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Geologic Sources and Concentrations of Selenium in the West-Central Denver Basin, Including the Toll Gate Creek Watershed, Aurora, Colorado, 2003–2007

Scientific Investigations Report 2013–5099

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

Cover. Photograph showing tonstein within Denver Formation claystone bedrock. Secondary evaporative deposits are evident on the surface of the outcrop along the Toll Gate Creek streambank, Aurora, Colorado, July 2007. Photograph by Suzanne Paschke.

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

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SALLY JEWELL, Secretary

U.S. Geological Survey
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Contents

Abstract....1
Introduction....1
    Purpose and Scope....2
Study Methods....2
    Data Compilation....2
    Well Installation and Groundwater Sampling....2
    Geologic Sampling and Analysis....5
Background....5
    Selenium Geochemistry....5
    Geologic Sources of Selenium....6
        Coal and Lignite....7
        Volcanic Rocks....8
        Bentonite Claystone....8
        Coal-Enclosed Volcanic Ash....8
        Cretaceous-Tertiary Boundary....9
        Weathering Processes and Secondary Weathering Deposits....9
Description of Study Area....9
    Physiographic Setting....9
    Hydrogeologic Setting....10
Geologic Sources of Selenium in the West-Central Denver Basin....13
    Denver Formation....13
    Denver Lignite Zone....13
    Denver Formation Weathering....14
Selenium Concentrations in the West-Central Denver Basin....14
    Groundwater....14
    Geologic Samples....20
    Mobilization and Transport of Selenium....20
Summary....25
Acknowledgments....26
References Cited....26

Figures

1. Map showing surface extent of Cretaceous shale in Colorado, Denver Basin, selenium-impaired streams on the Colorado 303(d) list in 2006, and location of the study area....3
2. Map showing locations of geologic sections, the Toll Gate Creek watershed, groundwater-monitoring wells, and geologic sampling sites, west-central Denver Basin, Colorado....4
3. Eh-pH relations, oxidation states, geologic examples, and chemical transformations for selenium....7
4. Map showing Denver Basin aquifer system, extent and thickness of the Denver lignite zone, and extent of the Cretaceous-Tertiary boundary in the Denver Basin....11
5. Map showing Denver Formation outcrop and water-table altitude contours, Toll Gate Creek, Aurora, Colorado....12

6. Geologic sections A-A' through F-F' through near-surface Denver Formation in the vicinity of Toll Gate Creek 15
7. Graph showing statistical distribution of concentrations of dissolved selenium in groundwater samples from agricultural and urban land-use wells in the west-central Denver Basin, Colorado, 2003 20
8. Map showing spatial distribution of monitoring wells, concentrations of dissolved selenium in groundwater, and Denver lignite-zone thickness, 2003 22
9. Map showing spatial distribution of monitoring wells, concentrations of dissolved selenium in groundwater, and Denver lignite-zone thickness, 2007 23
10. Conceptual diagram depicting selenium sources, mobilization, and transport in the Toll Gate Creek watershed 24

Tables

1. Sample information and selenium concentrations for geologic samples from land-use study wells in the west-central Denver Basin, Colorado, 2004 6
2. Station and sampling information and concentrations of dissolved selenium in groundwater samples from agricultural and urban land-use wells in the west-central Denver Basin, Colorado, 2003 21

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F–32)/1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Concentrations of chemical constituents in soil are given in either milligrams per kilogram (mg/kg) or parts per million (ppm)

Geologic Sources and Concentrations of Selenium in the West-Central Denver Basin, Including the Toll Gate Creek Watershed, Aurora, Colorado, 2003–2007

By Suzanne S. Paschke, Katherine Walton-Day, Jennifer A. Beck, Ank Webber, and Jean A. Dupree

Abstract

Toll Gate Creek, in the west-central part of the Denver Basin, is a perennial stream in which concentrations of dissolved selenium have consistently exceeded the Colorado aquatic-life standard of 4.6 micrograms per liter. Recent studies of selenium in Toll Gate Creek identified the Denver lignite zone of the non-marine Cretaceous to Tertiary-aged (Paleocene) Denver Formation underlying the watershed as the geologic source of dissolved selenium to shallow groundwater and surface water. Previous work led to this study by the U.S. Geological Survey, in cooperation with the City of Aurora Utilities Department, which investigated geologic sources of selenium and selenium concentrations in the watershed. This report documents the occurrence of selenium-bearing rocks and groundwater within the Cretaceous- to Tertiary-aged Denver Formation in the west-central part of the Denver Basin, including the Toll Gate Creek watershed. The report presents background information on geochemical processes controlling selenium concentrations in the aquatic environment and possible geologic sources of selenium; the hydrogeologic setting of the watershed; selenium results from groundwater-sampling programs; and chemical analyses of solids samples as evidence that weathering of the Denver Formation is a geologic source of selenium to groundwater and surface water in the west-central part of the Denver Basin, including Toll Gate Creek.

Analyses of water samples collected from 61 water-table wells in 2003 and from 19 water-table wells in 2007 indicate dissolved selenium concentrations in groundwater in the west-central Denver Basin frequently exceeded the Colorado aquatic-life standard and in some locations exceeded the primary drinking-water standard of 50 micrograms per liter. The greatest selenium concentrations were associated with oxidized groundwater samples from wells completed in bedrock materials. Selenium analysis of geologic core samples indicates that total selenium concentrations were greatest in samples containing indications of reducing conditions and organic matter (dark gray to black claystones and lignite horizons).

The Toll Gate Creek watershed is situated in a unique hydrogeologic setting in the west-central part of the Denver Basin such that weathering of Cretaceous- to Tertiary-aged, non-marine, selenium-bearing rocks releases selenium to groundwater and surface water under present-day semi-arid environmental conditions. The Denver Formation contains several known and suspected geologic sources of selenium including: (1) lignite deposits; (2) tonstein partings; (3) organic-rich bentonite claystones; (4) salts formed as secondary weathering products; and possibly (5) the Cretaceous-Tertiary boundary. Organically complexed selenium and/or selenium-bearing pyrite in the enclosing claystones are likely the primary mineral sources of selenium in the Denver Formation, and correlations between concentration of dissolved selenium and dissolved organic carbon in groundwater indicate weathering and dissolution of organically complexed selenium from organic-rich claystone is a primary process mobilizing selenium. Secondary salts accumulated along fractures and bedding planes in the weathered zone are another potential geologic source of selenium, although their composition was not specifically addressed by the solids analyses. Results from this and previous work indicate that shallow groundwater and streams similarly positioned over Denver Formation claystone units at other locations in the Denver Basin also may contain concentrations of dissolved selenium greater than the Colorado aquatic-life standard or the drinking-water standard.

Introduction

Selenium is an essential trace element and dietary micronutrient for humans and animals, but the intake of elevated levels of selenium can be toxic to humans, fish, and wildlife (Stadtman, 1974; Gissel-Nielson and others, 1984). In the semi-arid western United States, weathering of selenium-bearing rocks and derived sediments contributes dissolved selenium to draining rivers by natural and anthropogenic processes (Seiler and others, 1999). Rainfall-runoff, infiltration,

recharge, and groundwater/surface-water interaction processes naturally weather and erode the selenium-bearing rocks. The weathering processes result in mobilization of dissolved selenium, as well as major ions and other trace elements, by dissolution and desorption reactions. These processes are accelerated by increased water use on the land surface in irrigated areas (Butler and others, 1996), and irrigation of agricultural fields or suburbanized areas in semi-arid climates is considered a primary control on mobilization and movement of selenium from geologic sources to streams (Butler and others, 1996; Seiler and others, 1999). Once present in aquatic systems, selenium can cycle in and out of the water column because of complexation, adsorption, evaporation, and oxidation-reduction (redox) chemical reactions (McNeal and Balistrieri, 1989). Dissolved selenium in streams and other water bodies accumulates through the aquatic food chain, and its toxic effects can result in mortality, decreased reproduction, and deformities in offspring of fish and birds (Lemly, 1985; Ohlendorf and others, 1986; Ohlendorf, 1989; Presser, 1994). The U.S. Environmental Protection Agency (EPA) has established a primary drinking-water standard for selenium of 50 micrograms per liter (µg/L) (U.S. Environmental Protection Agency, 2003), and, in 1997, the State of Colorado established an aquatic-life standard for selenium of 4.6 µg/L (Colorado Department of Public Health and Environment, 2008).

In Colorado, numerous streams are included on the Colorado list of impaired waters under provisions of Section 303(d) of the Clean Water Act of 1972 (303(d) list) because concentrations of dissolved selenium exceed the aquatic-life standard of 4.6 µg/L (fig. 1). Many selenium-impaired streams in Colorado are associated with non-point source discharge from areas underlain by selenium-bearing Cretaceous marine rocks such as the Mancos Shale in western Colorado (Butler and others, 1996; Tuttle and others, 2005) or its equivalent, the Pierre Shale, in central and eastern Colorado (Gates and others, 2009) (fig. 1). Tertiary coal and organic shale deposits containing volcanic sediment also are known selenium sources (Kulp and Pratt, 2004).

Toll Gate Creek is a perennial stream that drains a suburban area of Aurora, Colorado (Colo.), where concentrations of dissolved selenium in groundwater and surface water have consistently exceeded the aquatic-life standard (Brown and Caldwell and Chadwick Ecological Consultants, 2003; Herring and Walton-Day, 2007; Paschke and others, 2012). Bedrock beneath the area is the Cretaceous- to Tertiary-aged (Paleocene) Denver Formation, and recent studies of selenium in Toll Gate Creek groundwater and surface water (Herring and Walton-Day, 2007; Paschke and others, 2012) identified the Denver Formation as a geologic source of dissolved selenium to shallow groundwater and surface water. This study by the U.S. Geological Survey (USGS), in cooperation with the City of Aurora Utilities Department, investigated the Denver Formation as a geologic source of selenium in the west-central part of the Denver Basin, including the Toll Gate Creek watershed.

Purpose and Scope

This report documents the occurrence of selenium-bearing rocks and groundwater within the Cretaceous- to Tertiary-aged Denver Formation in the west-central part of the Denver Basin, including the Toll Gate Creek watershed. The report presents results of a literature search and compilation of existing data including background information on selenium geochemistry, processes controlling selenium concentrations in the aquatic environment, and geologic sources of selenium. Geologic information on the extent and thickness of lignite beds and geologic sections constructed from well-driller logs are used to illustrate the geologic setting of the area. Groundwater-sampling results for selenium and chemical analyses of solids samples are provided as evidence that weathering of the Denver Formation is a primary source of selenium to groundwater in the west-central part of the Denver Basin, including the Toll Gate Creek watershed.

Study Methods

This study evaluated selenium geochemistry and geologic sources of selenium for the west-central Denver Basin, including Toll Gate Creek, on the basis of data compilation, groundwater-quality data, and geologic sampling and analysis. This report section describes the employed study methods.

Data Compilation

Information on selenium geochemistry, geologic sources of selenium, and the hydrogeologic setting of Toll Gate Creek was obtained through a literature search including compilation and analysis of existing data. Maps produced in previous studies (Kirkham and Ladwig, 1979; Robson, 1996) were used to depict the extent of Denver Formation outcrops and coal beds and the configuration of the water table. Well logs from the Colorado Division of Water Resources State Engineer's Office well-permit database and geologic logs from recent monitoring wells installed by the USGS were used to develop geologic sections using the geographic information system program ARCMap Version 10.1 (Environmental Systems Research Institute, Inc., 1999–2012) plug-in CrossView (A-Prime Software, 2012) (fig. 2).

Well Installation and Groundwater Sampling

In 2003, groundwater-monitoring wells were installed and sampled in the west-central part of the Denver Basin as part of the USGS National Water Quality Assessment (NAWQA) Program to evaluate the effects of targeted land uses on water quality in the shallow bedrock aquifers of

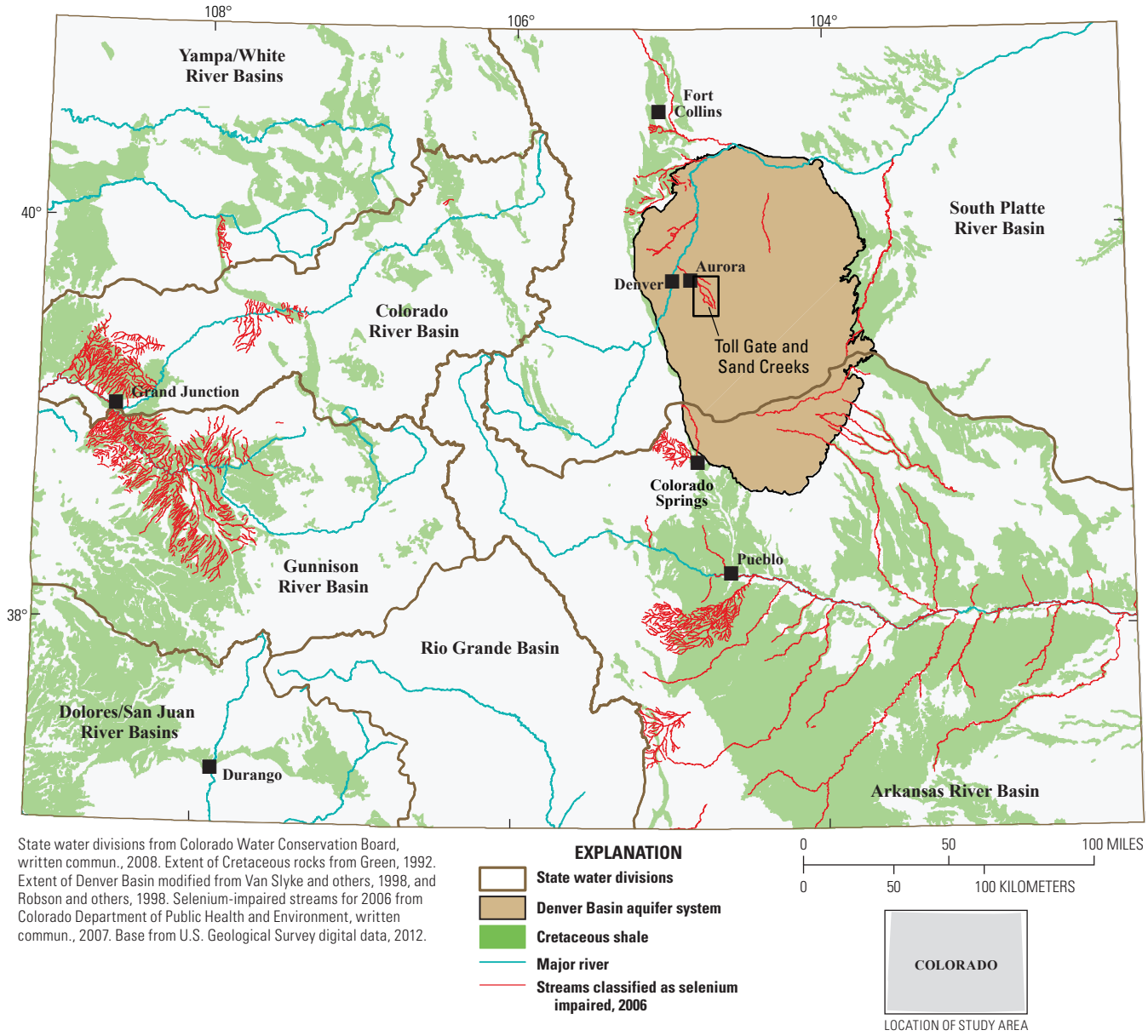


Figure 1. Map showing surface extent of Cretaceous shale in Colorado, Denver Basin, selenium-impaired streams on the Colorado 303(d) list in 2006, and location of the study area.

