Prepared in cooperation with the University of Minnesota-Duluth Natural Resources Research Institute

Assessing the Influence of Natural Copper-Nickel-Bearing Bedrocks of the Duluth Complex on Water Quality in Minnesota, 2013–15

Scientific Investigations Report 2020–5039

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

Cover background. St. Louis River in northeastern Minnesota, September 2014. Photograph by Sarah M. Elliott.

Cover foreground and photograph, this page. Filson Creek in northeastern Minnesota, August 2014. Photographs by Sarah M. Elliott.

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	0.004047	square kilometer (km^2)
square foot (ft^2)	0.09290	square meter (m^2)
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.3048	meter per second (m/s)

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C = (°F – 32) / 1.8.

Datum

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

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

Supplemental Information

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

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

Abbreviations

®	registered trademark
Al	aluminum
As	arsenic
B	boron
Ba	barium
Be	beryllium
Bi	bismuth
C	carbon
Ca	calcium
Ce	cerium
Co	cobalt
CO_2	carbon dioxide
Cr	chromium
Cu	copper
DEM	digital elevation model
DOC	dissolved organic carbon
Fe	iron
Hg	mercury
ID	identification
ICP–AES	inductively coupled plasma–atomic emission spectrometry
ICP–MS	inductively coupled plasma–mass spectrometry
ISO	International Organization for Standardization
K	potassium
La	lanthanum
Li	lithium
lidar	light detection and ranging
LLD	lower limit of determination
Mg	magnesium
Mn	manganese
Mo	molybdenum
MRS	Midcontinent Rift System
Na	sodium
Nb	niobium
Ni	nickel

NOAA	National Oceanic and Atmospheric Administration
NSE	Nash-Sutcliffe efficiency
NWQL	National Water Quality Laboratory
OM	organic matter
OUI	oxide ultramafic intrusion
P	phosphorus
Pb	lead
PGE	platinum-group element
QA	quality assurance
QC	quality control
Rb	rubidium
RPD	relative percent difference
RSD	relative standard deviation
S	sulfur
Sb	antimony
Sc	scandium
Se	selenium
SO_4^{-2}	sulfate
Sr	strontium
Th	thorium
Ti	titanium
TOC	total organic carbon
U	uranium
USGS	U.S. Geological Survey
V	vanadium
W	tungsten
WQS	water-quality standard
Zn	zinc

Assessing the Influence of Natural Copper-Nickel-Bearing Bedrocks of the Duluth Complex on Water Quality in Minnesota, 2013–15

By Sarah M. Elliott,[1] Perry M. Jones,[1] Laurel G. Woodruff,[1] Carrie E. Jennings,[2] Aliesha L. Krall,[1] and Daniel L. Morel[1]

Abstract

The U.S. Geological Survey, in cooperation with the University of Minnesota-Duluth Natural Resources Research Institute, completed an assessment of regional water quality in areas of potential base-metal mining in Minnesota. Bedrock, soil, streambed sediment, and surface-water samples were collected in three watersheds that cross the basal part of the Duluth Complex with different mineral-deposit settings: (1) copper-nickel-platinum group element mineralization (Filson Creek), (2) iron-titanium-oxide mineralization (headwaters of the St. Louis River), and (3) no identified mineralization (Keeley Creek). At least 10 bedrock, 30 soil (2 each from 15 sites), and as many as 13 streambed sediment samples were collected in each watershed and analyzed for 44 major and trace elements, total and inorganic carbon, and 10 loosely bound metals (when possible). Surface-water samples were collected at four to nine locations in each watershed three to four times per year for 2 years (total of 141 environmental samples). Surface-water samples were analyzed for 10 trace metals (total and dissolved concentrations), 8 trace elements, 8 major ions (dissolved concentrations), alkalinity, and total and dissolved organic carbon.

Metal and element concentrations in solid media varied by watershed, representing local geology. Copper-nickel sulfide mineralization in the Filson Creek watershed was evidenced in bedrock, soil, and streambed sediments. In the Keeley Creek watershed, silicate mineralogy of underlying bedrock contributed metals to streambed sediments. Thick glacial cover masked potential bedrock contributions to solid media in the St. Louis River watershed. Water-quality data indicate that waters in all three watersheds are dilute. Water quality is more similar between the Filson and Keeley Creek watersheds, compared to the St. Louis River watershed, because of the difference in glacial cover. Metal concentrations (copper and nickel, in particular) in surface-water samples follow similar patterns of concentrations in solid media, indicating the influence of bedrock on water quality in Filson and Keeley Creeks. Data from this study provide a baseline of metal concentrations and general water quality within an area of active mineral exploration.

