4.0	3.8	3.15	0.41	0.34	183	130	42
94DW S16	Bard Creek	39.751	105.686	9.0	4.6	3.21	0.93	0.38	199	188	113
94DW S17	Mad Creek	39.762	105.700	10.1	n.d.	2.73	1.30	0.34	189	281	72
94DW S18	W. Fork Clear Creek near Hoop Creek	39.776	105.793	15.5	7.2	2.84	1.35	0.25	233	242	62
94DW S19	W. Fork Clear Creek below Henderson	39.771	105.820	7.5	5.0	4.18	0.66	0.29	332	105	79
94DW S20	Jim Creek	39.882	105.754	12	14.4	2.43	0.81	0.43	151	150	81
94DW S21	Fraser River at trail campground	39.900	105.775	6.0	4.4	2.99	0.97	0.41	184	192	43
94DW S22	Vasquez Creek	39.921	105.785	9.0	5.4	2.71	1.80	0.36	152	216	44
94DW S23	Ralston Creek above reservoir	39.822	105.261	5.5	n.d.	2.73	2.05	0.55	101	215	55
94DW S24	Ralston Creek below Schwartzwalder	39.837	105.273	5.0	9.0	2.14	2.43	0.53	87	232	50
94DW S25	Ralston Creek trib. above reservoir	39.824	105.263	13	18	3.19	1.30	0.56	139	164	33
94DW S26	Ralston Creek at Ralston Roost	39.832	105.409	16	11.2	1.76	1.46	0.41	93	228	46
94DW S26(DUP.)				14	11.6	1.80	1.43	0.43	95	222	69
94DW S27	Deer Creek	39.851	105.346	14	4.5	2.37	1.23	0.40	121	211	48
94DW S28	Ralston Creek at lower Golden Gate Park	39.851	105.346	9.0	5.7	2.39	1.57	0.45	106	250	94
94DW S29	Ranch Creek	39.950	105.765	12	7.7	2.17	1.81	0.63	114	241	72
94DW S30	St Louis Creek	39.945	105.830	10	n.d.	2.18	1.61	0.43	141	167	46
94DW S31	Elk Creek	39.934	105.812	8.0	4.6	2.10	1.40	0.46	157	218	53
94DW S33	Tucker Gulch at Golden Gate Canyon	39.772	105.246	5.5	10.8	1.89	3.13	0.63	62	135	53
94DW S34	Crawford Gulch	39.779	105.286	7.0	8.2	2.68	1.59	0.52	150	132	45
94DW S35	Clear Creek below Loveland Ski area	39.688	105.881	4.0	5.3	3.67	0.87	0.36	205	208	52
94DW S36	Quayle Creek	39.691	105.805	10.2	n.d.	3.49	0.90	0.49	225	212	82
94DW S37	Clear Creek at Baker	39.692	105.804	5.5	4.0	3.86	0.86	0.38	220	202	46
94DW S38	Clear Creek at Silver Plume	39.696	105.746	3.1	n.d.	3.59	0.90	0.38	199	204	47
94DW S39	Clear Creek at Georgetown Loop	39.701	105.707	3.8	n.d.	3.64	0.83	0.35	211	201	57
94DW S40	Clear Creek above Georgetown Lake	39.718	105.694	5.0	5.4	3.35	1.11	0.38	180	196	74
94DW S41	Clear Creek at Empire	39.753	105.661	9.0	6.9	3.14	0.84	0.41	187	179	94

 Table 6.
 Location and chemical composition of fine-grained stream sediment (less than 0.09 millimeter) from the Denver West

 1:100,000 quadrangle, Colorado.—Continued

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[lat., latitude; long., longitude; DUP, duplicate field sample; n.d., not determined; LOI, loss on ignition; NAD27, North American datum, 1927; wt%, weight percent; $\mu g/g$, micrograms per gram; <, less than. Analyses by X-ray fluorescence and delayed neutron analysis (U and Th only)]

Zr (µg/g)	Nb (µg/g)	Ba (µg/g)	La (µg/g)	Ce (µg/g)	Cu (µg/g)	Zn (µg/g)	Pb (µg/g)	W (µg/g)	Th (μg/g)	U (µg/g)
458	17	744	121	184	127	203	93	25	33	17.8
754	17	685	164	266	108	215	30	<20	42	9.4
390	13	636	86	152	32	157	27	<20	34	10.2
1,000	16	662	230	379	53	122	45	<20	70	15.7
1,530	26	748	227	406	32	113	47	73	64	9.4
1,260	17	1,350	238	433	75	929	294	329	66	9.7
1,350	28	799	268	448	57	204	83	112	71	14.3
813	22	770	118	201	24	140	21	<20	29	7.4
993	21	675	223	367	46	220	57	<20	63	27.2
430	22	762	99	174	24	116	40	<20	41	8.6
561	21	746	134	232	24	99	35	<20	59	10.3
721	21	931	215	379	30	151	60	<20	102	14.4
891	16	584	198	332	150	255	128	<20	52	14.8
642	21	750	158	279	393	185	40	<20	57	17.5
448	17	777	107	193	156	521	55	47	32	14.7
827	18	663	324	557	28	632	62	<20	187	42.3
526	27	759	237	377	91	516	201	<20	93	34.7
401	14	960	238	405	258	7,620	234	113	127	47.7
760	28	596	467	825	68	1,500	203	<20	233	41.7
592	16	799	217	372	23	116	20	<20	63	39.1
485	16	695	114	209	22	119	40	<20	54	45.9
411	17	612	140	256	40	227	30	<20	64	28.0
597	15	624	86	162	31	181	34	<20	41	28.6
565	12	553	82	151	30	221	32	<20	42	38.1
366	17	708	67	142	46	122	41	<20	25	15.7
467	15	903	102	182	36	202	28	<20	36	18.2
769	17	935	142	239	29	179	28	<20	47	21.4
683	19	693	129	190	25	75	29	<20	58	41.6
1,380	17	697	247	385	21	86	28	<20	91	26.7
1,580	20	823	150	245	32	115	24	<20	41	13.9
378	15	570	137	211	22	104	30	<20	44	20.5
614	27	659	109	195	23	75	30	<20	43	8.7
278	13	509	55	86	35	148	20	<20	14	5.0
205	24	661	61	127	49	169	59	<20	19	5.0
533	22	781	176	328	33	170	70	<20	75	12.6
719	19	862	201	378	215	2,130	1,200	28	85	19.4
534	24	807	195	352	33	440	87	<20	88	14.3
607	18	786	249	453	45	363	95	<20	113	17.1
693	19	779	242	462	58	1,900	242	<20	128	15.3
762	21	760	193	363	80	2,150	294	49	83	13.0
906	18	810	240	437	124	4,100	603	42	107	18.6