the Denver Basin. The NAWQA Program was designed to uniformly assess, through consistent methods of data collection and analysis, the status and long-term trends in the quality of the Nation's surface-water and groundwater resources. The NAWQA program also works to develop an understanding of the natural and human factors that affect water quality in selected river basins and principal aquifers of the United States (Gilliom and others, 1995). Two groundwater-quality land-use studies (LUS) were implemented in the Denver Basin by the NAWQA program in areas of (1) predominantly non-irrigated wheat (or other small grain) crops (agricultural LUS or AGLUS), and (2) areas urbanized since 1970 (urban LUS or URLUS). Thirty-two wells were installed for the agricultural LUS, and 29 wells were installed for the urban LUS (fig. 2). The well locations were randomly distributed within the areas of targeted land use following the methods of Scott (1990). The agricultural LUS wells are located northeast of Toll Gate Creek. Urban LUS wells are located in Aurora, Parker, and Highlands Ranch, Colorado, with 9 of the 29 wells located in the Toll Gate Creek watershed (fig. 2). Wells were drilled, completed, and developed following USGS protocols (Lapham and others, 1995) and State of Colorado drilling rules (*http://water.state.co.us/groundwater/Pages/default.aspx*) to depths just below the water table such that the wells were completed in either alluvial material or near-surface bedrock. Well purging, sample collection, field measurements,

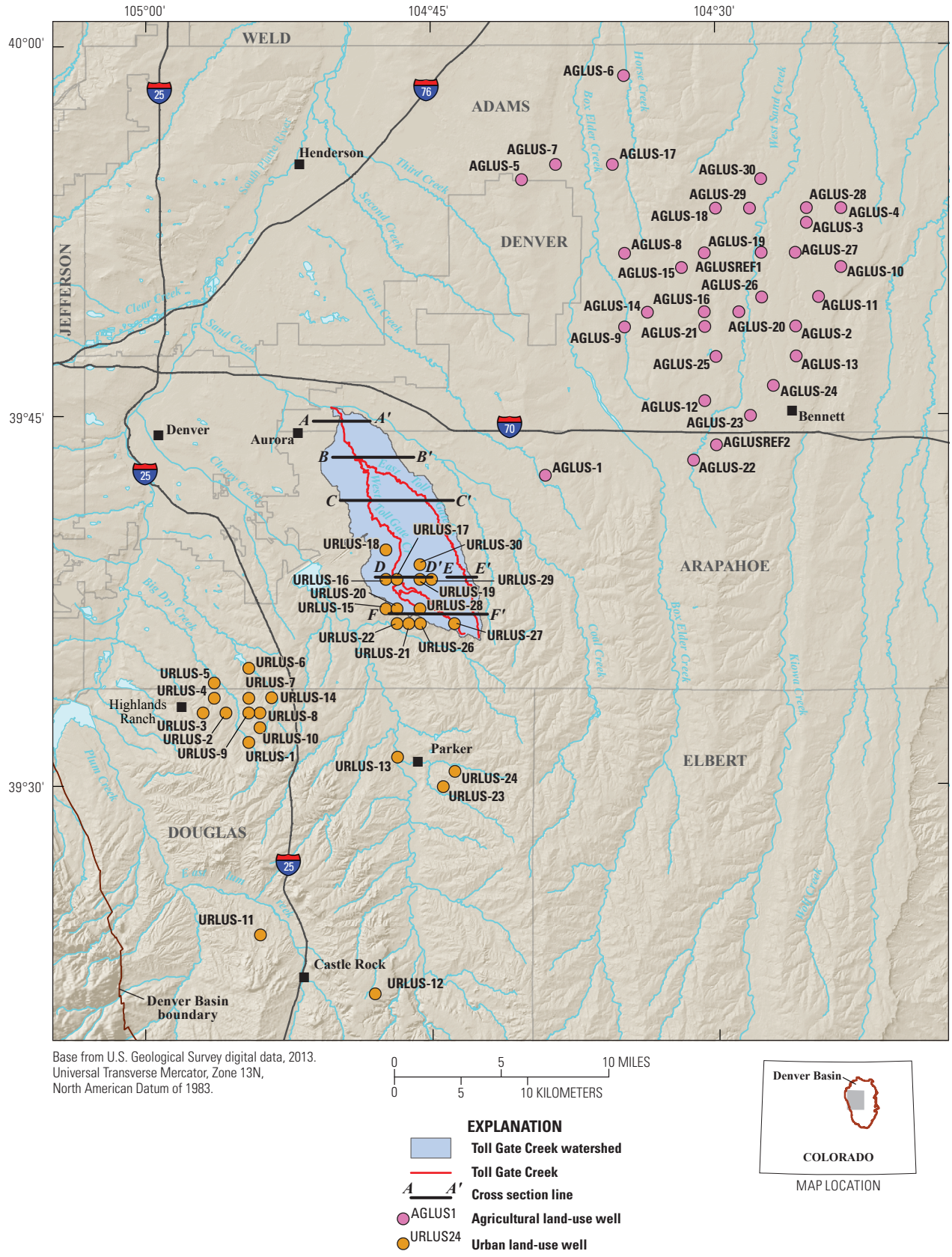


Figure 2. Map showing locations of geologic sections, the Toll Gate Creek watershed, groundwater-monitoring wells, and geologic sampling sites, west-central Denver Basin, Colorado.

and equipment cleaning methods followed standard USGS protocols established by Koterba and others (1995), Lapham and others (1995), and the USGS National Field Manual (U.S. Geological Survey, variously dated), and the samples were analyzed for a suite of inorganic and organic constituents including dissolved selenium. Samples collected for analysis of dissolved selenium were filtered through a 0.45-micron filter and acidified to a pH less than 2 with ultrapure nitric acid. The concentrations of dissolved selenium were determined using inductively coupled plasma, atomic absorption spectrometry following the methods of Fishman and Friedman (1989), Faires (1993), Fishman (1993), and Garbarino (1999).

In 2007, groundwater samples were collected from 19 existing monitoring wells to determine the concentrations of dissolved selenium and other constituents in and around the Toll Gate Creek watershed (Paschke and others, 2012). Three of the sampled wells (URLUS-18, URLUS-28, and URLUS-30) were installed as part of the NAWQA URLUS described in the previous paragraph, and the other 16 wells were installed in 2005 by the City of Aurora as part of a lawn-irrigation return-flow study (Richard Vidmar, City of Aurora, oral commun., 2007). Sixteen of the 19 wells are completed in surficial materials, two of the wells are completed in surficial materials and weathered Denver Formation claystone, and one wells is completed in surficial materials and weathered Denver Formation sandstone (Paschke and others, 2012). Well purging, sample collection, field measurements, and equipment cleaning methods followed standard USGS protocol (Koterba and others, 1995; Lapham and others, 1995; U.S. Geological Survey, variously dated), and the samples were analyzed for a suite of inorganic and organic constituents including dissolved selenium (Paschke and others, 2012). Samples collected for analysis of dissolved selenium were filtered through a 0.45-micron filter and acidified to a pH less than 2 with ultrapure nitric acid. The concentrations of dissolved selenium were determined using inductively coupled plasma, atomic absorption spectrometry following the methods of Fishman and Friedman (1989), Faires (1993), Fishman (1993), and Garbarino (1999).

Geologic Sampling and Analysis

The selenium content of Denver Formation bedrock material in the west-central part of the Denver Basin, including the Toll Gate Creek watershed, was evaluated by analyzing 14 core samples from the NAWQA groundwater monitoring wells for total and extractable selenium. Samples were chosen from AGLUS wells 5 (two samples), 6, 9, 18, and reference 2 (two samples) and from URLUS wells 16, 19 (two samples), 20, 22, 28, and 30 (two samples) (fig. 2 and table 1). Samples were selected from locations where groundwater had elevated concentrations of selenium or from horizons thought to contain elevated selenium (coal/lignite zones). Representative samples also were chosen from core sections that appeared to be oxidized by in-situ processes (as indicated by the presence of iron oxides and a light yellow to orange color) and reduced by in-situ processes (dark brown to black coal seams and light to dark gray mudstones and claystones). Samples were crushed and sieved according to methods described in Taylor and Theodorakos (2002) and were analyzed for selenium by hydride generation atomic-absorption spectrophotometry described in Hageman and others (2002).

Core samples with the greatest selenium concentrations were chosen for paste extraction and analysis of the extract for selenium (table 1). Saturated paste extraction was conducted by staff at the Bureau of Reclamation laboratories in Denver, Colo., following methods described by the U.S. Department of Agriculture (2004). The specific conductance and pH of the extraction solutions were measured immediately following extraction and percent saturation (weight of water divided by dry weight of sample extracted times 100) was calculated for each sample. Filtered paste-extraction (aqueous) samples were analyzed at the U.S. Geological Survey's National Water Quality Laboratory for selenium by collision/reaction cell ICP-MS (inductively coupled plasma—mass spectrometry) (Garbarino and others, 2006). Results were multiplied by percent saturation (in decimals) to correct back to dry weight of soil and to allow for direct comparison between samples.

Background

This report section provides an overview of selenium geochemistry, processes controlling selenium concentrations in the aquatic environment, and potential geologic sources of selenium on the basis of a literature search and data compilation. The report section "Geologic Sources of Selenium in the West-Central Denver Basin" relates the background information presented here to conditions observed in the study area.

Selenium Geochemistry

The chemistry of selenium resembles that of sulfur, and like sulfur, selenium can exist in the 2– (Se^{2-}, selenide), 0 (Se^{0}, elemental selenium), 4+ (SeO_3^{2-}, selenite), and 6+ (SeO_4^{2-}, selenate) oxidation states (McNeal and Balistrieri, 1989; fig. 3). Each oxidation state exhibits different chemical behavior such that the concentration, speciation, and association of selenium in the geologic and aquatic environments depend on the pH, oxidation-reduction (redox) conditions, solubility of its salts, and biological interactions (McNeal and Balistrieri, 1989). Reduced forms of selenium, selenide and elemental selenium, occur in acidic, reducing, and organic-rich environments (McNeal and Balistrieri, 1989; Naftz and Rice, 1989; Kulp and Pratt, 2004). Selenide can exist as insoluble sulfide and selenide minerals, substituted for sulfur in pyrite, or as organic-selenium compounds and complexes (Kulp and Pratt, 2004). Dissolved selenium, in the oxidized complexes of selenite or selenate, is soluble and thus readily transported by groundwater and surface water in the aquatic environment. For the near-neutral pH and

Table 1. Sample information and selenium concentrations for geologic samples from land-use study wells in the west-central Denver Basin, Colorado, 2004.

[Site ID, U.S. Geological Survey site identification number; AGLUS, agricultural land-use study well name; URLUS, urban land-use study well name; BLS, below land surface; Se, selenium; µg/L, micrograms per liter; mg/kg, milligrams per kilogram; w/, with; Fe, iron; NA, not analyzed; <, less than]

Well name	Site ID	Core description	Core sample depth interval BLS (feet)	Screened interval BLS (feet)	Se in groundwater (µg/L)	Se in core (mg/kg)	Se in paste extract corrected to dry weight basis (µg/L)
AGLUS-5	395450104402701	Dark gray claystone	68.5–70.0	79.8–89.6	408	13.0	4,600
AGLUS-5	395450104402701	Gray/black claystone (Coal interbeds above)	81.0–84.0	79.8–89.6	408	1.40	139
AGLUS-6	395909104350401	Yellow brown sand, unconsolidated	30.5–31.5	32.1–41.9	150	0.14	NA
AGLUS-9	394858104345901	Dark gray claystone w/coal interbeds	93.2–93.5	55.2–65.0	6.2	10.0	1,630
AGLUS-18	395352104302801	Yellow-orange sandstone, Fe stained	44.1–45.0	35.8–45.6	31.4	1.0	8.14
AGLUSREF2	394351104302901	Dark gray claystone	26.9–27.5	35.5–45.5	<0.50	1.20	264
AGLUSREF2	394351104302901	Black lignite	38.5–39.2	35.5–45.5	<0.50	1.30	50.2
URLUS-16	393836104474701	Yellowish-brown sand	20.0–20.6	13.5–23.3	19.3	0.11	NA
URLUS-19	393823104455801	Dark yellowish-orange silty claystone, Fe stained	39.0–40.0	32.8–42.6	306	0.70	NA
URLUS-19	393823104455801	Dark yellowish-orange silty claystone, Fe stained	42.0–43.0	32.8–42.6	306	0.20	NA
URLUS-20	393733104465101	Yellowish-orange sand, Fe stained	18.0–19.0	18.4–28.2	41.4	<0.10	NA
URLUS-22	393654104472001	Yellowish-orange sand	7.0–7.6	8.6–18.4	21.4	0.31	NA
URLUS-28	393742104453801	Yellow/brown sand (“Swamp deposit” above saturated interval)	23.5–24.5	18.3–28.1	242	0.22	NA
URLUS-30	393903104455701	Yellow brown to olive gray claystone w/ Fe stain and gypsum	24.0–24.6	28.0–37.5	301	0.16	NA
URLUS-30	393903104455701	Yellow claystone, Fe stained	33.5–34.1	28.0–37.5	301	1.00	79.2

oxidizing conditions present in most aquatic environments, oxidized forms of selenium such as selenite and selenate are generally the dominant forms of dissolved selenium (McNeal and Balistrieri, 1989). Selenite is generally mobile in the aquatic environment under mildly oxidizing conditions, but can be immobilized by adsorption onto bentonite clays at pH values less than 7 and onto iron oxides at pH values between 5 and 8 (Balistrieri and Chao, 1987; McNeal and Balistrieri, 1989; Boult and others, 1998). Selenate is highly mobile in the aquatic environment, especially under alkaline and oxidizing conditions (Naftz and Rice, 1989), forming soluble salts and weakly adsorbing to iron oxides and clay particles and organic matter (McNeal and Balistrieri, 1989, Naftz and Rice, 1989; Kulp and Pratt, 2004), and it is the chemical reactions of salt precipitation and dissolution, sorption to iron oxides and clays, and sorption and complexing with organic matter that can cause selenium to cycle in and out of the aquatic environment. Selenate can substitute for sulfate in gypsum (Fernández-González and others, 2006) and thenardite (Michele Tuttle, U.S. Geological Survey, oral commun., 2012), and it is the form of selenium most readily taken up by plants and algae (McNeal and Balistrieri, 1989; Kulp and Pratt, 2004).