Introduction

The world’s demands for copper (Cu), nickel (Ni), and platinum-group elements (PGEs) have grown since 1980 (Wilburn and Bleiwas, 2004; Doebrich, 2009; Boland, 2012; Yager and others, 2012) and will likely continue to grow with increases in population and high-technology applications. Important uses of these metals include wiring for home appliances (Cu), use in alloys to prevent corrosion (Ni), and catalysts to control vehicle pollution (PGEs). In the United States, there currently are more than 20 active Cu mines, but only 1 active Ni mine (located in Michigan) and 2 active PGE mines (located in south-central Montana), leaving the country dependent on Ni and PGE imports (McRae, 2015; Loferski and others, 2016).

The basal part of the Duluth Complex in northeastern Minnesota contains world-class mineral deposits that represent the third largest Cu and Ni resource and the fourth largest precious metals resource in the world (Miller and others, 2002). The Mesoproterozoic Duluth Complex is an intrusive component of the Midcontinent Rift System (MRS), emplaced at about 1.1 Ga (Paces and Miller, 1993). The MRS is a 1,370-mile (mi) long curvilinear continental rift system that extends from Kansas northward through Iowa, Minnesota, and Wisconsin to the Lake Superior region and then turns southeast through lower Michigan. Bedrock of the MRS is exposed at the surface only in the Lake Superior region. Eleven individual Cu-Ni-PGE deposits and several small iron (Fe)-titanium (Ti)-oxide bodies have been identified in the Duluth Complex (Miller and others, 2002) (fig. 1). Disseminated Cu-Ni-PGE sulfide mineralization occurs along the northern basal contact zone between mafic intrusions of the Duluth Complex and older rocks (Miller and others, 2002). The Fe-Ti-oxide

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[1] U.S. Geological Survey.

[2] Freshwater Society.

bodies (small plugs of oxide-bearing ultramafic rocks) occur along the southern one-half of the complex (Hauck and others, 1997).

In 2010, approximately 15 percent of the total gross regional product of the northeastern Minnesota economy relied on taconite Fe mining (Skula and others, 2012). Despite this mining legacy, no sulfide-bearing metal deposits have ever been developed. Mineral exploration along the basal part of the Duluth Complex for Cu, Ni, PGEs, and Ti is ongoing; a planned Cu-Ni-PGE mine (NorthMet Mining Project) has been issued permits to allow mining (Minnesota Department of Natural Resources, 2018). Minnesota faces a unique opportunity to determine how to promote economic development through possible Cu-Ni-PGE mining in northeastern Minnesota while protecting existing water quality and ecosystems.

The Cu-Ni-PGE deposits in northeastern Minnesota are in or near environmentally sensitive areas. One of the larger deposits (Maturi) is within the watershed of the Boundary Waters Canoe Area Wilderness (fig. 1), a unique wilderness area characterized by numerous lakes and streams in the northern one-third of the Superior National Forest. In Minnesota, State, Tribal, and Federal water-resource managers and scientists are concerned that mining sulfide-bearing Cu-Ni-PGE deposits could have detrimental effects on regional water resources and ecosystems. These concerns arise because mining of sulfide-bearing mineral deposits in other parts of the United States has resulted in water-quality problems such as increased acidity and high trace metal concentrations in downgradient streams, wetlands, and lakes (U.S. Environmental Protection Agency, 1994; Seal and others, 2010).

Northeastern Minnesota streams and lakes typically have low alkalinities, and low acid buffering capacity (Thingvold and others, 1979; Siegel and Ericson, 1980), and therefore are sensitive to changes in metal concentrations because they have a limited ability to complex metals in waters. Sulfate (SO_4^{-2}) concentrations in northeastern Minnesota stream and lake waters are typically low in undisturbed watersheds but can exceed Minnesota's current water-quality standard of 10 milligrams per liter (mg/L) (Siegel and Ericson, 1980; Berndt and Bavin, 2012) in waters downstream from taconite Fe mining activities (Thingvold and others, 1979).

The potential of metals leaching from exposed Duluth Complex mineralized rock raises concerns regarding potential effects on aquatic ecosystems downgradient from developed mines or waste rock sites. Elevated concentrations of Cu, Ni, and other trace metals can adversely affect fish, aquatic invertebrates and plants, and amphibians (U.S Environmental Protection Agency, 1993; Horne and Dunson, 1995; Seal and others, 2010). For example, wild rice, an important cultural and economic resource in Minnesota, is sensitive to SO_4^{-2} in waters where it grows. In water, SO_4^{-2} is converted to sulfide in sediment; as sulfide levels increase, the likely presence of wild rice decreases (Minnesota Pollution Control Agency, 2015).