36 Uranium in Surface Waters and Sediments Affected by Historical Mining in the Denver West 1:100,000 Quadrangle, Colorado

 Table 6.
 Location and chemical composition of fine-grained stream sediment (less than 0.09 millimeter) from the Denver West

 1:100,000 quadrangle, Colorado.—Continued

[lat., latitude; long., longitude; DUP, duplicate field sample; n.d., not determined; LOI, loss on ignition; NAD27, North American datum, 1927; wt%, weight percent; $\mu g/g$, micrograms per gram; <, less than. Analyses by X-ray fluorescence and delayed neutron analysis (U and Th only)]

Sample ID	Sampling site	NAD27 Decimal lat.	NAD27 Decimal long.	LOI (%)	Fe ₂ 0 ₃ (wt %)	K (wt %)	Ca (wt %)	Ti (wt %)	Rb (µg/g)	Sr (µg/g)	Y (µg/g)
94DW S42	Clear Creek at Lawson	39.766	105.626	5.0	6.5	3.16	0.93	0.36	164	193	68
94DW S43	Mill Creek	39.765	105.601	7.0	7.1	2.73	1.43	0.49	138	187	66
94DW S43(DUP.)				8.0	8.0	2.63	1.40	0.48	139	178	62
94DW S44	Clear Creek above Idaho Springs	39.757	105.567	5.5	n.d.	2.94	0.91	0.38	175	183	73
94DW S45	Virginia Canyon	39.746	105.513	3.0	10.2	2.45	1.57	0.66	112	140	122
94DW S46	Clear Creek below Idaho Springs	39.744	105.490	2.3	12.5	2.10	1.85	0.69	98	180	198
94DW S47	Clear Creek near junct I-70 and US 6	39.746	105.436	2.6	7.7	2.44	1.64	0.49	104	187	80
94DW S48	N. Fork Clear Creek at mouth	39.749	105.399	6.7	12.2	2.57	0.96	0.49	136	227	80
94DW S49	N. Fork Clear Creek above Missouri Creek	39.826	105.536	8.4	9.6	2.71	1.23	0.62	140	238	57
94DW S50	Missouri Canyon	39.820	105.510	6.4	9.1	2.62	1.30	0.60	143	188	4.8
94DW \$50(DUP.)				6.2	8.9	2.68	1.33	0.60	142	194	49
94DW S51	Eureka Gulch above Central City	39.805	105.527	7.7	12	2.18	1.43	0.52	128	217	53
94DW S52	Chase Gulch above Blackhawk	39.804	105.502	9.6	9.6	2.44	1.01	0.51	135	148	128
94DW S53	N. Fork Clear Creek below Blackhawk	39.797	105.476	4.8	11.4	2.59	1.36	0.57	120	193	85
94DW S54	Clear Creek at Golden gage	39.753	105.234	5.5	10	2.75	1.08	0.58	150	219	70
94DW S55	Guy Gulch	39.747	105.303	16.3	6.8	2.50	8.75	0.47	66	176	35
94DW S56	Elk Creek	39.742	105.331	9.5	6.3	2.44	12.42	0.49	66	222	42
94DW S57	Russell Gulch at mouth	39.764	105.447	4.4	9.4	2.49	1.60	0.60	132	305	130
94DW \$57(DUP.)				3.9	9.2	2.56	1.50	0.57	134	317	113
94DW S58	Smith Hill Gulch	39.783	105.455	8.8	7.3	1.85	2.02	0.42	49	166	49
94DW \$59	Clear Creek below N. fork of Clear Creek	39.741	105.332	4.3	8.9	2.81	1.12	0.54	144	243	51
94DW S60	Keystone Gulch	39.594	105.972	7.5	7.7	1.89	2.47	0.55	92	238	58
94DW S61	Snake River near Keystone Ski area	39.606	105.943	8.9	n.d.	2.09	1.12	0.38	136	240	82
94DW S62	Snake River above Montezuma	39.564	105.860	17.7	11.3	1.70	0.32	0.35	100	167	41
94DW S63	Deer Creek above Montezuma	39.563	105.860	14.9	12.9	1.55	1.89	0.45	80	166	54
94DW S64	N. Fork Snake River	39.608	105.940	7.3	6.6	2.67	1.21	0.42	150	211	81
94DW S65	Peru Creek	39.599	105.857	11.4	11.1	2.58	0.82	0.48	146	234	130
94DW S66	Snake River above Peru Creek	39.591	105.871	10.4	12.4	1.62	1.06	0.39	116	636	91
94DW S67	S. Fork Clear Creek above Georgetown	39.687	105.699	7.2	8.3	2.22	2.02	0.51	111	232	149
94DW S68	Leavenworth Creek at S. Clear Creek	39.687	105.700	6.3	8.0	3.19	0.80	0.44	164	188	91
94DW S69	Geneva Creek above Grant			5.6	5.7	2.99	1.09	0.35	133	240	81
94DW S70	Geneva Creek above Duck Creek	39.529	105.732	15.6	15.1	1.80	0.51	0.30	102	185	45
94DW S71	Duck Creek	39.529	105.731	3.6	n.d.	2.65	1.39	0.48	152	348	144
94DW S72	S. Fork Clear Creek above reservoir	39.653	105.707	10.6	11.7	2.27	1.28	0.58	131	231	78
94DW S73	W. Chicago Creek	39.693	105.617	3.6	10.2	1.85	2.43	0.61	71	220	82
94DW S74	S. Chicago Creek	39.693	105.616	5.8	n.d.	2.29	2.39	0.78	93	428	90
94DW S75	Chicago Creek gage near Devil's Canyon	39.717	105.571	4.2	n.d.	2.37	2.05	0.78	105	321	101
94DW \$75(DUP.)				4.7	n.d.	2.50	1.90	0.74	110	317	80
94DW S76	Chicago Creek at Clear Creek	39.737	105.524	1.9	10.9	1.73	3.00	0.74	64	210	112
94DW S77	Soda Creek at Idaho Springs	39.736	105.513	3.2	10.7	2.32	1.76	0.61	107	167	85