Geologic Sources of Selenium

Many rocks and minerals are selenium bearing, providing source material for environmental selenium (McNeal and Balistrieri, 1989). Coal and organic-rich fine-grained sediments tend to have high selenium concentrations (Adriano, 2001), on the order of 0.5 to 11 milligrams per kilogram, because of either the presence of selenium-bearing sulfide minerals or the complexation of selenium with organic matter (McNeal and Balistrieri, 1989; Yudovich and Ketris, 2006). Large selenium contents are common in sedimentary rocks associated with coal in the western United States (Lakin, 1961), and selenium is considered one of the most enriched trace elements in coal (Gluskoter and others, 1977; Valkovic, 1983; Coleman and others, 1993; Neuzil and others, 2005). Selenium also is associated with volcanic activity, and sedimentary rocks with volcanic input, such as tonsteins or bentonite claystones containing volcanic ash, frequently exhibit high selenium concentrations (Kulp and Pratt, 2004). Hydrothermal and volcanic-hosted sulfide deposits also can contain substantial selenium concentrations (Castor and Weiss, 1992; Layton-Matthews and others, 2008). Weathering of

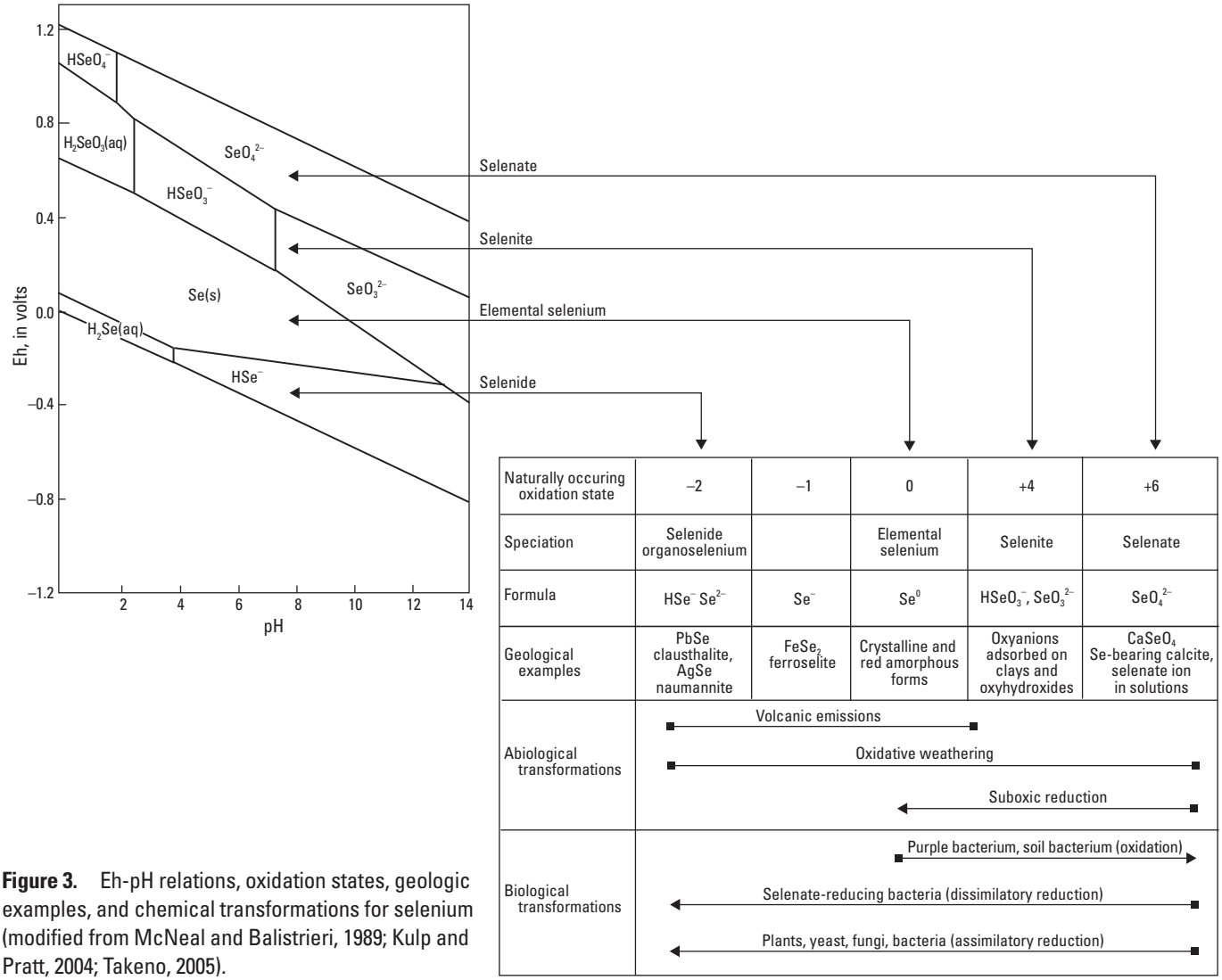


Figure 3. Eh-pH relations, oxidation states, geologic examples, and chemical transformations for selenium (modified from McNeal and Balistrieri, 1989; Kulp and Pratt, 2004; Takeno, 2005).

selenium-bearing rocks results in deposition of secondary selenium-bearing salts, which also are a geologic source of selenium to groundwater and surface water (Kulp and Pratt, 2004; Tuttle and others, 2005).

Coal and Lignite

Selenium in coal and lignite can be derived from a variety of sources, including detrital material, original plant material, volcanic ash, or adsorption from groundwater (Coleman and others, 1993), and can occur in either organic or inorganic form (Yudovich and Ketris, 2006). Organic selenium in coal and lignite appears to occur as an organic-selenium compound or as elemental selenium disseminated through the organic matter (Yudovich and Ketris, 2006) possibly substituting for organic sulfur (Coleman and others, 1993). Inorganic selenium in coal and lignite can occur as selenium-bearing pyrite, selenium-bearing galena, and lead selenide (Coleman and others, 1993; Yudovich and Ketris, 2006). The relative abundance of organic versus inorganic selenium in coal and lignite varies worldwide depending on the original depositional environment and subsequent diagenesis of the coal (Yudovich and Ketris, 2006). Water-soluble and ion-exchangeable selenium also has been reported in weathered and oxidized coal and lignite deposits (Coleman and others, 1993).

Selenium concentration data from about 9,000 coal and lignite samples from the United States (U.S.) indicate a total-selenium geometric-mean concentration in U.S. coal of about 1.7 parts per million (Coleman and others, 1993). Selenium concentrations in U.S. coals generally do not correlate to ash yield, pyritic sulfur, or organic sulfur concentrations, indicating an organic selenium source for many basins (Coleman and others, 1993). However, for western U.S. basins containing coal of Tertiary age, including the Denver Formation, peat accumulated in dominantly non-marine environments and selenium was positively correlated with ash yield (correlation coefficient of 0.53 for 59 samples from the Denver Formation lignite) (Coleman and others, 1993). The correlation between

selenium concentration and ash yield in these basins indicates that selenium and the inorganic coal fraction shared a common source (detrital material or ash) and that the coal underwent minimal diagenesis subsequent to deposition (Yudovich and Ketris, 2006).

Volcanic Rocks

Selenium is associated with volcanic activity and is present in lava, volcanic ash, volcanic-related sulfur deposits, and weathered volcanic deposits (Santmyers, 1930; Byers and others, 1936; Davidson and Powers, 1959; Koch, 1967; Meyer and others, 1992; Presser, 1994). In the western U.S., volcanic-ash deposition was widespread during the late Cretaceous and early Tertiary ages (Koch, 1967; Noe and others, 2007a), and the resulting claystone deposits are enriched in selenium (Kulp and Pratt, 2004). Selenium present in the volcanic ash likely was deposited as aeolian outfall (Davidson and Powers, 1959; Presser, 1994; Witham and others, 2005), and selenium also was carried by lava, which was subsequently eroded and redistributed (Koch, 1967; Presser, 1994).

Tonsteins are thin (typically less than 2–3 inches), laterally persistent, distinct white kaolinite clay beds. Tonsteins are formed by the alteration and leaching of volcanic-ash layers deposited in coal-forming swamps (Zielinski, 1985; Triplehorn, 1990; Timofeev and Admakin, 2002). Because their original composition was volcanic ash, tonsteins also are a potential source of selenium to coal beds. Tonsteins are found in coal-bearing sedimentary basins as partings within coal beds, and tonstein occurrences are recognized worldwide in rocks of Paleozoic, Mesozoic, and Cenozoic age (Timofeev and Admakin, 2002).

Bentonite Claystone

Dark gray bentonite claystone, such as that found in the Denver Formation, was formed from the inclusion of volcanic ash in mud and fine-grained sediment deposited in relatively shallow lacustrine or shallow sea environments (Boles and Surdam, 1979; Altaner and Grim, 1990; Christidis and others, 1995). The term bentonite is used for a clay (including lithified claystone or shale) that is generally dark grey in color and consists predominantly of smectite minerals, usually montmorillonite (Grim and Guven, 1978; Industrial Minerals Association of America, 2012). Because of its unique chemical and physical properties, bentonite clay is an important industrial mineral used in a variety of manufacturing, drilling, and construction applications. The smectite clay structure creates a slight negative charge within the clay such that the cations calcium, magnesium, and sodium are incorporated into the structure and are easily exchanged between the clay and porewater (Gates and others, 2002). Bentonite clay also possesses colloidal properties, and its volume can increase several times when it comes in contact with water. This phenomenon of swelling clay soils can lead to problems with building foundations and roadways (see for example, Noe and others, 2007a).

Because of the volcanic-ash content, bentonite claystone and shale also can contain selenium (Byers and others, 1938; Davidson and Powers, 1959; See and others, 1991; Kulp and Pratt, 2004). Total selenium content ranging from 0.3 to 3 parts per million is reported for bentonite shales in Colorado (Byers and others, 1938), and selenium in shales can occur complexed with organic matter or in a reduced mineralized form such as a trace element in pyrite (Kulp and Pratt, 2004). Sequential-extraction experiments on the Pierre Shale from South Dakota and Wyoming indicate organic selenium is the predominant form of selenium present in Cretaceous-age organic-rich shale and bentonite claystone (Kulp and Pratt, 2004). Additional experiments comparing weathered and unweathered organic-rich Pierre Shale suggest that humic, organic-selenium compounds found in shale are formed during oxidative weathering, whereas selenium enrichment in bentonite claystone was inferred to result from secondary processes including (1) the adsorption of selenium mobilized by groundwater from the surrounding organic-rich sediments onto clay particles and iron hydroxides; and (2) microbial reduction of selenium within the bentonite intervals (Kulp and Pratt, 2004). Naftz and Rice (1989) note that the concentrations of dissolved selenium in groundwater from Tertiary sandstones and organic shales in the Powder River Basin, Wyoming, were directly related to the concentrations of dissolved organic carbon (DOC), indicating oxidation of organic matter in coal and carbonaceous shale as a primary mechanism converting insoluble selenide to soluble selenite and selenate.

Coal-Enclosed Volcanic Ash

Several studies have examined the mobility and distribution of trace elements from volcanic ash and clay to surrounding rocks during diagenesis, chemical weathering, and alteration (Zielinski, 1982; Zielinski, 1985; Crowley and others, 1989; Triplehorn and others, 1991; Warwick and others, 1997; Flores and others, 2006). Plant decay in coal-forming swamps creates acidic, organic-rich pore fluids that promote alteration of volcanic-ash deposits to kaolinite (Zielinski, 1985). Trace elements present in the volcanic ash can be mobilized under acidic conditions and generally have an affinity for organic matter, which suggests a source-sink relation between volcanic ash (and tonsteins) and the enclosing coal deposits (Zielinski, 1985). The organic matter creates a gradient to reducing geochemical conditions that can lead to the formation of organic complexes or sulfides such that element enrichment in the organic matter occurs near contacts with the altered ash (Zielinski, 1985). Some actinides (uranium and thorium), rare earth elements, and heavy metals (copper, lead, vanadium, and titanium) are enriched at the contact redox boundaries, whereas iron, manganese, and alkaline elements were strongly leached from ash and tonsteins and more readily dispersed throughout the enclosing coal (Zielinski, 1985).

The work of Zielinski (1985) does not specifically address selenium, but on the basis of its known geochemical behavior, selenium would be expected to complex with

organic matter in coal or clay and also could be coprecipitated with sulfide minerals such as pyrite in the enclosing coal or clay. Flores and others (2006) note elevated selenium concentrations (0.069–1.5 part per million) for tonsteins in the upper Paleocene Wyodak-Anderson coal of the Powder River Basin, Wyoming, as evidence that the partings survived strong leaching of acids from plant decomposition, which in turn implies that selenium concentration was elevated in the original volcanic ash. Crowley and others (1989) examined the mobility of elements from tonsteins into surrounding coal beds for the Cretaceous C coal bed, Emery Coal Field, Utah, and their results generally agreed with those of Zielinski (1985) except for differences related to the apparent migration range of elements. Some elements (such as zircon and hafnium) that remained in the tonstein of the Felix coal bed during alteration also were found in coal beds of the Emery C coal, which Crowley and others (1989) explain by the greater tonstein thickness, which in turn exerted greater influence on coal geochemistry in the C coal bed. Selenium analyses were included in the Crowley and others (1989) study, and on the basis of cluster analyses, selenium was grouped with uranium and rare earth elements found in abundance near the tonstein/coal contact suggesting selenium mobilized from the tonsteins was complexed or coprecipitated near the contact redox boundary by the same mechanism as uranium (Crowley and others, 1989). Warwick and others (1997) conducted another study of element mobility from tonsteins to coal for the Paleocene Manning Formation of east-central Texas, and grouped selenium with uranium and most of the rare earth elements. All of these studies indicate that tonsteins and bentonite claystone are selenium bearing because of their volcanic-ash content, and that selenium can be mobilized from the ash-derived deposits into surrounding coal.

Cretaceous-Tertiary Boundary

The Cretaceous-Tertiary (K-T) boundary is marked worldwide by sediments (commonly a tonstein deposit) with anomalous iridium (Ir) concentrations that were deposited during a short period, 65 million years ago (Alvarez and others, 1984; Tschudy and others, 1984; Nichols and others, 1986; Pollastro and Pillmore, 1987; Meyer and others, 1992). In the Denver Basin, the K-T boundary is marked by an iridium-enriched tonstein and by a distinct change in plant and pollen assemblages (Nichols and Fleming, 2002) related to meteorite impact (Alvarez and others, 1980; Pollastro and Pillmore, 1987; Meyer and others, 1992). Iridium also has been observed in volcanic gases, dust, and ash (Egger and Brückl, 2006) and is correlated to other highly volatile elements like gold (Au) and selenium at the K-T boundary and in volcanic sublimates (Meyer and others, 1992). In the Raton Basin of southern Colorado and New Mexico, concentrations of iridium, titanium, vanadium, antimony, arsenic, cobalt, and selenium in the K-T boundary layer are greater than their concentrations in other tonsteins in the basin (Gilmore and others, 1984).