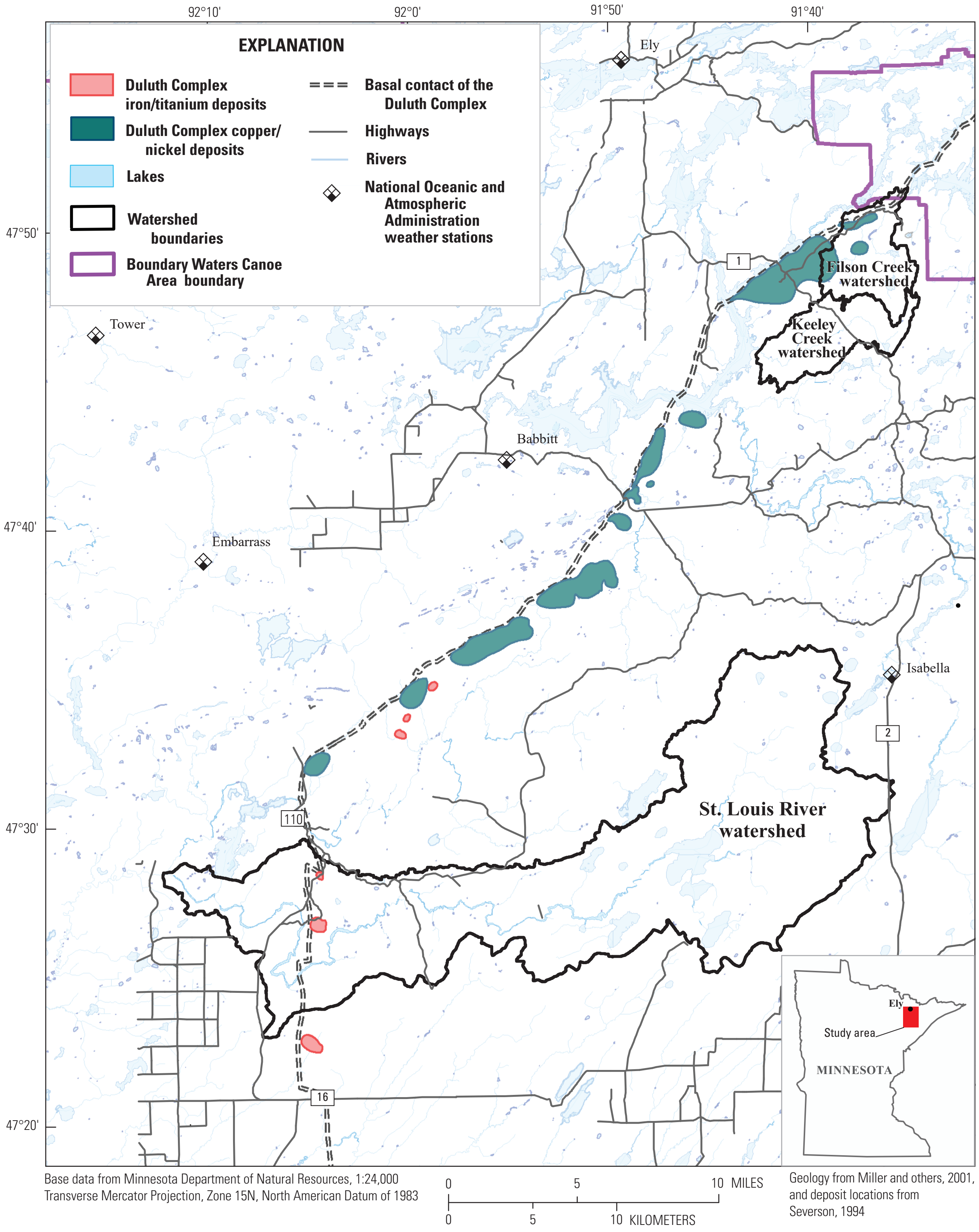
An understanding of the premining status of bedrock, soil, and streambed sediment chemistry and regional water quality is needed to establish the background conditions of water resources. Localized water-quality studies are part of the permitting process for potential mines (Minnesota Minerals Coordinating Committee, 2013). However, a more regional assessment of premining, natural geochemical, and water-quality variability in watersheds across the basal part of the Duluth Complex will improve our understanding of water quality in areas of mineral exploration and possible mine development. Regional geochemistry and hydrologic studies were completed in the late 1970s as part of a study to examine the environmental, social, and economic effects associated with the potential development of Cu-Ni sulfide mineral resources of the Duluth Complex (Minnesota Environmental Quality Board, 1979). Since that time, logging and other land use activities have occurred in the area, potentially changing local water quality. The objective of this study is to provide an update of regional water-quality conditions in three watersheds that transect the basal section of the Duluth Complex.