Table 6.Location and chemical composition of fine-grained stream sediment (less than 0.09 millimeter) from the Denver West1:100,000 quadrangle, Colorado.—Continued

[lat., latitude; long., longitude; DUP, duplicate field sample; n.d., not determined; LOI, loss on ignition; NAD27, North American datum, 1927; wt%, weight
percent; µg/g, micrograms per gram; <, less than. Analyses by X-ray fluorescence and delayed neutron analysis (U and Th only)]

Zr (µg/g)	Nb (µg/g)	Ba (µg/g)	La (µg/g)	Ce (µg/g)	Cu (µg/g)	Zn (µg/g)	Pb (µg/g)	W (µg/g)	Th (µg/g)	U (µg/g)
790	18	961	159	312	130	1,970	190	54	73	16.8
577	18	657	129	239	42	219	72	<20	44	12.4
580	18	658	132	238	45	204	86	<20	67	15.8
932	22	935	196	347	144	2,920	191	48	84	21.0
870	17	560	136	266	181	772	410	<20	52	14.8
1,550	14	601	338	570	220	1,400	302	21	90	21.6
505	12	590	102	201	183	1,500	244	28	38	10.9
322	16	776	109	188	672	1,360	484	<20	18	11.3
530	18	752	127	217	64	192	49	<20	34	7.4
371	19	636	74	141	55	218	89	<20	22	5.9
391	20	646	82	144	51	208	82	<20	20	6.2
395	18	753	56	111	122	1,920	250	26	19	9.1
781	14	582	211	230	335	4,340	657	54	30	13.8
522	17	662	88	168	484	1,100	386	27	19	8.9
476	16	801	110	182	253	1,130	324	<20	33	14.0
272	14	566	47	83	42	148	30	29	19	7.4
313	13	588	49	92	49	129	57	<20	17	4.2
992	17	833	202	331	388	974	322	39	54	17.8
879	14	878	200	338	312	646	332	<20	43	16.3
316	9.5	593	69	107	31	100	23	<20	14	11.5
313	17	811	75	139	223	610	386	<20	16	9.0
827	14	660	95	174	24	204	30	<20	36	24.4
508	18	2,580	94	214	536	2,990	483	45	52	28.5
414	16	510	85	172	82	148	173	<20	33	10.5
491	12	636	87	153	50	604	137	<20	35	32.5
721	17	689	285	482	31	147	33	<20	112	35.4
1,340	24	833	248	401	663	1,230	592	<20	58	27.3
387	7	25,000	n.d.	n.d.	230	7,250	1,930	81	< 7.5	25.9
1,650	11	666	339	550	31	249	159	23	99	21.9
698	20	956	128	244	121	2,500	704	36	50	14.1
759	20	798	122	214	62	602	18	<20	39	20.6
354	11	591	109	195	132	209	68	<20	42	34.2
2,240	30	751	386	624	21	61	38	<20	160	31.2
565	19	710	166	240	35	117	34	<20	35	21.5
713	13	684	97	161	29	132	17	<20	34	8.6
1,610	23	1,140	113	235	29	110	39	<20	29	10.3
1,970	23	861	174	319	32	228	63	<20	51	17.2
1,180	23	879	136	244	33	255	60	<20	45	16.2
688	11	579	131	238	52	272	58	<20	42	9.5
531	18	610	103	187	56	269	69	<20	39	9.3

 Table 6.
 Location and chemical composition of fine-grained stream sediment (less than 0.09 millimeter) from the Denver West