Weathering Processes and Secondary Weathering Deposits

Coal and claystone bedrock can contain both organically bound selenium and selenium-bearing pyrite that can be released to the aquatic environment or be redeposited as secondary selenium-bearing salts during the weathering process.

Present-day oxidative weathering of coal and organic matter in claystone releases selenium bound to organic matter to soluble selenite and selenate and generates DOC (Naftz and Rice, 1989). Sequential extraction experiments on the Pierre Shale from South Dakota and Wyoming indicate organic selenium is a predominant form of selenium present in organic-rich shale and bentonite claystone (Kulp and Pratt, 2004), and concentrations of dissolved selenium in groundwater from Tertiary sandstones and organic shales in the Powder River Basin were directly related to DOC concentrations (Naftz and Rice, 1989). These results indicate oxidation of organic matter in coal and organic-rich claystone can be an important mechanism converting insoluble selenide to soluble selenite and selenate and generating DOC.

Selenium-bearing pyrite also can be present in coals and organic-rich claystone, and oxidative weathering of this pyrite releases of iron, sulfur, and selenium to the environment, which can react with calcium and sodium released from bentonite claystones, to form secondary deposits of iron oxide and selenium-bearing salts in the weathered zone of the subsurface (Tuttle and others, 2005). Selenate can substitute for sulfate in gypsum (Fernández-González and others, 2006) and thenardite (Michele Tuttle, U.S. Geological Survey, oral commun., 2012), and these salts can, in turn, serve as soluble geologic sources of selenium to groundwater and surface water (Kulp and Pratt, 2004; Tuttle and others, 2005). Secondary iron oxide deposits can serve as sources or sinks of adsorped selenium depending on the system pH.

Description of Study Area

The Denver Basin is located in eastern Colorado at the base of the Rocky Mountain Front Range. Toll Gate Creek is a perennial tributary of Sand Creek located in the west-central part of the Denver Basin east of Denver (fig. 2).

Physiographic Setting

Toll Gate Creek is a perennial tributary of Sand Creek located near the eastern edge of the Denver metropolitan area in the municipality of Aurora, Colo. Toll Gate Creek drains a suburban area, where surface water is derived from rainfall and snowmelt runoff, urban storm-water drainage, and groundwater discharge from the encompassing watershed. The drainage flows north-northwesterly toward its confluence with Sand Creek, which in turn flows into the South Platte River north of Denver. Neither Toll Gate Creek or Sand Creek are used for drinking-water supply, and Toll Gate Creek does not receive wastewater discharge.

The west-central part of the Denver Basin including Toll Gate Creek is in the Great Plains physiographic province (Trimble, 1980), where topography is characterized by rolling hills and dissected plains. Land-surface altitude in the Toll Gate Creek watershed ranges from approximately 5,900 feet (ft) in the headwaters of West Toll Gate Creek to approximately 5,300 ft near its confluence with Sand Creek. The climate of the region is semi-arid, with mean annual precipitation averaging about 14 to 16 inches in the watershed for the period 1931–2003 (National Oceanic and Atmospheric Administration, 1931–2003). About 70 percent of the precipitation falls during the 6-month period from April to September as summer thundershowers, and the remaining 30 percent of precipitation occurs as winter snowfall (Hansen and others, 1978). Native vegetation consists of grasslands with mixed-grass prairie and rangeland shrubs (Keith and Maberry, 1973). Phreatophytes such as cottonwoods, willows, and cattails grow immediately adjacent to streams in valley bottom lands and flood plains (Keith and Maberry, 1973; Driscoll, 1975).

Residential and commercial development in the Toll Gate Creek watershed since the 1940s has changed the land use, vegetation, and hydrology of the area. Vegetation is predominantly lawns with trees and gardens in residential areas, and paved areas and other impervious surfaces predominate in transportation corridors and commercial developments. Small tributaries to Toll Gate Creek were piped through culverts beneath roads and highways, and the creek itself has undergone engineered channelization over much of its length (Jill Piatt-Kemper, City of Aurora, oral commun., 2007).

Toll Gate Creek is presently (2012) a perennial stream; however, it was likely intermittent and/or ephemeral prior to urbanization, with only occasional or local flow, similar to Sand Creek, Coal Creek, and other plains streams originating in the central part of the Denver Basin and eastern Colorado (Nadler and Schumm, 1981; Friedman and Lee, 2002). Topographic maps from the 1960s show springs along West Toll Gate Creek near its confluence with East Toll Gate Creek, and historical accounts of the creek from the 1950s indicate perennial flow in some reaches at that time (Pyle, 1998). The channelized tributaries and culverts collect and carry shallow groundwater to the creek, and at low-flow (base flow) conditions, flow in Toll Gate Creek is supported primarily by groundwater inflow from the encompassing watershed (Paschke and others, 2012).

Hydrogeologic Setting

Near-surface groundwater hydrology in the Toll Gate Creek watershed is characterized by variably saturated Quaternary-aged unconsolidated surficial materials overlying the Cretaceous to early Tertiary-aged Denver Formation bedrock (Robson, 1996; Paschke, 2011).

The Denver Basin bedrock aquifer system is defined as the sandstone, siltstone, and claystone units of upper Cretaceous to Tertiary-aged rocks above the Pierre Shale (Romero, 1976; Van Slyke and others, 1988). Four primary aquifers compose the aquifer system, which from oldest to youngest are the Laramie-Fox Hills, Arapahoe, Denver, and Dawson (Romero, 1976; Robson, 1987; Graham and Van Slyke, 2004). The synclinal structure of the Denver Basin causes the bedrock units of the aquifer system to crop out in a ring pattern in which the oldest rocks of the Laramie-Fox Hills aquifer are exposed around the outer margins of the basin and the youngest rocks of the Dawson aquifer are exposed in the center of the basin (Paschke, 2011; fig. 4). Unconsolidated surficial materials overlie the Denver Basin bedrock aquifers, primarily along present-day stream channels, and form unconfined aquifers where saturated (Robson, 1987; Robson, 1996; fig. 4). In Toll Gate Creek, surficial materials include alluvial, colluvial, and aeolian deposits.

The Denver Formation underlying the unconsolidated sediments in the west-central part of the Denver Basin, including the Toll Gate Creek watershed, includes three of the Denver Basin hydrogeological units: (1) the Tertiary-aged lower Dawson aquifer, (2) the Tertiary-aged confining unit between the lower Dawson and Denver aquifers (Denver upper confining unit), and (3) the Cretaceous to Tertiary-aged Denver aquifer (fig. 4). These aquifer and confining units contain the Denver lignite zone of the Cretaceous to Tertiary-aged Denver Formation (Denver lignite zone), which consists of poorly consolidated claystone and occasional beds of consolidated siltstone or sandstone, local seams of low-rank coal (lignite), and volcanic-ash layers (Kirkham and Ladwig, 1979; Robson and Romero, 1981). Robson (1996) shows bedrock outcrops along the channel of upper West Toll Gate Creek, upstream from (south of) Quincy Reservoir and along the edges of valley-fill surficial materials downstream from the reservoir (fig. 5).

Where claystones are present at the land surface or beneath surficial materials, they generally form a confining unit, which inhibits the downward movement of shallow groundwater. The uppermost layers of outcropping claystones are commonly weathered to yellow-brown color, caused by the presence of secondary iron oxides, have a blocky appearance, and contain salt deposits (Paschke and others, 2012). The weathered bedrock is in hydraulic connection with the overlying surficial materials. The water table may occur in surficial deposits or in the weathered top of bedrock with depths to water generally less than 50 ft below land surface and saturated thickness generally less than 20 ft (Robson, 1996; Richard Vidmar, City of Aurora, written commun., 2007; Paschke and others, 2012). Groundwater in the surficial materials and weathered bedrock flows generally down valley and toward Toll Gate Creek (fig. 5). Toll Gate Creek is incised into weathered bedrock along much of its length such that the stream flows directly on bedrock. Seeps and springs are observed along the Toll Gate Creek channel margins and occur where groundwater emerges from the contact between the surficial materials and the underlying less-permeable claystone bedrock.

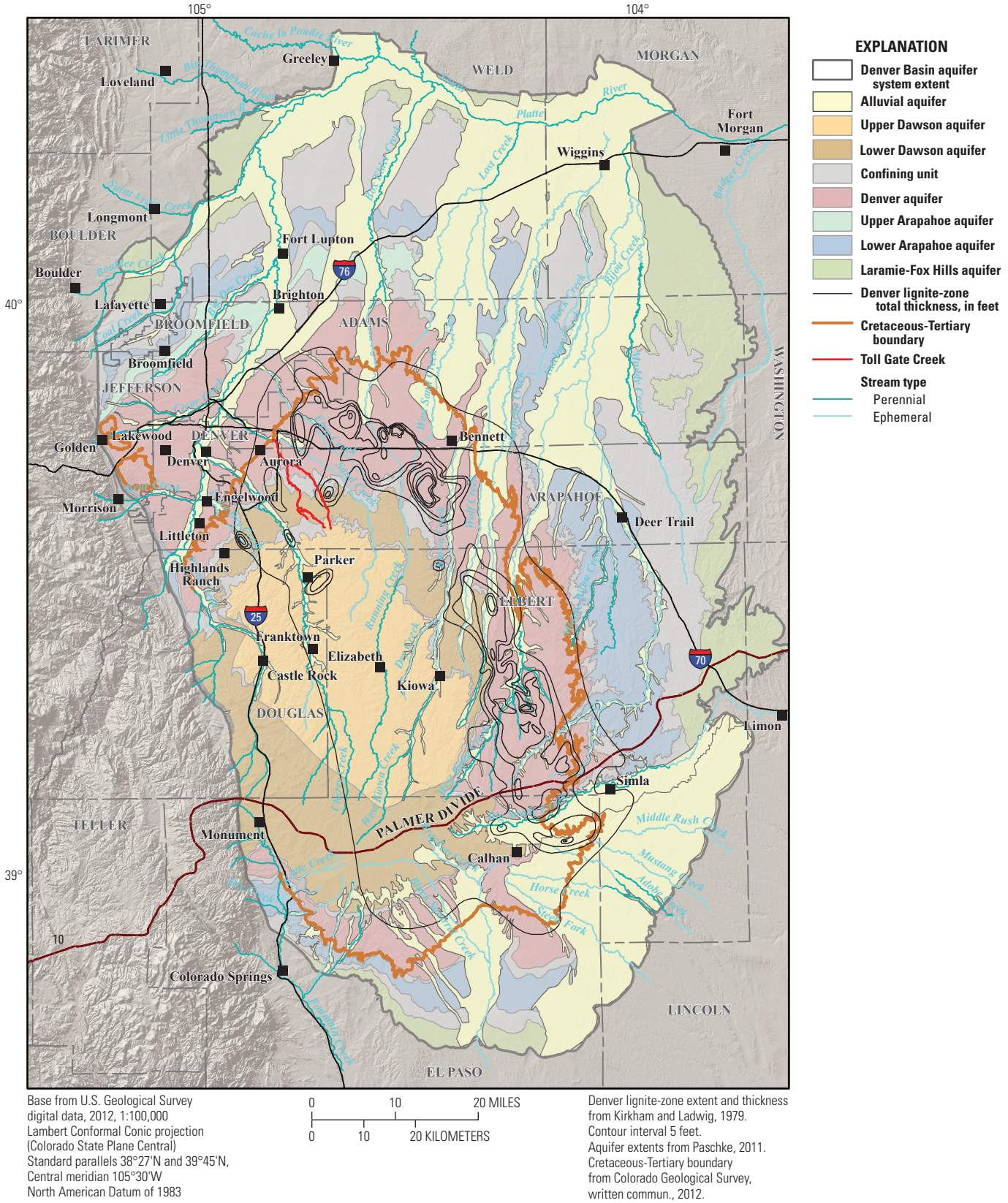


Figure 4. Map showing Denver Basin aquifer system, extent and thickness of the Denver lignite zone, and extent of the Cretaceous-Tertiary boundary in the Denver Basin.

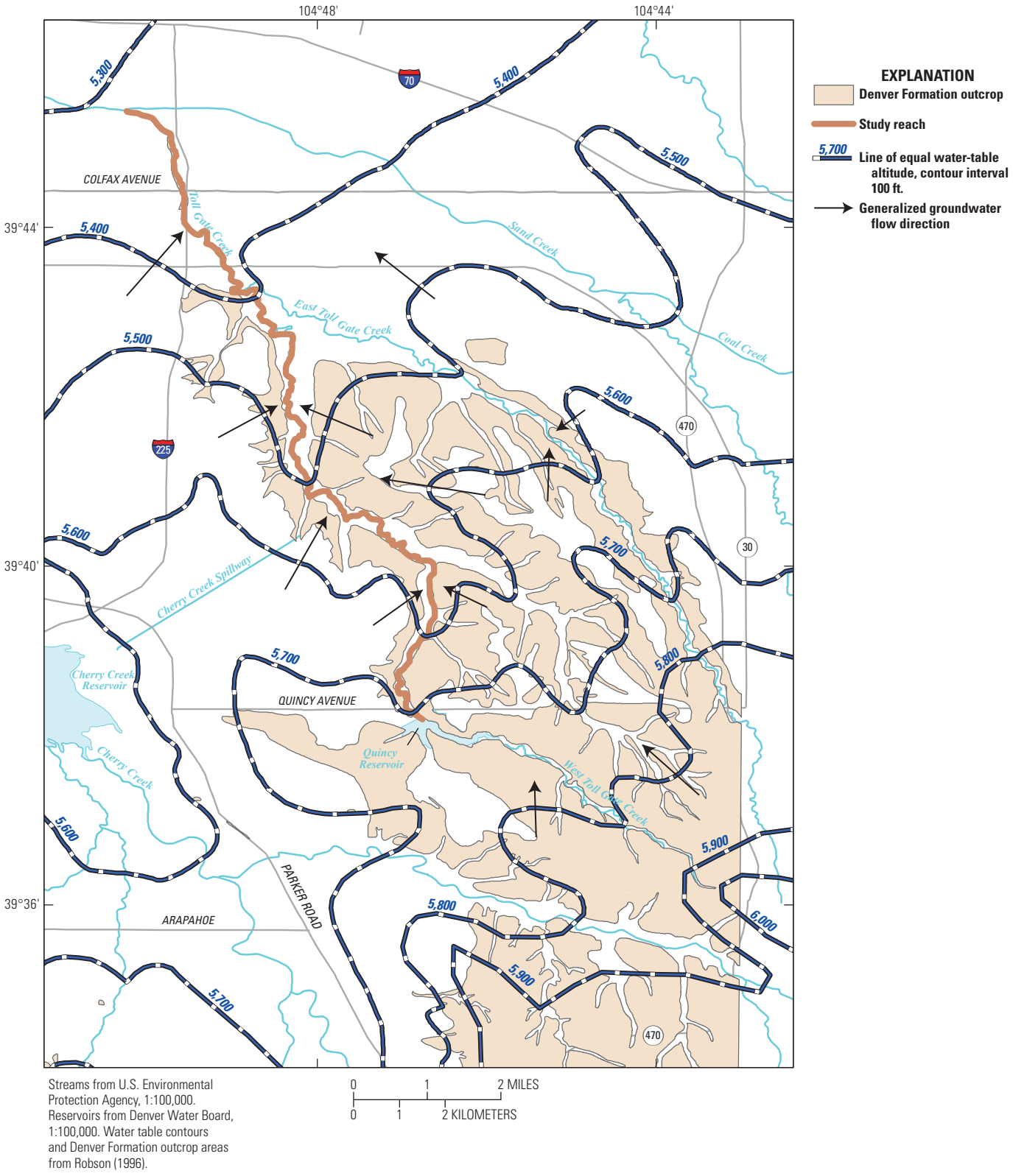


Figure 5. Map showing Denver Formation outcrop and water-table altitude contours, Toll Gate Creek, Aurora, Colorado.