Purpose and Scope

This report describes the influence of naturally mineralized bedrock along the basal section of the Duluth Complex on water quality in three northeastern Minnesota watersheds: Filson Creek, Keeley Creek, and the headwaters of the St. Louis River east of its confluence with the Partridge River. These watersheds represent different mineral-deposit settings with no current or past mining activity. In each watershed, solid media data, water-quality data, and streamflow measurements were collected in 2013, 2014, and 2015. Solid-media data were compared with water-quality data to assess the influence of bedrock on water quality. Water-quality data also were compared to the sparse water-quality data from the 1979 regional copper-nickel study (Minnesota Environmental Quality Board, 1979) to assess possible changes in water quality with time. Water-quality and streamflow data were used to create synthetic hydrographs for calculating instantaneous loads of metals in the sampled waters.

Description of Study Areas

The study areas include the Filson Creek, Keeley Creek, and headwaters of the St. Louis River watersheds in northeastern Minnesota (fig. 1). These watersheds cross the basal part of the Duluth Complex and have different mineral-deposit settings: (1) exposed surficial Cu-Ni-PGE mineralization (Filson Creek), (2) no identified surficial mineralized deposits (Keeley Creek), and (3) buried Fe-Ti-oxide mineralization (St. Louis River).



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Miller and others, 2001, and deposit locations from Severson, 1994

Figure 1. Locations of precipitation stations, mineral deposits, and basal contact of the Duluth Complex in Filson Creek, Keeley Creek, and headwaters of the St. Louis River watersheds, northeastern Minnesota.

Physiography

The three study watersheds are within the Superior Upland Province of the Laurentian Upland Region (Fenneman and Johnson, 1946). The region was glaciated by numerous advances of the Rainy and Superior lobes during the Wisconsinan and pre-Wisconsinan. The northern part of the region is dominated by bedrock-controlled uplands and intervening bogs and wetlands, whereas the southern part is a glacial surface dominated by drumlin fields, moraines, small glacial lakes, and outwash plains. Most of the area within the three watersheds is within the Superior National Forest. The U.S. Forest Service practices sustainable forest and resource management to support multiple uses, including timber production, recreation, and mineral exploration in the Superior National Forest.

The two northern watersheds (Filson and Keeley Creeks) are north of the Laurentian Divide and ultimately drain into Hudson Bay. This drainage path includes Birch Lake, parts of the Boundary Waters Canoe Area Wilderness, a 1-million-acre wilderness unit of the National Wilderness Preservation System administered by the U.S. Forest Service, and the Rainy Lake system along the United States–Canada international border. The third watershed (headwaters of the St. Louis River) is south of the Laurentian Divide and drains into Lake Superior and ultimately the St. Lawrence River.

Climate

The climate of northeastern Minnesota is continental and locally affected by Lake Superior, with cold winters and warm summers. A weather station at Embarrass, Minnesota (National Oceanic and Atmospheric Administration [NOAA] station identification (ID) number GHCND:USC00212576), is approximately 12 mi north of the St. Louis River watershed and approximately 22 mi southwest of the Filson and Keeley Creek watersheds (fig. 1). The normal annual temperature (1981–2010) recorded at this station is about 34 degrees Fahrenheit (°F), with monthly mean temperatures ranging from about 1.4 °F in January to 63 °F in July (National Climatic Data Center, 2015). The 30-year (1981–2010) normal annual precipitation from the Embarrass weather station and another station at Ely, Minnesota (NOAA station ID number GHCND:USC00212543, approximately 8 mi northwest of the Filson and Keeley Creek watersheds; fig. 1) were both 30 inches (in.) (National Climatic Data Center, 2015). Multiple studies have estimated the mean annual evapotranspiration for the Filson and Keeley Creek watersheds as between 41 and 53 in. (Ericson and others, 1976; Baker and others, 1979; Lindholm and others, 1979; Sanford and Selnick, 2012).

Bedrock Geology

The three water courses all rise in the Duluth Complex and flow over the basal contact between the Duluth Complex and older country rock. The following sections describe the bedrock geology of the Filson Creek, Keeley Creek, and headwaters of the St. Louis River watersheds in more detail.