 1:100,000 quadrangle, Colorado.—Continued

[lat., latitude; long., longitude; DUP, duplicate field sample; n.d., not determined; LOI, loss on ignition; NAD27, North American datum, 1927; wt%, weight percent; µg/g, micrograms per gram; <, less than. Analyses by X-ray fluorescence and delayed neutron analysis (U and Th only)]

Sample ID	Sampling site	NAD27 Decimal lat.	NAD27 Decimal long.	LOI (%)	Fe ₂ 0 ₃ (wt %)	K (wt %)	Ca (wt %)	Ti (wt %)	Rb (µg/g)	Sr (µg/g)	Ү (µg/g)
94DW S78	Beaver Brook at I-70	39.715	105.392	6.8	9.7	2.19	2.00	0.52	93	170	85
94DW S79	Soda Creek above El Rancho	39.710	105.368	3.4	11.7	1.72	3.59	0.70	57	172	194
94DW S80	Kerr Gulch	39.660	105.290	4.7	8.2	2.37	2.29	0.49	94	174	116
94DW S81	Bear Creek at Morrison	39.653	105.195	4.3	n.d.	2.74	1.36	0.50	119	193	133
94DW S81(DUP.)				4.6	n.d.	2.67	1.31	0.48	118	190	106
94DW S82	Corral Creek	39.628	105.430	10.5	9.6	2.37	1.73	0.76	129	226	86
94DW S83	Bear Creek at Singing River Ranch	39.624	105.444	11.3	10	2.16	2.11	0.91	106	292	125
94DW S84	Bear Creek at Evergreen Lake golfcourse	39.633	105.333	2.6	n.d.	2.43	1.74	0.69	127	242	535
94DW S84(DUP.)				4.0	6.9	2.66	1.73	0.56	134	213	189
94DW S85	Cub Creek	39.624	105.323	3.6	5.9	3.19	1.16	0.39	167	183	81
94DW S86	N. Turkey Creek west of Hwy 285	39.592	105.224	5.6	4.5	2.80	1.14	0.44	154	178	152
94DW S87	S. Turkey Creek east of Hwy 285	39.592	105.218	6.9	7.6	2.80	1.21	0.50	140	168	69
94DW S88	Turkey Creek near mouth of canyon	39.618	105.217	4.8	5.4	2.56	1.32	0.41	126	193	99
94DW S89	Deer Creek at Hogback	39.549	105.134	9.0	n.d.	3.27	1.28	0.59	178	239	42

iron oxides can incorporate dissolved uranium when they first form as precipitates during neutralization of acid drainage (Wanty and others, 1999), and over longer periods in streams these oxides can provide sites for additional adsorptive uptake of dissolved uranium. Note that stream waters from the Central City area are generally low in dissolved uranium concentration (fig. 9, table 4). Suspended fine-grained particles of iron oxyhydroxides and oxides could contribute to the strong particle-association of uranium and iron in stream water from this site (RA/FA>4; see previous discussion, p. 16). Other elements showing strong particle association at this site included aluminum, copper, lead, and arsenic (Asher-Bolinder, 1995).

Scanning Electron Microscope Observations

Five sediment samples containing anomalously high concentrations of uranium and thorium were selected for investigation by SEM–EDX to further identify specific uranium- and thorium-rich minerals in Denver West sediments. Observations of uranium-rich and barium-rich grains from sediments below the Schwartzwalder uranium mine (sites 23, 24, and 25, fig. 1) are discussed in a subsequent section. Other observations included abundant detrital monazite (fig. 16) and zircon in relatively thorium- and uranium-rich samples 84 and 19, respectively (fig. 1, table 6). Sample 19 is from the West Fork of Clear Creek that drains the thorium- and uranium-rich Silver Plume batholith (figs. 1, 2). Sample 19 also contained rare grains rich in iron, oxygen, and molybdenum that were

tentatively identified as altered molybdenum-bearing pyrite, probably derived from the Red Mountain intrusive complex to the west. Note that water samples 15, 18, and 19 from the West Fork of Clear Creek contained anomalous concentrations of dissolved molybdenum (table 4), which are additional indications of molybdenum mineralization in the intrusive complex. Other trace minerals identified in at least one of the five sediment samples included apatite $[Ca_5(PO_4)_3(OH,F)]$, barite (BaSO₄), pyrite (FeS₂), and sphalerite (ZnS).

The Schwartzwalder Uranium Deposit

Description and Mining History

The occurrence, mining, and possible environmental impact of the Schwartzwalder uranium deposit deserve expanded discussion because this large deposit has produced much more uranium than all the other deposits in the Denver West quadrangle combined (table 3). In addition, the deposit has been more recently mined than most others in the quadrangle, and it is located close to Ralston Creek and to the western suburbs of Denver (fig. 1).