Geologic Sources of Selenium in the West-Central Denver Basin

The Cretaceous- to Tertiary-aged (Paleocene) aquifers and confining units that crop out in the west-central part of the Denver Basin contain the Denver lignite zone, and the weathering of these bedrock units is the hypothesized source of selenium to groundwater and surface water.

Denver Formation

The stratigraphic sequence that encompasses the Denver lignite zonc has been defined by various naming conventions. On the basis of aquifer and confining-unit extents (Paschke, 2011) and the spatial distribution for the lignite (Kirkham and Ladwig, 1979), the Denver lignite zone is stratigraphically associated with the upper part of the Denver aquifer, the upper Denver confining unit, and the lower Dawson aquifer in the west-central part of the Denver Basin including Toll Gate Creek (fig. 4). This sequence has been named the Denver Formation by previous researchers and consists of a 600 to 1,100 foot-thick sequence of interbedded shale, claystone, siltstone, sandstone, lignite, and volcanic-ash deposits (Romero, 1976; Robson and Romero 1981; Robson, 1987) that includes the K-T boundary (Nicols and Flemming, 2002).

The Denver Formation is part of the D1 sequence of Raynolds (2002) and represents the synorogenic deposition of sediments in the Denver Basin during Laramide uplift of the Rocky Mountain Front Range to the west. The depositional environment during Denver Formation sedimentation consisted of alluvial fan deposition near the mountain front, where sandstone beds are prevalent (Weimer, 1972; Soister, 1978; Crifasi, 1992; Raynolds, 2002). Farther from the mountain front, finer grained sediments and coal were deposited in swamps in the northern, central, and eastern parts of the basin (Weimer, 1972; Soister, 1978; Kirkham and Ladwig, 1979; Robson and Romero, 1981; Robson, 1987; Crisfasi, 1992). Volcanic activity also increased in the Rocky Mountain Front Range during deposition of the Denver Formation, so that the sequence contains andesitic sandstones, volcanic-ash layers, and extensive claystone deposits (Kirkham and Ladwig, 1979; Tweto, 1980; Robson and Romero, 1981). The K-T boundary lies within the upper part of the Denver Formation in the west-central part of the Denver Basin and is closely defined by vertebrate fossils (Tweto, 1980) and palynological evidence (Nichols and Fleming, 2002).

Denver Lignite Zone

Lignite beds occurring in the top 300 to 500 ft of the Denver Formation form the Denver lignite zone (Kirkham and Ladwig, 1979; Gaggiani and others, 1987; Eakins and Ellis, 1987), which extends over a roughly kidney-shaped area from just northeast of Toll Gate Creek to several miles south of Calhan, encompassing about 1,700 square miles (mi^2) (Kirkham and Ladwig, 1979) and parts of the K-T boundary (fig. 4).

The Denver lignite zone consists of three to eight mapped lignite beds with several thinner and carbonaceous beds (Kirkham and Ladwig, 1979). The zone also contains claystone, siltstone, and sandstone beds, and most lignite beds contain numerous non-coal clay partings that range from less than 0.1 inch to about 2 ft (0.3 to 61 centimeters) in thickness (Kirkham and Ladwig, 1979). Many partings are composed of kaolinite clay, the origin of which has not been studied in detail. However, Kirkham and Ladwig (1979) indicate that at least a few of the partings are altered volcanic-ash layers (tonsteins) similar to those described by Bohor and others (1976) for other basins in the Rocky Mountain area. The Denver lignite zone has been dated by palynological evidence as Early Paleocene (Soister and Tschudy, 1978) above the K-T boundary. More recent work on the K-T boundary in the Denver Basin identifies tonsteins and associated lignites as both Cretaceous and Paleocene in age based on palynological samples from West Bijou Creek (Nichols and Fleming, 2002). Nichols and Fleming (2002) identify an approximately 1.5-inch (3-centimeters) thick tonstein parting within a lignite bed along West Bijou Creek as the K-T boundary on the basis of pollen assemblages, the presence of shock-metamorphosed quartz grains (Barclay and others, 2003), and an iridium-abundance anomaly. Results from Nichols and Fleming (2002) indicate that the Denver lignite zone contains the K-T boundary in some parts of the Denver Basin.

Coal beds and volcanic-ash partings in the Denver Formation were exposed during excavation and construction at the Denver International Airport (DIA) just north of Toll Gate Creek (Nichols and Fleming, 2002). The coal deposit exposed at DIA is considered an unnamed bed probably associated with the "northern lignite area" of the Denver Basin as described by Kirkham and Ladwig (1979) and is stratigraphically below the E lignite bed (Nichols and Fleming, 2002). Palynological analysis of the unnamed DIA coal bed provided insight to the depositional environment and plant community of the area during earliest Paleocene time and indicates a peat swamp with a plant community dominated by ferns and sphagnum moss developed in a fluvial setting forested by palms and other angiosperms (Nichols and Fleming, 2002). The uppermost Cretaceous plant species become extinct at the K-T boundary as they are absent from the Paleocene coal deposits (Nichols and Fleming, 2002). Volcanic ash fell into the Paleocene peat swamp at fairly regular intervals and formed the claystone partings observed within the coal (Kirkham and Ladwig, 1979; Nichols and Fleming, 2002). However, the ash falls did not seem to have had a destructive effect on the plant community of the swamp as spore and pollen assemblages below and above the ash beds are quite similar in composition (Nichols and Fleming, 2002). Forty-seven ash falls were identified in an 8-ft thick coal bed, and an estimated 15,000 to 20,000 years were required to deposit the earliest Paleocene DIA coal bed (Nichols and Fleming, 2002).

The extent of lignite and claystone beds in the vicinity of the Toll Gate Creek watershed was investigated by constructing a series of geologic cross sections. The sections were constructed on the basis of drilling logs from water-well permits and thus the geologic descriptions are somewhat generalized to terms such as "clay," "shale," "sand," and "coal," for example. The constructed sections A-A' through F-F' (figs. 6*A*–6*F*) confirm that Denver Formation lignite and claystone occur commonly near land surface beneath the Toll Gate Creek watershed, which is consistent with regional geologic information. The presence of claystone bedrock also was noted along stream banks during tracer-injection and synoptic sampling activities in Toll Gate Creek in 2007 (Paschke and others, 2012).

Denver Formation Weathering

In the Denver Basin, total uplift and erosion have resulted in removal of about 10,500 ft of sediment on the western edge of the basin and about 2,000 ft of sediment removal in the northern and eastern parts of the basin (Noe and others, 2007a). Present-day topography of the Denver Basin has evolved over the past 2 million years during glacial and interglacial periods, with downcutting and erosion of pediment surfaces and alluvial valleys and deposition of late Pliocene to Holocene terrace and flood-plain alluvial deposits (Hunt, 1955; Noe and others, 2007a). The near-surface bedrock has been subject to rebound and weathering processes for the past 10,000 years beneath valleys and modern streams and up to 2 million years beneath the highest pediment surfaces because of the erosion and sediment removal (Hunt, 1955; Noe and others, 2007a).

Erosion, rebound, and weathering have created variably weathered zones in the near-surface claystone bedrock of the Denver Formation that are up to about 70 ft thick (Noe and others, 2007a). These weathered zones contain a high density of fractures and are oxidized compared to unweathered bedrock (Noe and others, 2007a; 2007b; Paschke and others, 2012). Weathering and oxidation of claystone bedrock can oxidize selenium-bearing organic materials and pyrite, releasing DOC and trace elements to the environment and leaving secondary deposits of iron oxide and salts in the weathered zone (Naftz and Rice, 1989; Kulp and Pratt, 2004). Concentrations of dissolved selenium in groundwater were correlated to DOC concentrations for shallow groundwater in the Toll Gate Creek watershed (Paschke and others, 2012) and secondary iron oxide and gypsum deposits are observed in the weathered Denver Formation (Paschke and others, 2012). Selenium released by weathering processes can occur as a trace element in the structure of gypsum ($CaSO_4$) and other secondary salts (for example, thenardite ($NaSO_4$) in the weathered zone) (Fernández-González and others, 2006; Tuttle and others, 2005). Selenium-bearing secondary salts that have accumulated along fractures and bedding planes in the weathered zone are readily dissolved by groundwater and surface watear and constitute a potential geologic source of selenium in the west-central Denver Basin.

Selenium Concentrations in the West-Central Denver Basin

Selenium concentrations in groundwater and geologic materials in the west-central Denver Basin are discussed in this report section and provide evidence that the Denver Formation is a geologic source of selenium.

Groundwater

Results of the analyses of water samples collected from 60 monitoring wells in 2003 (well AGLUS 28 was a dry well) indicate that the concentrations of dissolved selenium in groundwater in the west-central Denver Basin ranged from 0.2 to 969 µg/L (fig. 7; table 2). Concentrations of dissolved selenium exceeded the Colorado aquatic-life standard (4.6 µg/L) in 19 of 31 samples (61 percent of samples) and exceeded the primary drinking-water standard (50 µg/L) in 5 of 31 samples (16 percent of samples) from the non-irrigated agricultural land-use study wells. For the urban land-use study wells, concentrations of dissolved selenium exceeded the Colorado aquatic-life standard in 19 of 29 samples (66 percent of samples) and exceeded the primary drinking-water standard in 6 of 29 samples (21 percent of samples). The mean and median concentrations of selenium in samples from urban land-use monitoring wells (81.5 and 9.7 µg/L, respectively) were greater than the mean and median concentrations in samples from non-irrigated agricultural land-use monitoring wells (35.6 and 6.2 µg/L, respectively) (fig. 7). In the semi-arid climate, infiltrating agricultural or urban irrigation water can potentially mobilize selenium from the unsaturated zone at rates greater than native recharge, and elevated selenium concentrations are expected in irrigated areas (Seiler and others, 1999; DeSimone and others, 2009). However, results from a Wilcoxon two-sided rank-sum test (Helsel and Hirsch, 1992) indicate that there was not a statistically significant difference between the mean concentrations of selenium for the two different land-use areas (p-value of 1.0 for the two-sided test).

The spatial distribution of concentrations of dissolved selenium in groundwater for 2003 (fig. 8) shows that the Colorado aquatic-life standard of 4.6 µg/L and the primary drinking-water standard of 50 µg/L were exceeded near Highlands Ranch, in the Toll Gate Creek watershed, and in the northeastern extent of the Denver lignite zone. The spatial distribution of the selenium concentrations is somewhat biased by the locations of installed wells, whose locations were selected on the basis of land use rather than targeting suspected sources of selenium. However, the results indicate that concentrations of dissolved selenium at the water table are greater than the Colorado aquatic-life and primary drinking-water standards in areas underlain by Denver Formation claystone and lignite.