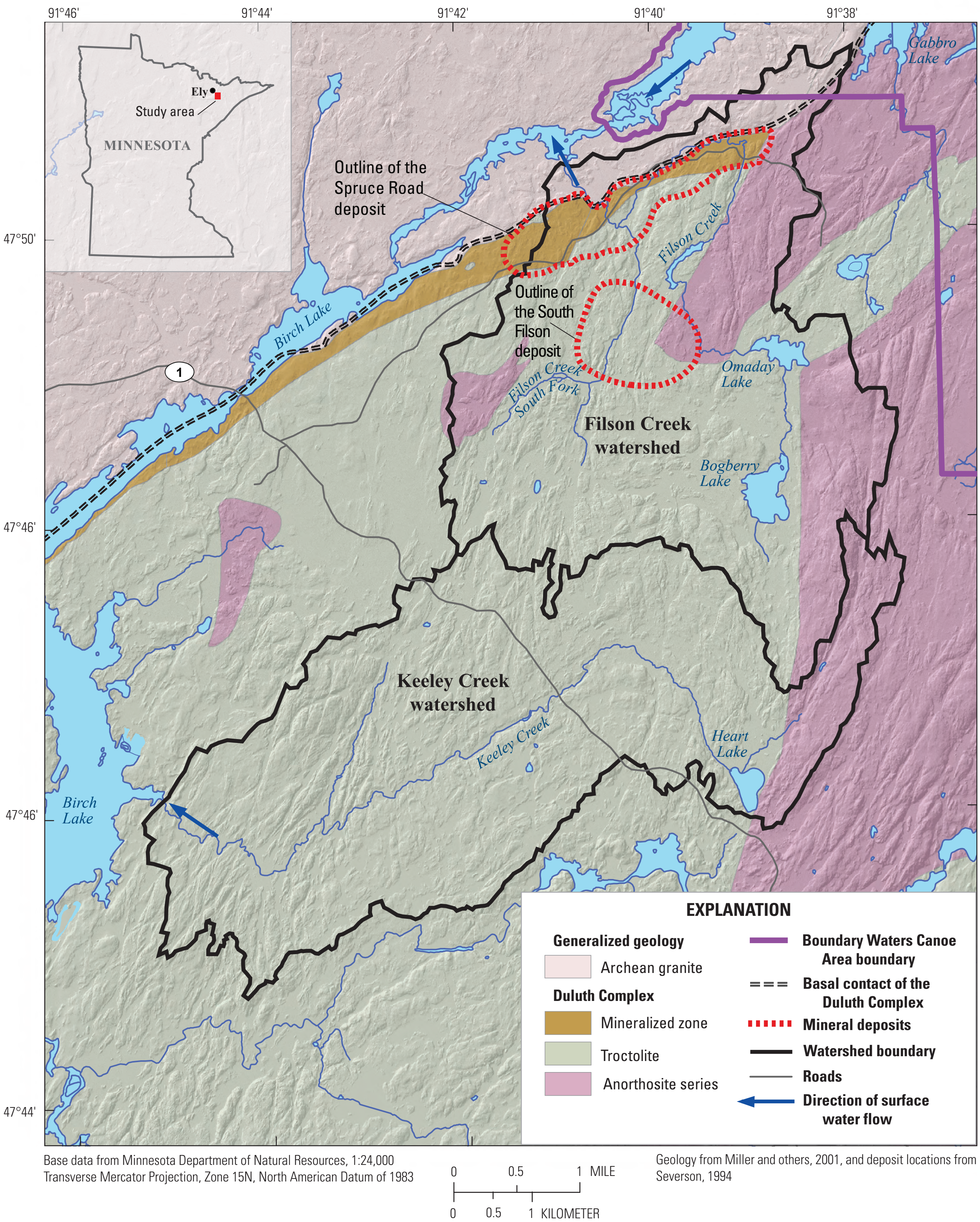
Filson Creek

The bedrock geology of the Filson Creek watershed is complex. Bedrock units include the Archean Giants Range batholith, a large composite granitoid body, and the Mesoproterozoic Duluth Complex (fig. 2). Duluth Complex bedrock in the Filson Creek watershed is represented largely by (1) the South Kawishiwi intrusion, a thick sequence of troctolite; (2) the anorthosite series, composed of medium- to coarse-grained plagioclase-rich cumulates; and (3) a band of oxide-rich gabbro and foliated troctolite (Miller and others, 2001; Peterson and Albers, 2007). Hornfels inclusions of the Paleoproterozoic Biwabik Iron-Formation and basalt of the Mesoproterozoic North Shore Volcanic Group are exposed near the basal contact of the South Kawishiwi intrusion.

Two mineral deposits within the Filson Creek watershed are the Spruce Road deposit and the South Filson deposit (fig. 2). The Spruce Road deposit is exposed at the surface with mineralization consisting of discontinuous sulfide-bearing heterogeneous troctolite and melatroctolite. The South Filson deposit is a combination of primary disseminated Cu-Ni sulfide mineralization and secondary hydrothermal mineralization (Kuhns and others, 1990; Gál and others, 2011). Neither the Spruce Road deposit nor the South Filson deposit is currently considered to be economic, nor is there any active exploration within the watershed.