The Schwartzwalder uranium deposit was discovered in 1949 by surface prospecting that detected anomalous radioactivity in a weathered outcrop adjacent to Ralston Creek. The discovery site was in Precambrian metamorphic rock located within a northwest-trending, steeply dipping
 Table 6.
 Location and chemical composition of fine-grained stream sediment (less than 0.09 millimeter) from the Denver West

 1:100,000 quadrangle, Colorado.—Continued

Zr (µg/g)	Nb (µg/g)	Ba (µg/g)	La (µg/g)	Се (µg/g)	Cu (µg/g)	Zn (µg/g)	Pb (µg/g)	W (µg/g)	Th (μg/g)	Մ (µg/g)
499	16	680	93	173	57	282	41	27	38	8.4
1,400	9	534	373	633	35	120	37	<20	138	21.0
793	17	651	152	271	35	160	25	<20	69	12.2
1,130	21	630	257	428	33	124	45	<20	105	20.1
978	22	645	213	348	33	129	32	<20	91	17.7
1,170	25	821	119	199	35	125	25	<20	45	13.6
3,710	30	773	148	238	32	99	37	<20	53	15.7
5,150	16	495	1,100	1,800	28	109	76	<20	464	85.6
1,440	20	618	332	553	27	104	60	<20	132	30.6
694	30	704	136	239	25	125	47	<20	57	11.1
1,220	41	669	346	567	28	133	58	<20	148	22.9
542	25	778	105	198	40	156	57	<20	42	8.7
827	30	698	136	236	34	138	57	<20	79	14.4
297	29	705	80	113	33	155	29	<20	32	11.1

[lat., latitude; long., longitude; DUP, duplicate field sample; n.d., not determined; LOI, loss on ignition; NAD27, North American datum, 1927; wt%, weight percent; µg/g, micrograms per gram; <, less than. Analyses by X-ray fluorescence and delayed neutron analysis (U and Th only)]

fault system (Wallace and Karlson, 1985). Uranium mineralization as pitchblende (amorphous or microcrystalline UO_2) was deposited with sulfide and carbonate minerals in steeply dipping fractures that conducted deep-circulating and ascending hydrothermal fluids (Wallace and Whelan, 1986). Isotopic analysis of the pitchblende gave an approximate U-Pb age of 69 Ma, indicating that mineralization coincided with earliest Laramide uplift of the Colorado Front Range (Ludwig and others, 1985). Paleogeographic reconstruction indicated that at the time of ore formation the deposit was buried under approximately 3 km of pre-Tertiary rocks.

Mining of the deposit was initially through adits in the hillside but later extended through vertical shafts to multiple deep working levels. Mining continued intermittently from 1953 to 2000 and extended to depths of more than 700 m (Wallace and Karlson, 1985; Cotter Corporation, 2005). Surface processing of ore included washing, sorting, and stockpiling prior to loading onto trucks for transport to Golden, Colorado, and eventually to a uranium mill in Cañon City, Colorado. Truck transport from the mine site was to the south over an improved gravel road that followed Ralston Creek for approximately 4.5 km before leaving the creek and intersecting with paved roads.

Previous Studies of Mining Effects

Lammering (1973) reported highly anomalous concentrations of dissolved uranium (>400 μ g/L) and ²²⁶Ra (2.2 to 81 picocuries per liter [pCi/L]) in Ralston Creek downstream

from the Schwartzwalder mine (1.0 pCi/L= 2.22 dpm). At that time, mine effluent of slightly alkaline pH (~8), derived from dewatering operations, was minimally treated in a small pond to remove suspended solids prior to its discharge to the creek. Two grab samples of mine effluent contained 14.2 and 15.6 mg/L of dissolved uranium and 72 and 86 pCi/L of dissolved ²²⁶Ra. For comparison, current USEPA drinking-water standards are 30 µg/L for uranium and 5 pCi/L for total dissolved radium (²²⁶Ra + ²²⁸Ra). Based on these results and additional water-quality data from the Colorado Department of Public Health, chemical treatment of mine effluent was begun in late 1972. Treatment consisted of addition of BaCl, to initiate precipitation of highly insoluble barite (BaSO₄), which is a highly efficient scavenger of dissolved radium (Doerner and Hoskins, 1925). A series of settling ponds was constructed for collection of suspended solids, including radium-bearing barite precipitate, from the treated water (Carrasco, 1977). Water from the final settling pond was allowed to enter Ralston Creek, which was monitored for dissolved radium and uranium.

A report by Wang and Edwards (1984) described a 1980–81 sampling of water, suspended solids, and sediments along Ralston Creek. Additional sampling included dissolved and suspended solids in discharge water from the final settling pond. Separation and analysis of sediment-size fractions and some selective extractions were performed to characterize the mode of occurrence of uranium and radium in the sediments. Wang and Edwards (1984) confirmed that the post-1972 water-treatment system effectively reduced dissolved radium in final settling-pond discharge to less than 3 pCi/L but also





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Figure 14. Geochemical "dot maps" indicating the distribution of uranium in fine-grained (less than 0.09 millimeter) stream sediments of the Denver West quadrangle. Dot size increases with increasing ranges of uranium concentration. Samples collected in 1994 during this study (*A*) are compared with a 1976 sampling under the NURE program (*B*). μg/g, micrograms per gram.



Figure 15. Photomicrographs (left) and corresponding fissiontrack radiographs (right) showing representative uranium hosts in fine-grained sediments (less than 0.09 millimeter) of the Denver West quadrangle. Higher densities of fission tracks indicate higher uranium concentrations and produce darker areas on the radiographs. (A) grain coating of uranium-rich, reddishbrown secondary iron oxide (short axis of view, 0.15 millimeter); (B) carbonized wood fragment of high uranium concentration (short axis of view, 0.15 millimeter); (C) zircon grain (short axis of view, 0.15 millimeter); (D) unidentified mafic mineral grain coated with uranium-rich secondary iron oxides. Uranium is much less concentrated in other mineral grains including fluorite, unaltered hornblende, and clear quartz grains (short axis of view is 0.6 millimeter); (E) low-power view of assorted mineral grains coated by uranium-bearing secondary iron oxides. Some uranium detected in the epoxy matrix was redistributed from the grain coatings during preparation of the thin section (short axis of view is 1.5 millimeters). Photomicrographs A-E are from sampling sites 2, 21, 23, 24, and 48, respectively (fig. 1).