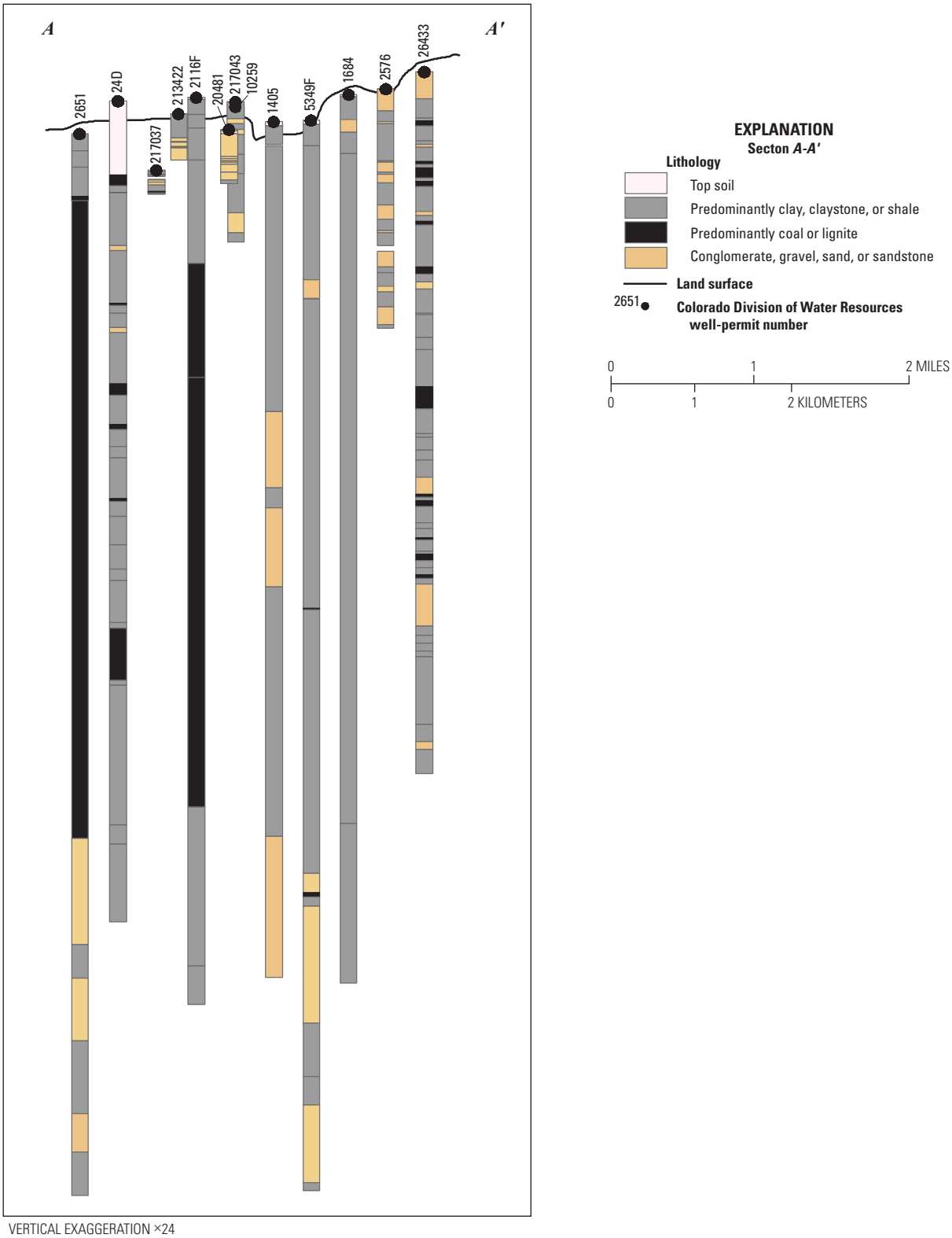
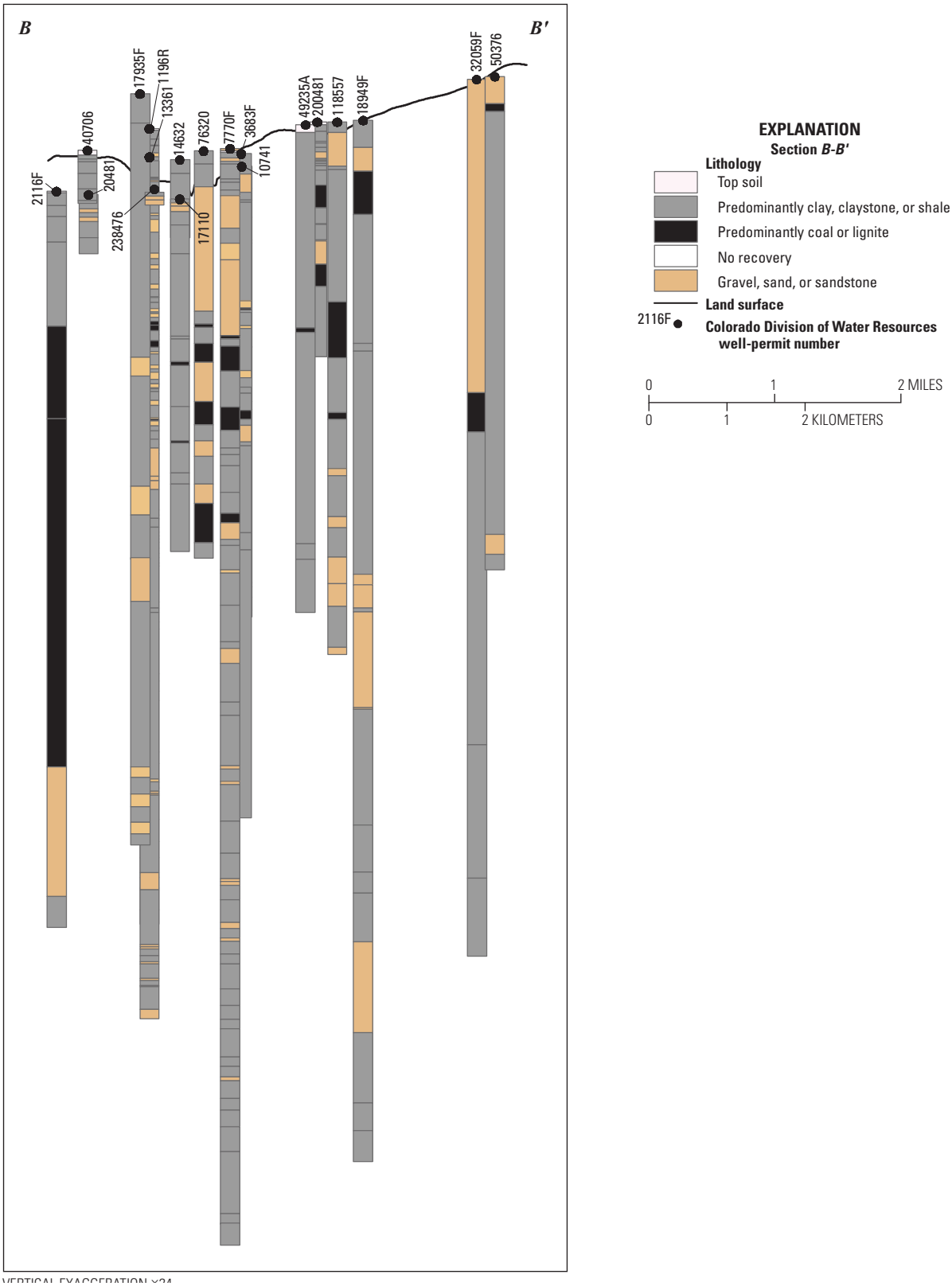
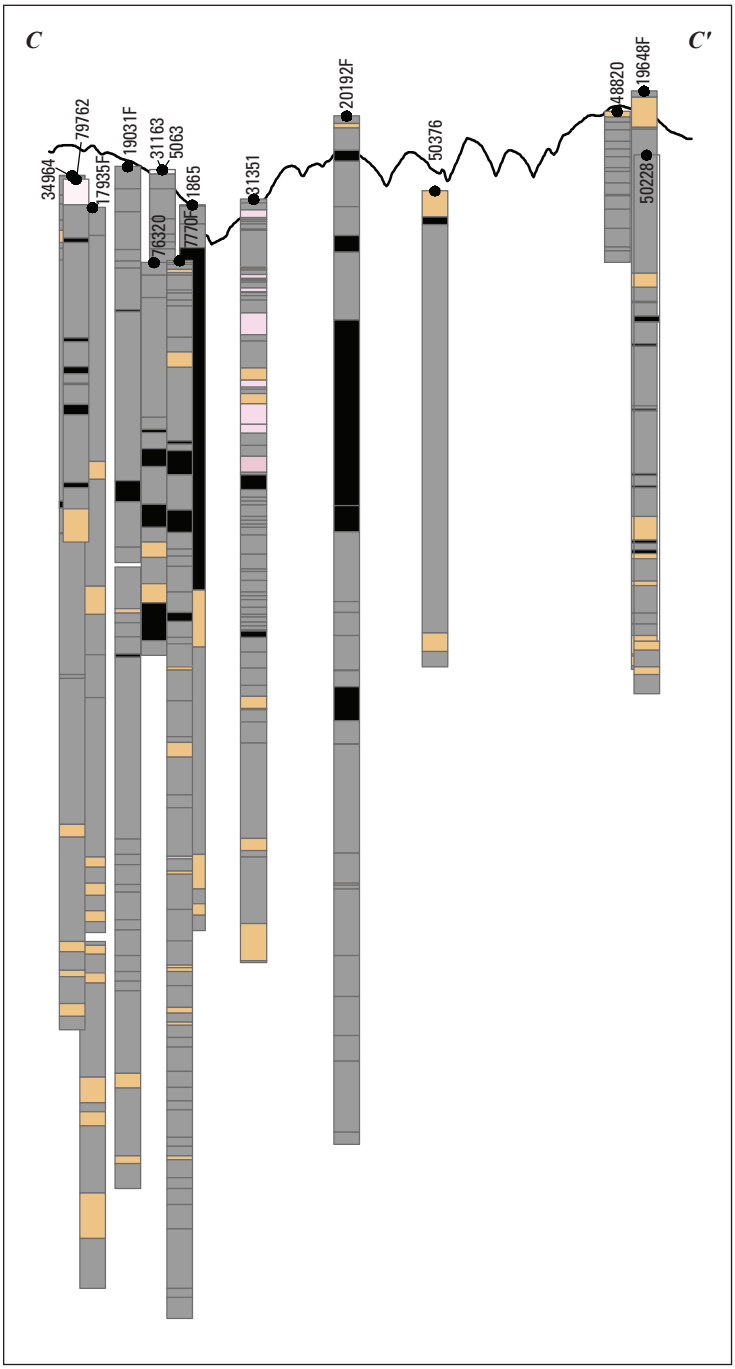


Figure 6 (above and following pages). Geologic sections *A-A′* through *F-F′* through near-surface Denver Formation in the vicinity of Toll Gate Creek.


B
B′
2116F
40706
20481
238476
17935F
13361
1196R
14632
76320
17110
7770F
3683F
10741
49235A
200481
118557
18949F
32059F
50376
EXPLANATION
Section B-B′
Lithology
Top soil
Predominantly clay, claystone, or shale
Predominantly coal or lignite
No recovery
Gravel, sand, or sandstone
Land surface
2116F
Colorado Division of Water Resources well-permit number
0
1
2 MILES
0
1
2 KILOMETERS
VERTICAL EXAGGERATION ×24



VERTICAL EXAGGERATION ×24

EXPLANATION

Section *C-C′*

Lithology

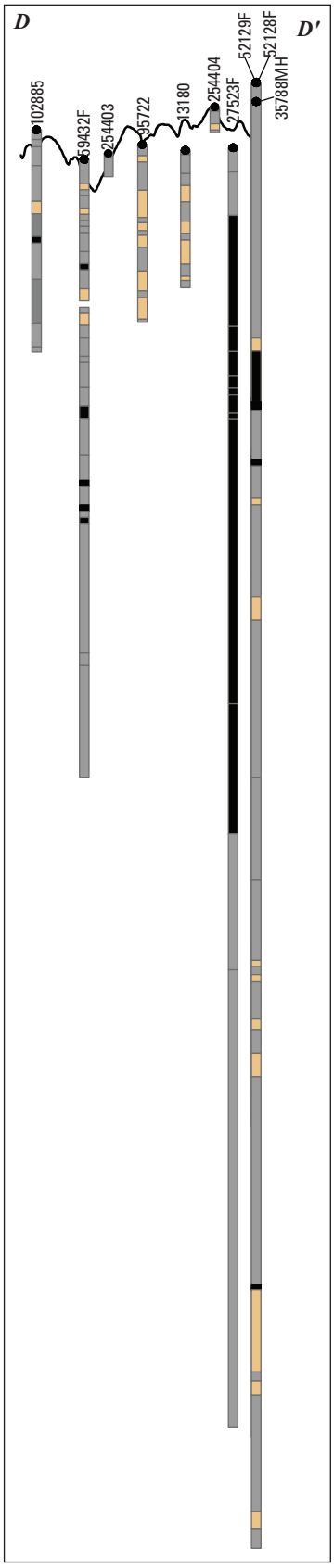
- Top soil
- Predominantly clay, claystone, or shale
- Predominantly coal or lignite
- No recovery
- Sand or sandstone
- Silt or siltstone

Land surface

34964 ● **Colorado Division of Water Resources well-permit number**

0 1 2 3 MILES

0 1 2 3 KILOMETERS



VERTICAL EXAGGERATION ×24

EXPLANATION

Section *D-D′*

Lithology

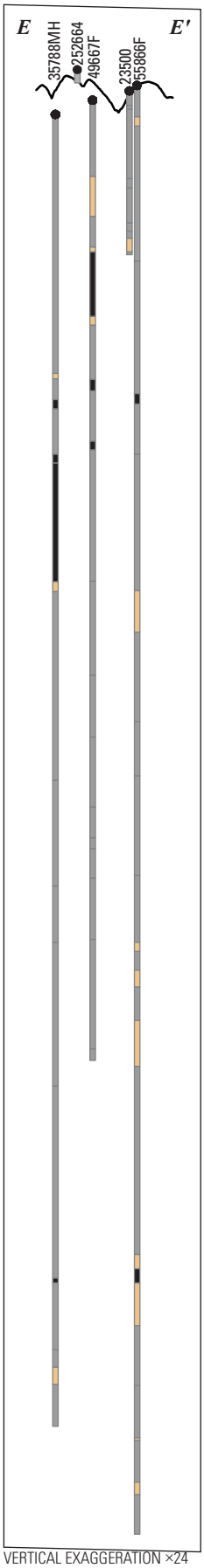
- Top soil
- Predominantly clay, claystone, or shale
- Predominantly coal or lignite
- Gravel, sand, or sandstone

Land surface

13180 **Colorado Division of Water Resources well-permit number**

0 1 2 MILES

0 1 2 KILOMETERS



VERTICAL EXAGGERATION ×24

EXPLANATION

Section *E-E′*

Lithology

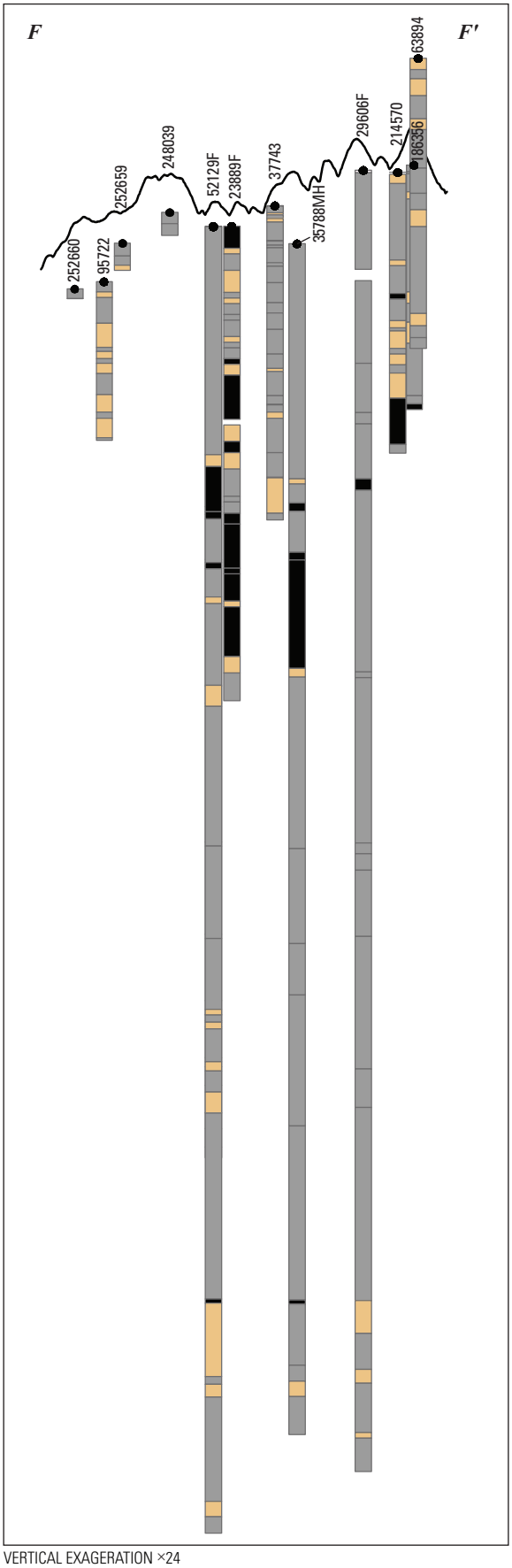
- Top soil
- Predominantly clay, claystone, or shale
- Predominantly coal or lignite
- Sand or sandstone

Land surface

23500 **Colorado Division of Water Resources well-permit number**

0 1 2 3 MILES

0 1 2 3 KILOMETERS



VERTICAL EXAGERATION ×24

EXPLANATION

Section *F-F′*

Lithology

- Top soil
- Predominantly clay, claystone, or shale
- Predominantly coal or lignite
- Gravel, sand, or sandstone

Land surface

37743 ● **Colorado Division of Water Resources well-permit number**

0 1 2 3 MILES

0 1 2 3 KILOMETERS

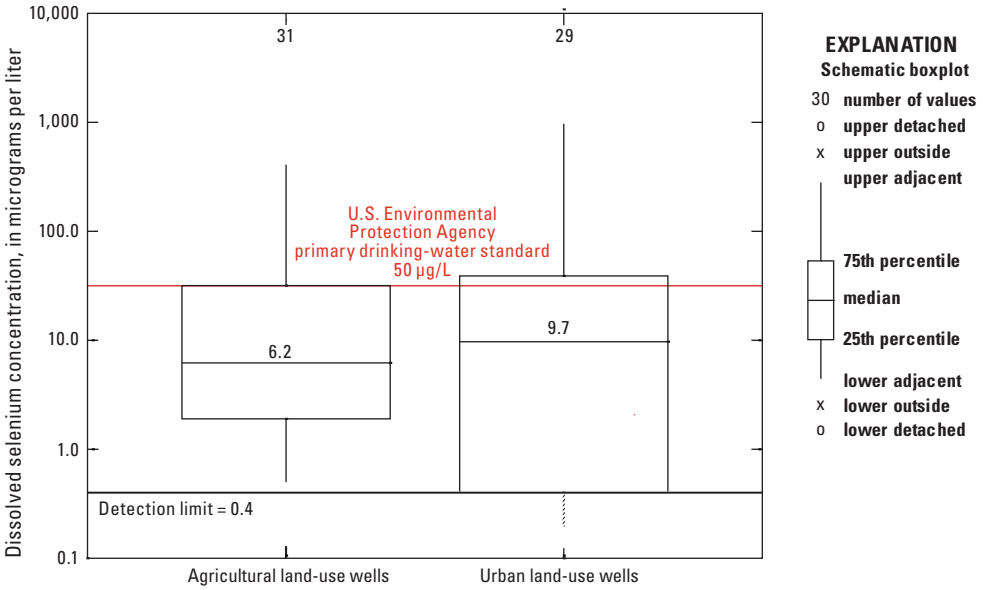


Figure 7. Graph showing statistical distribution of concentrations of dissolved selenium in groundwater samples from agricultural and urban land-use wells in the west-central Denver Basin, Colorado, 2003.