Keeley Creek

In contrast to the Filson Creek watershed, the bedrock geology of the Keeley Creek watershed is dominated by relatively homogeneous anorthositic troctolite of the South Kawishiwi intrusion; the far northern part of the watershed is underlain by gabbroic anorthosite of the anorthosite series (fig. 2) (Miller and others, 2001). Bedrock in the Keeley Creek watershed is typically not mineralized at the surface, although extensive disseminated sulfide mineralization at great depth has been identified by exploration drilling. In 2013, when this study began, the Keeley Creek watershed had no known mineralization, although recent mineral exploration has revealed minor Cu-Ni mineralization within the watershed (Dean Peterson, University of Minnesota-Duluth Natural Resources Research Institute, oral commun., 2014).



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Miller and others, 2001, and deposit locations from Severson, 1994

Figure 2. Mineral deposits and bedrock geology in the Filson Creek and Keeley Creek watersheds, northeastern Minnesota.

Headwaters of the St. Louis River

Within this portion of the St. Louis River watershed, bedrock of the Paleoproterozoic Virginia Formation (Lucente and Morey, 1983) is in contact with the Partridge River intrusion of the Duluth Complex (Miller and others, 2001). Bedrock outcrop in the St. Louis River watershed is sparse. The major rock units are the Virginia Formation, a thick sedimentary sequence of argillite, siltstone, shale, and graywacke (Lucente and Morey, 1983); and the Duluth Complex. The few exposed rocks of the Duluth Complex in the watershed include small, weathered outcrops of troctolite and gabbro along banks of the St. Louis River and a single prominent anorthosite plug. Nearly flat-lying argillites and siltstones of the Virginia Formation crop out in the western part of the headwaters of the St. Louis River watershed, upstream from the Whitewater Lake inlet. The actual contact between the Virginia Formation and the Duluth Complex is covered by glacial materials. This contact is exposed, however, along the south branch of Water Hen Creek, about 2.5 mi south of the southern boundary of the study watershed. Virginia Formation bedrock at that vicinity was highly metamorphosed by the heat of intrusion of the Duluth Complex. Hornfels contact metamorphic rocks collected from this location are assumed to be representative of the buried, metamorphosed Virginia Formation/Partridge River intrusion contact within the St. Louis River watershed.

No substantial Cu-Ni-PGE sulfide mineralization is known within the St. Louis River watershed, but three Fe-Ti-bearing oxide ultramafic intrusions (OUIs) near the base of the Partridge River intrusion have been recognized from geophysical surveys and explored as possible Fe and Ti resources (fig. 3) (Hauck and others, 1997). The OUIs typically have a high percentage of coarse-grained Fe-Ti-oxides and may also carry small concentrations of Cu-Ni sulfides (Severson, 1995). A drill core from the Skibo OUI has an abnormally thick weathered zone of mineralized troctolite at the bedrock subsurface, which Severson (1995) indicates is evidence of preglacial weathering.

Surficial Geology

The surficial geology in all three study watersheds mainly consists of glacial materials deposited by the Wisconsinan Rainy lobe. The large-scale southwest ice-flow direction of the Rainy lobe is from the Labrador sector of the Laurentide Ice Sheet, which traversed the high ground between the Lake Superior Basin and the Red River Valley-Winnipeg lowland (Lehr and Hobbs, 1992).

Filson and Keeley Creeks

Glacial sediment in the Filson and Keeley Creek watersheds is very thin, generally less than (<) 26 feet (ft) thick. The multiple glacial advances of the Rainy lobe that crossed the region removed older glacial sediment and weathered rock, leaving a landscape that primarily reflects the relative resistance of the different rock types to chemical weathering (Lehr and Hobbs, 1992). The most commonly encountered surficial sediments in these two watersheds are silt in upland locations and clay in low-lying areas. Clay is presumed to be lacustrine in origin based on its elevation and widespread distribution. Silt may also have been lacustrine in origin, but its variable thickness indicates that it may have been redistributed by wind.