Figure 16. Scanning electron microscope image and corresponding X-ray fluorescence spectrum of a large (120-micrometer-diameter) detrital monazite grain from sampling site 84 (fig. 1).

found that small amounts of suspended solids (6 mg/L) in the discharge contained 1,300 pCi/g radium in an insoluble form, probably as radium-bearing barite. The same discharge contained 1,700 µg/L of dissolved uranium plus 2,400 µg/g uranium in suspended solids. Suspended solids and bottom sediments collected from the creek downstream from the mine had much higher concentrations of uranium and radium than upstream from the mine, and concentrations decreased with downstream distance from the mine. Uranium and radium in sediments were primarily hosted by insoluble phases within the finest size fractions. Wang and Edwards (1984) speculated that radioactive particles in the streambed were partly uranium-ore particles washed from the site during early, poorly controlled mining practices and partly uranium- and radiumbearing particles delivered by outflow of the final settling pond.

In 1983, the water-treatment system that utilized settling ponds was replaced by a fully contained water-treatment plant that removed dissolved radium and uranium by barite precipitation and ion exchange, respectively (Thomas Lepry, Cotter Corporation, oral commun., 1994). Treated water of <60-µg/L uranium concentration was allowed to enter Ralston Creek. Water quality in Ralston Creek is of particular concern because the creek flows into Ralston Reservoir, which supplies drinking water to Denver and some western suburbs. Fortunately, the discharge from Ralston Creek is highly diluted in the reservoir, which receives most of its water through a tunnel from transmountain sources. Concentrations of dissolved uranium and radium in Ralston Creek and Ralston Reservoir are routinely measured on a monthly or quarterly basis, and results are closely monitored by the Colorado Department of Public Health and Environment and the Denver Water Board.

Mining Effects Determined in this Study

As part of this study, sediment and water were collected at two sites located 3.6 and 1.2 km downstream from the Schwartzwalder uranium mine (sites 23, 24; fig. 1). Uranium concentrations in the fine-grained fraction (<0.09 mm) of sediment samples 23 and 24 were 29 μ g/g and 38 μ g/g, respectively (table 6), which compare to concentrations of approximately 20 and 50 μ g/g in similarly sized fractions of sediment collected at similar locations by Wang and Edwards (1984, their samples 13 and 8). These uranium concentrations are near the upper end of concentrations for Denver West sediments (table 6, fig. 17C) and are clearly high compared to a value of 16 μ g/g in a small tributary to Ralston Creek downstream from the mine site (sample 25, table 6). Dissolved uranium concentrations in stream waters at sites 23 and 24 were 65 and 34 μ g/L, respectively (table 4), which were the highest and third highest concentrations measured (fig. 17A). The tributary that provided sediment sample 25 was dry, but water from site 28 some 10 km upstream from the mine had only 1.5 µg/L uranium. Wang and Edwards (1984) reported dissolved uranium of 4 µg/L immediately upstream from the mine and 600–1,200 µg/L immediately downstream from the mine. Anomalously high dissolved uranium in 1980-81 was clearly influenced by outflow from the final settling pond. Dissolved ²²⁶Ra concentrations at sites 23 and 24 were 0.84 and 0.91 pCi/L, respectively (table 4). Although still well below the drinking-water standard for total radium of 5 pCi/L, these were the highest ²²⁶Ra concentrations measured in the Denver West sampling (fig. 17A).

Another indication of nearby uranium occurrence included low Th/U ratios of <1.0 in whole sediment from sites 23 and 24 (table 5, fig. 17*B*). Most crustal rocks have Th/U ratios in the range of 1–6 (Wedepohl, 1969). Thorium is highly insoluble in most surface and ground water, so a low Th/U ratio in sediments indicates selective enrichment of uranium as uranium-rich detritus or as uranium sorbed onto sediment particles. In samples 23 and 24, the ratio of uranium



Figure 17. Plots indicating distinctive chemical characteristics of water and sediment from locations 23 and 24 along Ralston Creek below the Schwartzwalder uranium mine. (*A*) concentrations of dissolved uranium and radium are both high compared to other stream waters; (*B*) the Th/U ratio in fine-grained stream sediments is low (less than 1.0) compared to other locations in the Denver West quadrangle; (*C*) the relative degree of enrichment of uranium in fine-grained compared to coarse-grained sediment fractions is low (less than 2:1) compared to most other locations. pCi/L, picocuries per liter; µg/g, micrograms per gram.

concentration in the fine-grained fraction compared to the whole sediment is relatively low (<2X) compared to most other sediments (fig. 17*C*). This indicates that a disproportionate fraction of uranium is associated with larger particles, perhaps as uranium-bearing veinlets and surface coatings, or as small uranium-rich grains attached to larger grains.

Fission-track radiographs of polished thin sections indicated that samples 23 and 24 produced unusual "hot spots" of radiation damage in the mica detector (fig. 18B–D). These hot spots differed in appearance from the fission-track images generated by uranium-rich mineral grains such as zircon (fig. 18A). Hot spots had distinctive, optically bright (transmissive) interiors caused by a high density of fission tracks. Acid etching of the mica to reveal fission tracks also revealed additional areas of apparent damage radiating from the hot spots and extending beyond the range of fission tracks. This latter feature probably resulted from radiation damage caused by prolonged contact of a naturally radioactive uranium-rich particle with the mica detector. Close contact occurred during the 6-8 weeks that the reactor-irradiated thin section and overlying mica detector were stored prior to further processing. The hot spots could not be referenced to obvious zircon grains in the thin section but were of sufficiently large diameter (several tens of micrometers in diameter) to make such referencing possible if similar-sized zircons were present. Based on these observations, the hot spots are attributed to small, uraniumrich, highly radioactive point sources in the underlying thin section.