Groundwater-selenium concentrations for 14 monitoring wells sampled in 2007 in the vicinity of Toll Gate Creek (Paschke and others, 2012; fig. 9) were, in general, substantially greater than the Toll Gate Creek inflow and stream selenium concentrations, greater than the Colorado aquatic-life standard, and at some locations greater than the primary drinking-water standard. Concentrations of selenium in groundwater ranged from a minimum of 0.1 µg/L to a maximum of 264 µg/L, with a mean value of 48.1 µg/L and a median value of 27.9 µg/L. Concentrations of selenium in groundwater were greatest in monitoring wells completed in the weathered Denver Formation claystone and lignite, providing further evidence that the Denver Formation is a geologic source of selenium.

Geologic Samples

Results of the core-sample analyses for selenium (table 1) indicate that total selenium was present above the detection limit of 0.1 parts per million in 13 of the 14 samples. Total selenium concentrations in the geologic core samples ranged from 0.11 to 13 parts per million and were greatest in samples containing indications of in-situ reducing conditions and organic matter (dark gray to black claystones and lignite horizons).

The seven core samples containing the greatest concentrations of total selenium were selected for paste extraction. These samples included five samples of dark gray to black claystone and lignite and two samples of oxidized (yellow to orange) claystone and sandstone (table 1). Selenium concentrations in the paste extractions ranged from 8.14 to 4,600 µg/L and were greatest in dark gray claystone from well AGLUS 5. The lowest selenium concentration was measured in one of the more oxidized samples that contained staining from oxidized iron minerals. The lignite sample had the second lowest selenium concentration in the paste extractions. The paste-extraction results indicate that water-soluble forms of selenium are most abundant in organic-rich reduced claystones of the Denver Formation and that water-soluble forms of selenium are least abundant in weathered iron-rich sediments of the Denver Formation. These finding support the conclusion that water-soluble forms of selenium have been leached from weathered zones.

Mobilization and Transport of Selenium

The Toll Gate Creek watershed is situated in a unique hydrogeologic setting in the west-central part of the Denver Basin such that weathering of Cretaceous- to Tertiary-aged, non-marine, selenium-bearing rocks releases selenium to groundwater and surface water under present-day semi-arid environmental conditions (fig. 10). The Denver Formation contains several known and suspected geologic sources of selenium in the west-central part of the Denver Basin including (1) lignite deposits; (2) tonstein partings; (3) organic-rich bentonite claystones; (4) salts formed as secondary weathering products; and possibly (5) the K-T boundary. Solids sampling and paste-extraction results indicate that water-soluble forms of selenium in paste extractions were greatest for less weathered dark gray organic-rich claystones of the Denver Formation. Organically complexed selenium and/or selenium-bearing pyrite in the enclosing claystones are likely the primary mineral sources of selenium in the Denver Formation (Michele Tuttle, U.S. Geological Survey, oral commun., 2012). Paste extraction results and correlations between concentrations of dissolved selenium and DOC in groundwater (Paschke and others, 2012) indicate weathering and dissolution of organically complexed selenium from organic-rich claystone is a primary process mobilizing selenium. Secondary salts accumulated along fractures and bedding planes in the weathered zone are another potential geologic source of

Table 2. Station and sampling information and concentrations of dissolved selenium in groundwater samples from agricultural and urban land-use wells in the west-central Denver Basin, Colorado, 2003.

[Horizontal datum provided in Universal Transverse Mercator (UTM), Zone 13, North American Datum of 1983 (NAD83); NAWQA, National Water-Quality Assessment; USGS, U.S. Geological Survey; ft, feet; NGVD29, National Geodetic Vertical Datum of 1929; µg/L, micrograms per liter; mg/L, milligrams per liter; <, less than; E, estimated value less than long-term method detection limit]

Associated study	USGS site identification number	Local well name	Sample date	Dissolved selenium concentration (µg/L)	Dissolved oxygen concentration (mg/L)
NAWQA Agricultural land-use study	394310104393401	AGLUS-1	7/29/2003	6.6	2.4
	394838104255301	AGLUS-2	7/22/2003	1.5	7.2
	395300104253301	AGLUS-3	7/17/2003	5.3	8.6
	395324104234301	AGLUS-4	7/17/2003	5.8	9.0
	395450104402701	AGLUS-5	8/12/2003	408	1.6
	395909104350401	AGLUS-6	7/28/2003	150	6.6
	395541104385701	AGLUS-7	7/28/2003	137	4.3
	395211104351601	AGLUS-8	7/24/2003	31.8	4.6
	394858104345901	AGLUS-9	8/13/2003	6.2	1.2
	395115104234401	AGLUS-10	8/19/2003	40.4	7.7
	394953104244601	AGLUS-11	7/15/2003	3.9	2.6
	394539104305901	AGLUS-12	8/4/2003	92.6	2.8
	394731104260001	AGLUS-13	7/24/2003	8.8	7.6
	394947104335201	AGLUS-14	7/31/2003	0.6	8.6
	395119104321001	AGLUS-15	8/6/2003	0.6	1.5
	394933104304101	AGLUS-16	8/13/2003	26.8	16.3
	395540104353601	AGLUS-17	8/7/2003	1.9	3.8
	395352104302801	AGLUS-18	7/31/2003	31.4	9.2
	395208104310201	AGLUS-19	8/5/2003	50.3	17.4
	394919104291001	AGLUS-20	8/4/2003	4.9	11.5
	394838104310001	AGLUS-21	7/21/2003	21.8	8.3
	394339104313601	AGLUS-22	8/14/2003	0.6	3.6
	394530104283901	AGLUS-23	8/14/2003	3.4	0.4
	394614104270701	AGLUS-24	7/16/2003	<0.5	0.5
	394746104301901	AGLUS-25	8/6/2003	1.0	5.2
	394956104274101	AGLUS-26	7/7/2003	36.0	11.8
	395149104260701	AGLUS-27	7/14/2003	9.7	7.6
	395352104252801	AGLUS-28	7/23/2003	dry well	dry well
	395324104281401	AGLUS-29	7/23/2003	7.3	8.9
	395443104275901	AGLUS-30	7/18/2003	4.4	8.0
	395201104274001	AGLUSREF1	7/10/2003	2.8	7.3
	394351104302901	AGLUSREF2	7/30/2003	<0.5	0.5
NAWQA Urban land-use study	393158104550701	URLUS-1	10/29/2003	E0.4	9.3
	393301104561601	URLUS-2	10/28/2003	969	11.1
	393306104570201	URLUS-3	10/28/2003	9.7	5.4
	393404104565101	URLUS-4	11/12/2003	<0.4	0.1
	393445104563501	URLUS-5	11/12/2003	<0.4	0.1
	393458104544101	URLUS-6	11/20/2003	30.6	0.2
	393408104544001	URLUS-7	11/20/2003	6.4	0.8
	393327104542001	URLUS-8	10/27/2003	0.4	7.5
	393304104545101	URLUS-9	10/27/2003	167	6.1
	393229104541101	URLUS-10	10/29/2003	142	9.7
	392433104541101	URLUS-11	11/17/2003	38.9	11.9
	392210104482901	URLUS-12	11/18/2003	15.8	10.3
	393138104471901	URLUS-13	11/14/2003	<0.4	1.3
	393412104534601	URLUS-14	11/13/2003	<0.4	0.1
	393726104474101	URLUS-15	11/13/2003	<0.4	0.8
	393836104474701	URLUS-16	11/18/2003	19.3	4.1
	393947104473801	URLUS-17	12/8/2003	2.9	1.9
	393846104465601	URLUS-18	12/8/2003	9.1	0.8
	393823104455801	URLUS-19	12/10/2003	306	5.7
	393733104465101	URLUS-20	12/10/2003	41.4	0.1
	393655104463001	URLUS-21	12/1/2003	8.0	0.3
	393654104472001	URLUS-22	12/1/2003	21.4	0.5
	393003104450001	URLUS-23	11/25/2003	0.8	3.0
	393057104441101	URLUS-24	11/25/2003	E0.2	0.3
	393700104454101	URLUS-26	12/2/2003	3.5	7.5
	393655104441901	URLUS-27	12/2/2003	10.1	0.6
	393742104453801	URLUS-28	11/19/2003	242	1.6
	393837104450101	URLUS-29	11/19/2003	15.4	0.3
	393903104455701	URLUS-30	11/21/2003	301	2.3

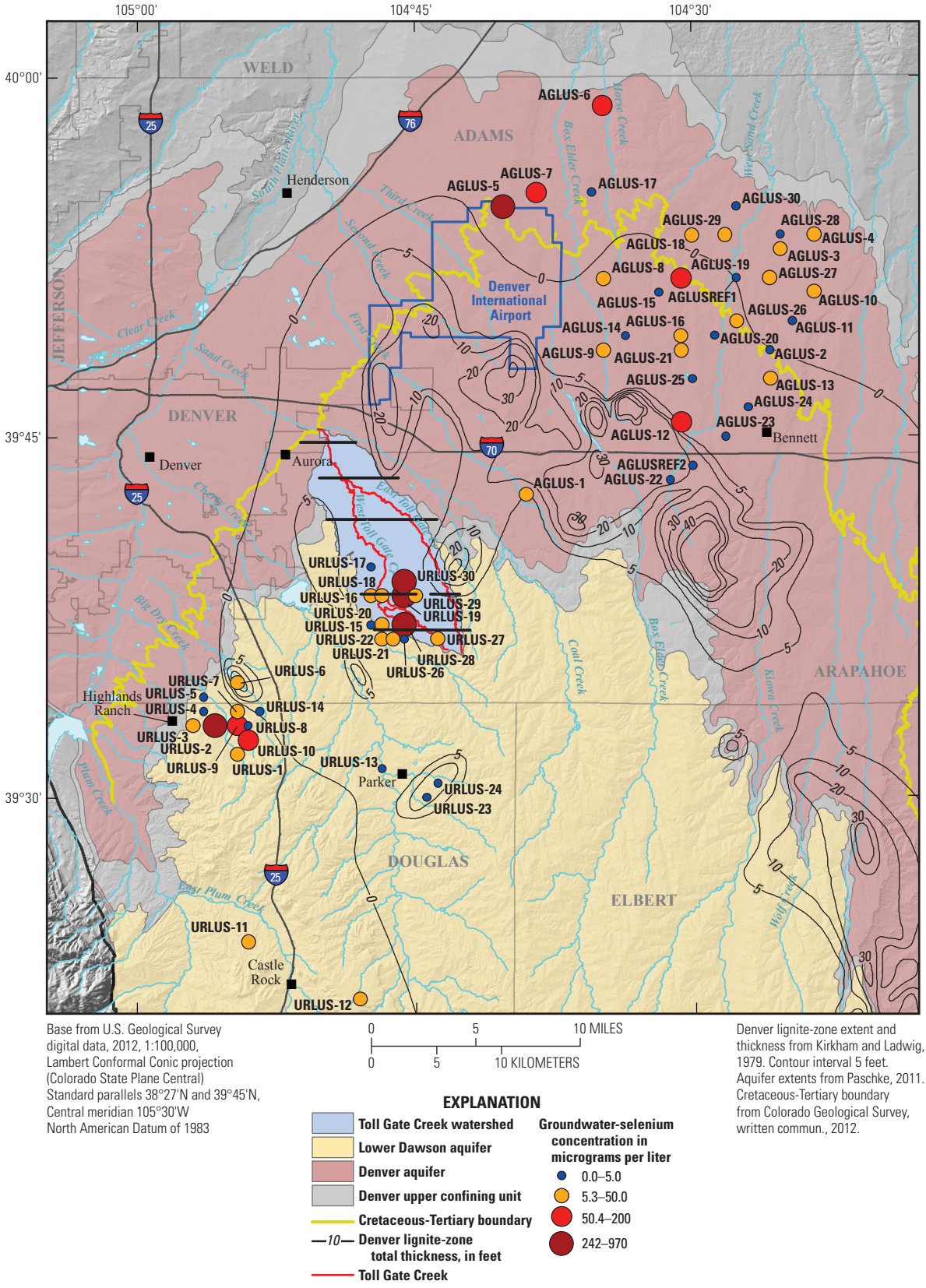


Figure 8. Map showing spatial distribution of monitoring wells, concentrations of dissolved selenium in groundwater, and Denver lignite-zone thickness, 2003.