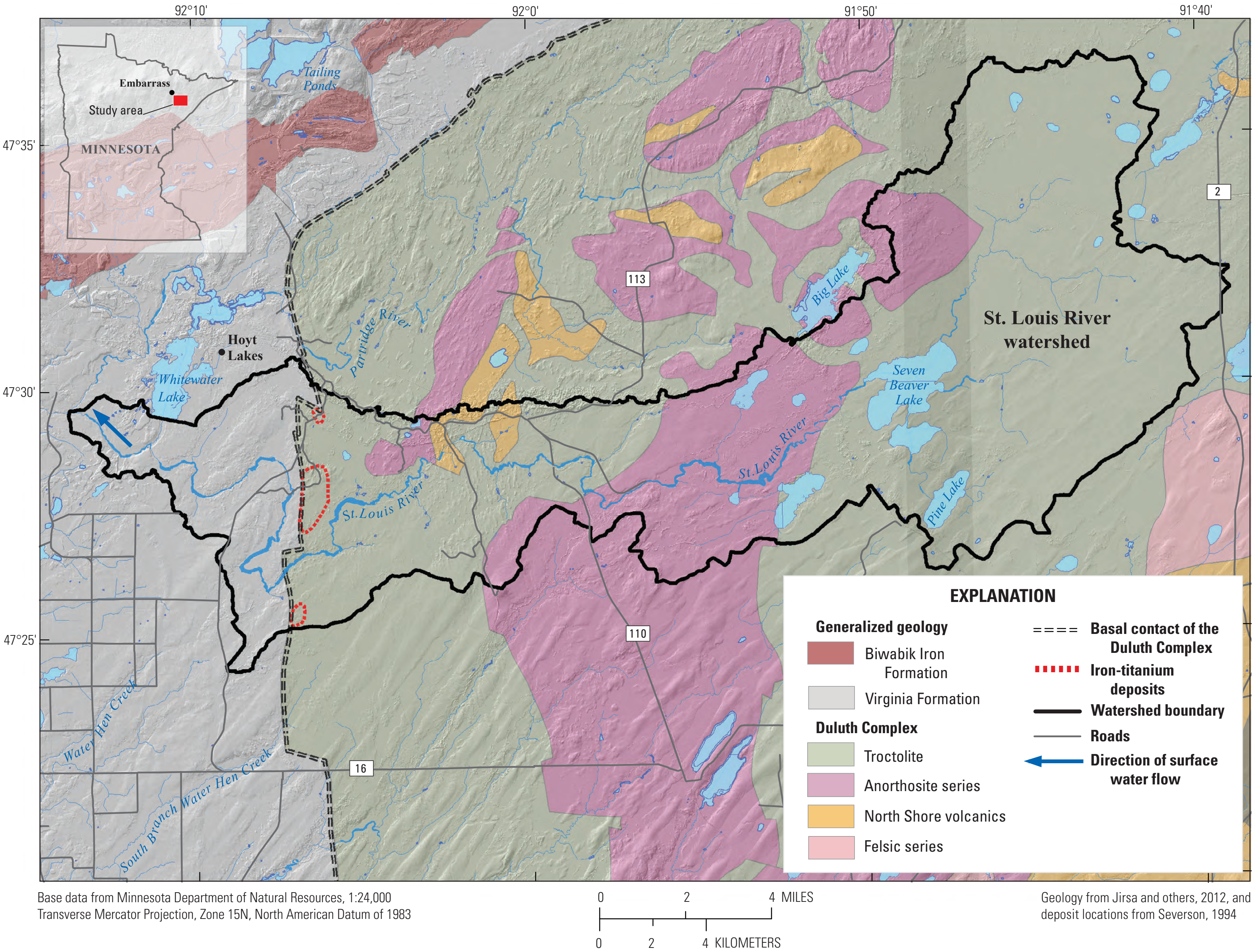
Where glacial till is thin, as it is in the bedrock-dominated Filson and Keeley Creek watersheds, Rainy lobe deposits strongly reflect underlying local bedrock (Lehr and Hobbs, 1992). The two watersheds lie within the Boundary Waters Formation (Wisconsinan, about 14,000 calendar years before present), which is characterized by thin, patchy, coarse-grained, locally derived diamicton and fine-grained, sorted sediment (Jennings and Gowan, 2016, and references therein). Diamicton, interpreted to be till or reworked till, is dominated by locally derived clasts with short mean transport distances and very few far-traveled clasts. The till matrix is variable, but where it is silty and sandy, it is non-cohesive and therefore easily reworked by wind and water (Jennings and Gowan, 2016).

Headwaters of the St. Louis River

A surficial geology map for the St. Louis River watershed was constructed using a glacial landform-sediment association approach to interpret landforms visible in a high-resolution 3.3-ft digital elevation model (DEM) derived from light detection and ranging (lidar) technology (http://www.mngeo.state.mn.us/). This approach assumes that it is possible to associate landforms to soil types as the landform and soil have common attributes that relate back to the depositional processes that created them. The 3.3-ft DEM provides a direct measurement of landforms using simulated solar shading, which can enhance subtle features. Mapping was done by on-screen digitizing directly into a geographical information system. Interpretations were checked in the field at various locations and compared to prior mapping in the area by Hobbs and Goebel (1982), Lehr and Hobbs (1992), Lehr (2000), and Jennings and Reynolds (2005). The resulting figure 4 shows geomorphology and interpreted surficial geology of the headwaters of the St. Louis River watershed.

The St. Louis River watershed is covered by relatively thick glacial sediment. Lithologic logs from scattered exploration drill holes that intersect the small OUI bodies in the west-central part of the watershed report glacial-sediment thickness between 28 and 134 ft (Severson, 1995). A line of nine shallow drill holes in the eastern end of the watershed indicates glacial-sediment thickness in that area between 69 and 138 ft (Minnesota Department of Health, 2016).