Small uranium-rich particles in thin sections of samples 23 and 24 were identified with SEM–EDX because they appeared as bright spots in the backscatter imaging mode. The EDX spectra of these particles displayed major peaks corresponding to uranium and oxygen (fig. 19). Another major peak, attributed to carbon, is from the conductive carbon coating applied to facilitate SEM observations and analysis. Uranium-rich particles were of the order of 10–20 micrometers in diameter and exhibited a range of morphologies from anhedral to euhedral to compositionally zoned (fig. 19). The zoned sample is tentatively identified as a colloform variety of pitchblende. Zoning that is apparent in the backscatter image is due to variable iron content.



Figure 18. Fission-track radiographs of a detrital zircon grain (*A*) and distinctive uranium-rich radioactive particles (*B*, *C*, *D*) from sediment sample 23 (fig. 1) downstream from the Schwartzwalder uranium mine. Short axis of all views is 0.15 millimeter.

Fine-grained U(IV) minerals such as uraninite (pitchblende) are highly unstable in the oxidizing environment of a stream but may persist for short times in portions of the streambed where the supply of dissolved oxygen from passing water is limited, or where sulfide or organic matter is sufficiently abundant to maintain anoxic conditions (Abdelouas and others, 1999). In addition, U(IV) minerals may be armored by coatings of secondary U(VI) minerals such as hydrous U(VI) oxide (for example, schoepite), or becquerelite, a hydrous U(VI) oxide with some structural calcium (Finch and Murakami, 1999). Fine-grained U(VI) minerals are also soluble enough to preclude long-term survival in a streambed; therefore, the observed uranium-rich particles are almost certainly of modern origin related to upstream mining activities at the Schwartzwalder mine. Mineral/solution equilibria calculations with PHREEQC confirmed that Ralston Creek waters are highly undersaturated with U(VI) minerals but that schoepite is closest to saturation. Similar uraniumrich particles were not observed in sample 25 from the small tributary to Ralston Creek.

Additional bright particles of high average atomic weight and <5-micrometer diameter observed in samples 23 and 24 were identified as barite (fig. 20). Barite of larger size was not identified, and none was detected in sample 25. Barite is not described in the local country rock near the mine or in the vein mineral and alteration assemblage of the Schwartzwalder ore (Wallace and Karlson, 1985; Wallace and Whelan, 1986). The tentative conclusion is that the barite originates from the period of 1972–1983 when suspended solids of very fine grained radium-bearing barite were allowed to enter Ralston Creek as discharge from the final settling pond. Individual particle analysis with SEM-EDX is not capable of detecting very small concentrations of radium in the barite, but the intense radioactivity of ²²⁶Ra and its daughter products is detectable in sediment fractions using high-resolution gamma-ray spectrometry. Gamma-ray spectrometry of the fine-grained fractions of samples 23 and 24 indicated a small but analytically significant disequilibrium excess of ²²⁶Ra activity (20 percent) above what could be supported by decay of uranium in the same samples (J.R. Budahn, U.S. Geological Survey, written commun., 2006). No such excess of radium activity was detected in the fine-grained sediment of sample 25. Relatively insoluble rock and mineral fragments should closely approximate radioactive equilibrium, so excess ²²⁶Ra activity is attributable to radium-bearing barite or preferential leaching of uranium from uraninite.

Anomalous concentrations of dissolved uranium and radium in Ralston Creek are likely influenced by slow dissolution of uraninite and radiobarite particles introduced from mining operations. Dissolution and progressive burial of these particles in the streambed will eventually diminish their influence on water quality. Similar particles have likely been transported into Ralston Reservoir. Particle tracking in cores taken from locations of continuous deposition within the reservoir could provide a record of past barite supply and progressive burial (Lo and others, 2006).

Conclusions

Stream waters and sediments in mountainous portions of the Denver West 1:100,000 quadrangle were sampled for uranium and other constituents in October 1994, a period considered to represent low-flow conditions in this area, which hosts radioelement-rich country rock and uranium deposits. Chemical, radiometric, and microbeam analyses designed to characterize the aqueous chemistry, mode of occurrence, mobility, and spatial distribution of uranium in the quadrangle have produced the following conclusions.

The speciation of dissolved uranium in stream waters is a strong function of solution pH, and for most waters uranium occurs as a variety of U(VI) complexes with dissolved carbonate. All stream waters in the study area are greatly undersaturated with uranium minerals, and dissolved uranium concentrations of less than 1 to 65 μ g/L are limited by sorption reactions. Dissolved uranium occurs primarily as an



Figure 19. Scanning electron microscope images of assorted small uranium mineral grains (UO_2) ? in sediment sample 24 (fig. 1) downstream from the Schwartzwalder uranium mine. Bar scale in all views is 10 micrometers. A representative X-ray fluorescence spectrum is included.

oxyanion and does not correlate strongly with other dissolved heavy metals, which occur as cationic species and are partially sourced by sulfide ores.