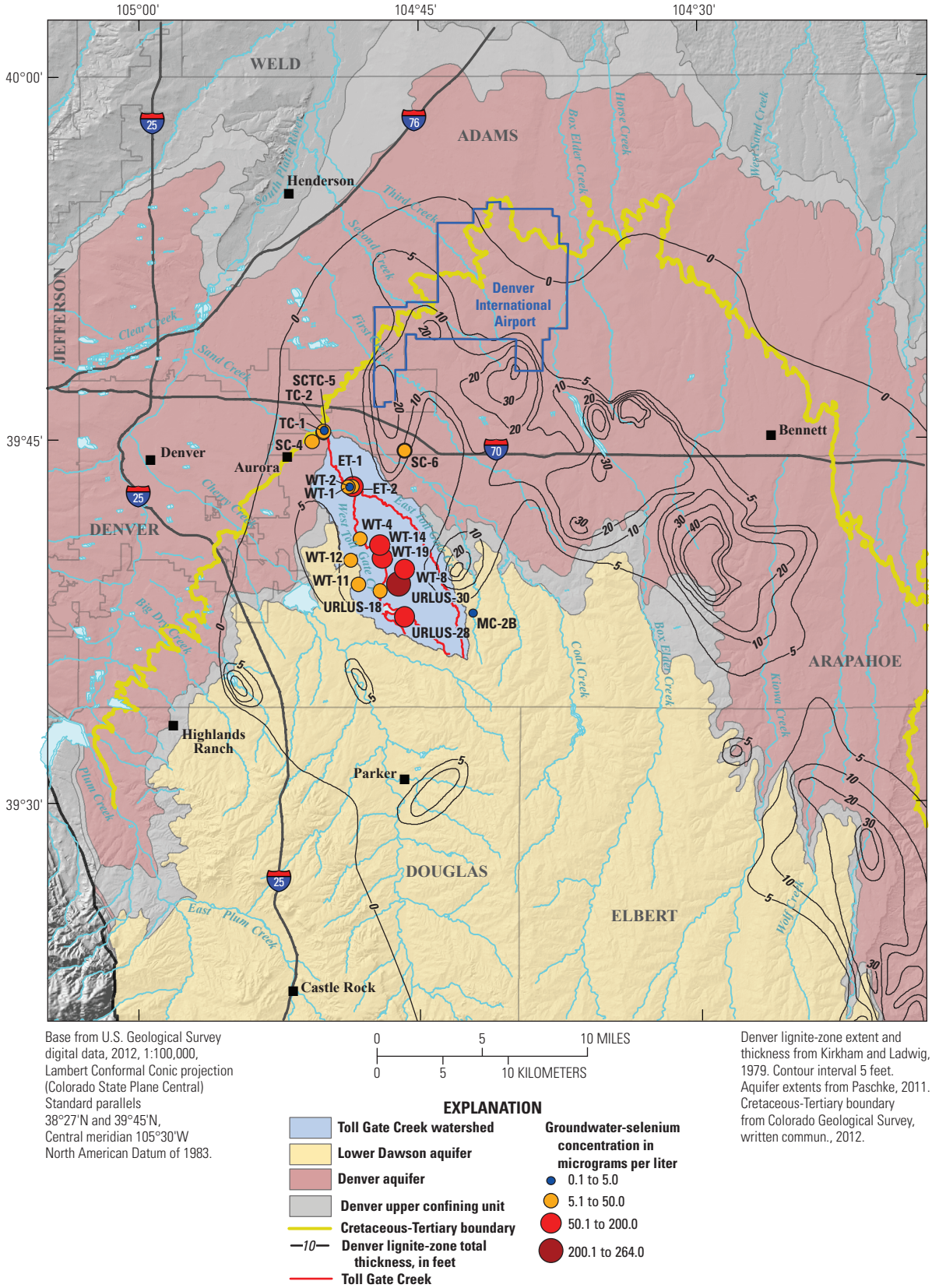


Figure 9. Map showing spatial distribution of monitoring wells, concentrations of dissolved selenium in groundwater, and Denver lignite-zone thickness, 2007.

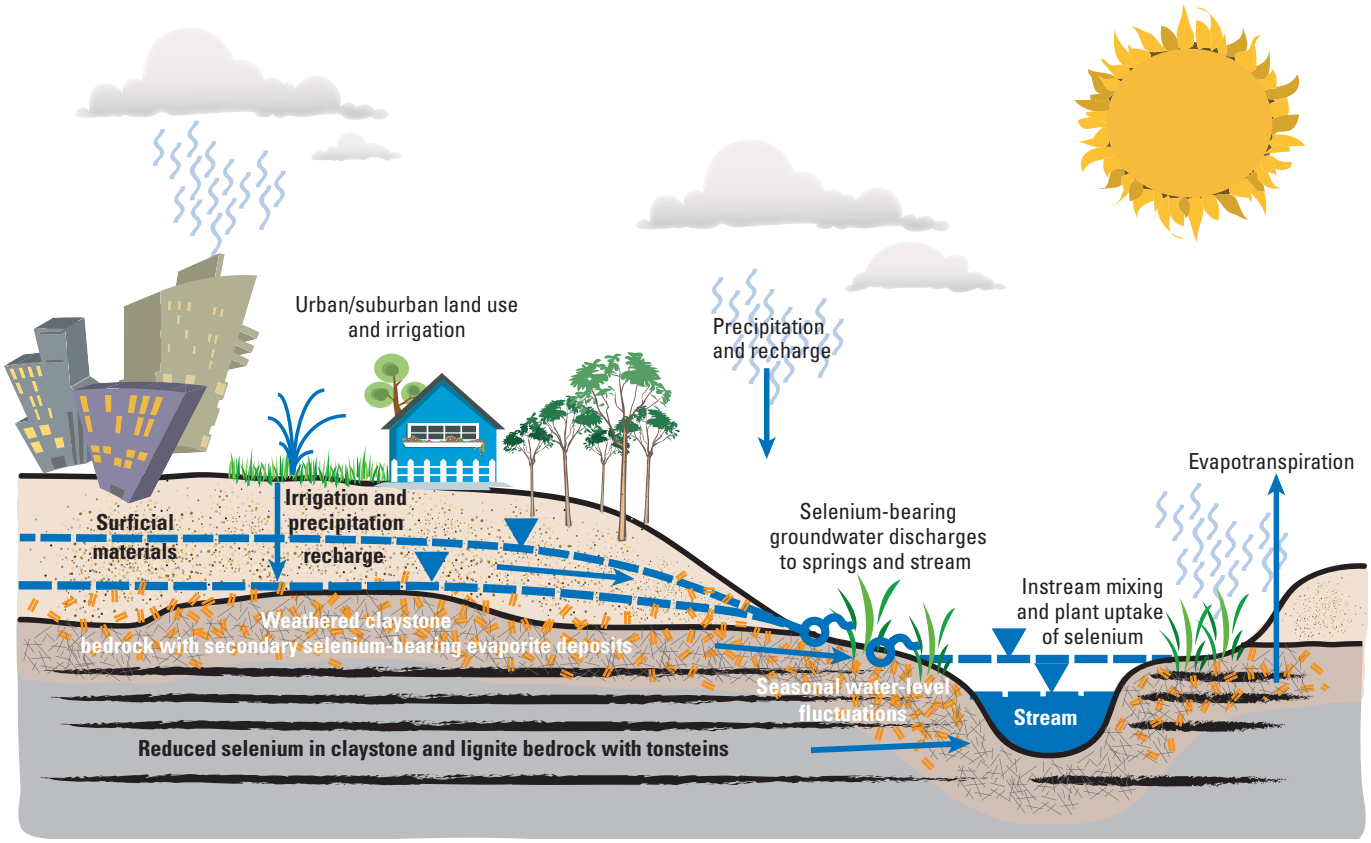


Figure 10. Conceptual diagram depicting selenium sources, mobilization, and transport in the Toll Gate Creek watershed.

water-soluble selenium (Tuttle and others, 2005), although their composition was not specifically addressed by the solids analyses.

Multiple weathering processes can release water-soluble selenium from the claystone bedrock into the shallow groundwater system where it is transported to downgradient discharge areas such as Toll Gate Creek. Exposure of the selenium-bearing rocks to the atmosphere, surface water, and groundwater results in the oxidation of selenide, held in complexes with organic matter or as a trace element in pyrite, to selenite and selenate. Oxidized (weathered) claystone samples with iron oxides contained lesser water-soluble selenium concentrations than the less-weathered samples, indicating that selenium may be somewhat leached from weathered bedrock or that selenite may be strongly sorbing to iron oxides. Secondary selenium-bearing salts in the weathered zone can later dissolve and release oxidized forms of selenium to groundwater and surface water (Michele Tuttle, U.S. Geological Survey, written commun., 2012). Results from this and previous work (Herring and Walton-Day, 2007; Paschke and others, 2012) indicate that shallow groundwater and streams similarly positioned over Denver Formation claystone units in other parts of the Denver Basin also may contain concentrations of dissolved selenium greater than the Colorado aquatic-life standard or the primary drinking-water standard.

Water-quality and solids-sampling results from this and previous studies (Herring and Walton-Day, 2007; Paschke and others, 2012) indicate ongoing weathering processes release water-soluble selenium from underlying claystone bedrock with subsequent cycling of selenium in the aquatic environment by evaporative and oxidation/reduction reactions (fig. 10). In the near surface, as stream and groundwater levels fluctuate, evaporative concentration and subsequent dissolution can cause selenium cycling between dissolved and solid phases. Ongoing evaporative processes can concentrate selenium in surface water, and evaporative salts are observed along stream banks, some of which have been identified as selenium bearing (Herring and Walton-Day, 2007). These evaporative deposits are rapidly dissolved during rainfall-runoff events, contributing selenium and other dissolved constituents to streams (Paschke and others, 2012). When water levels recede, evaporative deposits can again rapidly precipitate as evidenced by the presence of evaporative deposits along the banks of Toll Gate Creek (Herring and Walton-Day, 2007; Paschke and others, 2012). Oxidation/reduction reactions in groundwater and streams also promote selenium cycling. Oxidizing conditions favor selenium dissolution (mobilization), whereas reducing conditions promote reduction of selenium to immobile forms by either complexing with or sorbing to organic matter or precipitation as a selenium-bearing pyrite. In 2007, decreases in surface-water selenium concentrations were observed for samples from the reaches of Toll Gate Creek flowing through wetlands, where stagnant water and plant material created reducing conditions (Paschke and others, 2012).

Summary

In the semi-arid western United States, rainfall-runoff, infiltration, recharge, and groundwater/surface-water interaction processes naturally weather and erode selenium-bearing rocks and derived sediments, thereby contributing dissolved selenium to draining streams. Once present in aquatic systems, selenium can cycle in and out of the water column because of complexation, adsorption, evaporation, and oxidation-reduction (redox) chemical reactions. Dissolved selenium in streams and water bodies accumulates through the aquatic food chain, and its toxic effects can result in mortality, decreased reproduction, and deformities in offspring of fish and birds. The U.S. Environmental Protection Agency has established a primary drinking-water standard for selenium of 50 micrograms per liter (µg/L), and, in 1997, the State of Colorado established an aquatic-life standard for selenium of 4.6 µg/L. In Colorado, numerous streams are included on the Colorado list of impaired waters under provisions of Section 303(d) of the Clean Water Act of 1972 because concentrations of dissolved selenium exceed the aquatic-life standard, and many of these streams are in areas underlain by Cretaceous marine shale.

Toll Gate Creek, in the west-central part of the Denver Basin, is a perennial stream in which concentrations of dissolved selenium have consistently exceeded the Colorado aquatic-life standard. Recent studies of selenium in Toll Gate Creek identified the Denver lignite zone of the non-marine Cretaceous to Tertiary-aged (Paleocene) Denver Formation underlying the watershed as the geologic source of dissolved selenium to shallow groundwater and surface water. This report documents the occurrence of selenium-bearing rocks and groundwater within the Cretaceous- to Tertiary-aged Denver Formation in the west-central part of the Denver Basin, including the Toll Gate Creek watershed. The report presents background information on geochemical processes controlling selenium concentrations in the aquatic environment and possible geologic sources of selenium; the hydrogeologic setting of the watershed; selenium results from groundwater-sampling programs; and chemical analyses of solids samples from the present study as evidence that weathering of the Denver Formation is a geologic source of selenium to groundwater in the west-central part of the Denver Basin, including Toll Gate Creek.

Groundwater hydrology in the vicinity is characterized by variably saturated Quaternary unconsolidated surficial materials overlying the Cretaceous to early Tertiary-aged Denver Formation. The bedrock consists of poorly consolidated claystone and occasional beds of consolidated siltstone or sandstone, local seams of low-rank coal (lignite), and volcanic-ash layers. Where claystones are present at the land surface or beneath surficial materials, they generally form a confining unit, which inhibits the downward migration of shallow groundwater. Groundwater in the surficial materials and weathered bedrock generally flows down valley and toward streams. Seeps and springs are observed along the Toll Gate Creek channel margins and occur at the contact between the permeable surficial materials and the underlying claystone bedrock.

Analyses of samples collected from 60 monitoring wells in 2003 and from 14 monitoring wells in 2007 indicate concentrations of dissolved selenium in groundwater in the west-central Denver Basin frequently exceeded the Colorado aquatic-life standard and in some locations exceeded the primary drinking-water standard. The greatest selenium concentrations were associated with samples from wells completed in bedrock materials. Analytical results support the conclusion that selenium in groundwater is derived from geologic sources, although there was no statistical difference between concentrations of selenium in the water from wells in non-irrigated agricultural areas and water from wells in urban land-use study areas.

Results from selenium analysis of geologic core samples indicate that total selenium concentrations were greatest in samples containing indications of reducing conditions and organic matter (dark gray to black claystones and lignite horizons). Paste-extraction results for the seven core samples containing the greatest concentrations of total selenium indicate that water-soluble forms of selenium are most abundant in organic-rich, reduced claystones of the Denver Formation, and correlations between concentration of dissolved selenium and dissolved organic carbon in groundwater indicates weathering and dissolution of organically complexed selenium from organic-rich claystone is a primary process mobilizing selenium. Oxidized (weathered) claystone samples with iron oxides contained lesser water-soluble selenium concentrations than the less-weathered samples, indicating that selenium may be somewhat leached from weathered bedrock or that selenite may be strongly sorbing to iron oxides.

The Toll Gate Creek watershed is situated in a unique hydrogeologic setting in the west-central part of the Denver Basin such that weathering of Cretaceous- to Tertiary-aged, non-marine, selenium-bearing rocks releases selenium to groundwater and surface water under present-day semi-arid environmental conditions. The Denver Formation contains several known and suspected geologic sources of selenium including: (1) lignite deposits; (2) tonstein partings; (3) organic-rich bentonite claystones; (4) salts formed as secondary weathering products; and possibly (5) the Cretaceous-Tertiary boundary. Organically complexed selenium and/or selenium-bearing pyrite in the enclosing claystones are likely the primary mineral sources of selenium in the Denver Formation. Secondary salts accumulated along fractures and bedding planes in the weathered zone are another potential geologic source of selenium, although their composition was not specifically addressed by the solids analyses. Results from this and previous work indicate that shallow groundwater and streams similarly positioned over the Denver lignite zone at other locations in the Denver Basin also may contain concentrations of dissolved selenium greater than the Colorado aquatic-life standard or the primary drinking-water standard.

Acknowledgments

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