In the majority of sampled stream waters, uranium is truly dissolved or is present as a colloid that is able to pass a 0.45-micrometer filter membrane. A subset of stream waters shows stronger affinity of uranium with suspended fine particulates, and these waters tend to be located near or downstream from mining areas or discharges of acid mine drainage. Similar apparent particle association of iron, aluminum, and other metals in the same subset of mining-affected waters is consistent with the formation of chemical precipitates of iron and aluminum that can sorb uranium and other metals and contribute to their particle-associated mobility in streams.

Within mountainous areas underlain primarily by Precambrian crystalline rocks, the 1,400-Ma Silver Plume batholith is a relatively good local source of soluble uranium and sediments rich in uranium and thorium. Streams draining heavily mined areas that contain hydrothermally altered rocks and uranium-rich acid mine drainage do not contain particularly high concentrations of dissolved uranium. This indicates that dilution of acid drainage and (or) uptake of dissolved uranium by stream sediments are sufficient to limit dissolved uranium.



Figure 20. Scanning electron microscope images of assorted small barite (BaSO₄) grains in sediment samples 23 and 24 (fig. 1) downstream from the Schwartzwalder uranium mine. Bar scale in all views is 2 micrometers. A representative X-ray fluorescence spectrum is included.

The ²³⁴U/²³⁸U activity ratio (AR) of acid mine drainage in the quadrangle is less than 1.0 and is distinct from AR values greater than 1.0 in local stream waters. Chemical precipitates of iron-oxyhydroxides collected downstream from acid mine drainage should record the uranium isotopic signature of acid drainage. Selective chemical extractions of iron-oxyhydroxides in sediments followed by uranium isotopic analysis may provide a means to track downstream transport of iron- and uranium-rich precipitates produced during neutralization of acid drainage.

The fine-grained (<0.09 mm) fraction of stream sediments contains $5-50 \ \mu g/g$ uranium and hosts greater

abundance of small uranium- and thorium-bearing accessory minerals such as zircon, apatite, and monazite. Granitic rocks tend to be richer in these accessory minerals than metamorphic rocks, and thus fine-grained sediments derived from granitic sources tend to contain more uranium and thorium. Secondary iron oxides are ubiquitous uranium hosts that coat grain surfaces and can incorporate additional uranium by sorption. In areas underlain by Precambrian granitic and metamorphic rock, insoluble uranium-bearing minerals or strong sorptive uptake of uranium under ambient conditions of weathering, transport, and deposition produces relatively uranium-rich sediment, but uranium-poor stream water. Historical metal sulfide mining and associated uranium mining within central portions of the Denver West quadrangle have not produced highly elevated concentrations of uranium in local stream sediments. Some uranium enrichment can occur in sediments that contain iron-oxyhydroxide precipitates, which originally formed at sites of sulfide ore oxidation or acid drainage. Such precipitates can have high uranium content, may continue to sorb (or desorb) uranium in response to changing conditions, and also are subject to resuspension and downstream transport, particularly during spring runoff or storms. Similar conclusions likely apply to other metals incorporated in these minor, but relatively mobile precipitates.

Fine-grained sediments collected from Ralston Creek several kilometers downstream from the Schwartzwalder uranium mine have locally anomalous concentrations of uranium and contain rare particles of uraninite and radium-bearing barite that are the products of mining-related activities. Slow dissolution of such particles contributes to the locally anomalous concentrations of dissolved uranium and radium in Ralston Creek downstream from the mine.

With three exceptions, concentrations of dissolved uranium in the sampled streams are below the USEPA drinking-water standard of 30 μ g/L, and all dissolved concentrations are well below locally applied aquatic-life toxicity standards. Concentrations of uranium in stream sediments are also below a proposed aquatic-life toxicity standard for sediment of 100 μ g/g.

The methodologies applied in this regional-scale study are readily transferable to other sites and scales of investigation and could contribute to the design of future studies that attempt to describe uranium abundance and mobility in uranium-mineralized and mined areas.

Acknowledgments

Field sampling was assisted by Sigrid Asher-Bolinder, W.M. Aubrey III, R.L. Driscoll, L.C.S. Gundersen, F.A. Hills, A.L. Meier, D.E. Owen, C.T. Pierson, C.J. Potter, J.F. Robertson, M.R. Stanton, K.J. Wenrich, and USGS volunteer P.K. Cavey. Sample analysis was aided or provided by I.K. Brownfield, J.R. Budahn, R.J. Knight, H.A. Lowers, B.D. Marshall, M. McCoy, J.B. McHugh, A.L. Meier, and E.L. Mosier. Advice regarding sampling techniques, stream-gage measurements, and sample handling was provided by K.F. Dennehy, R.A. Kimbrough, J.S. Heiny, G.B. O'Neill, and K.S. Smith. Helpful information regarding the geology, rock chemistry, aqueous chemistry, and mining history of the area was provided by R.A. Crovelli, E.H. DeWitt, T.L. Klein, R.B. Wanty, and A.B. Wilson. Geographic information system (GIS) support and graphics were provided by D.R. Van Sistine. Uranium isotope analyses were provided by Dr. M.E. Ketterer of the University of Northern Arizona.

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Supplemental Files

The following photographs can be accessed on figure 1 by clicking on the sampling sites (online version only).





Site 73.jpg

Site 74.jpg

Site 75.jpg

Site 76.jpg

Site 77.jpg

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Site 82.jpg

Site 83.jpg

Site 84.jpg

Site 85.jpg

Site 86.jpg



Site 88.jpg

Site 89.jpg