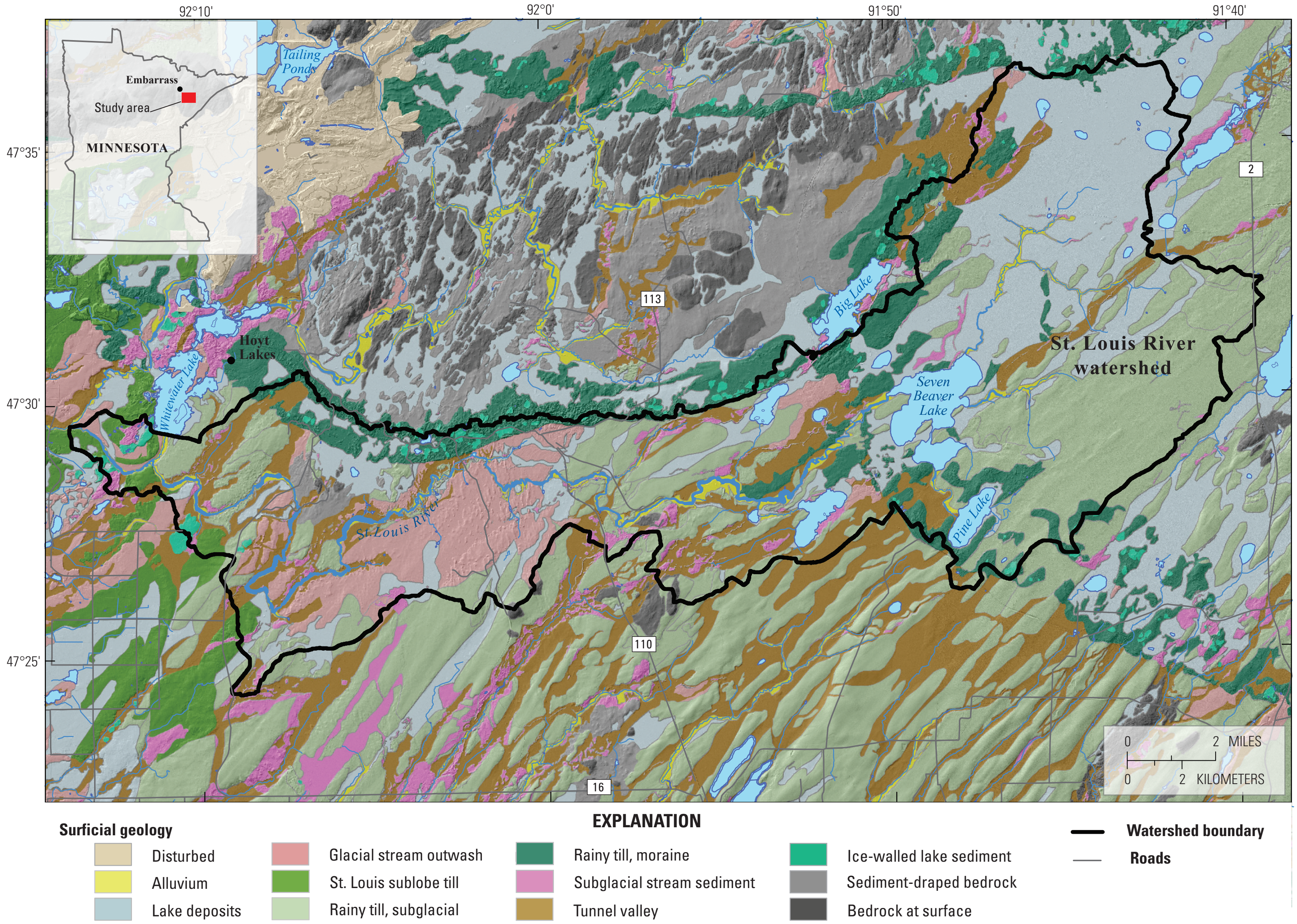
The bulk of the glacial deposits in the St. Louis River watershed belong to a late Wisconsinan lithostratigraphic unit called the Independence Formation, a rocky, sandy loam to loamy sand diamicton strongly influenced by the composition



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Jirsa and others, 2012, and
deposit locations from Severson, 1994

Figure 3. Mineral deposits and bedrock geology in the headwaters of the St. Louis River, northeastern Minnesota.



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Figure 4. Geomorphology and interpreted surficial geology for area including the headwaters of the St. Louis River watershed, Minnesota.

of local bedrock (Hobbs, 2016). Till is typically gray to pinkish gray, non-calcareous, with a matrix texture ranging from 48 to 87 percent sand, 9 to 40 percent silt, and 0 to 13 percent clay. Because the till is clay-poor and thereby non-cohesive, it was easily reworked in proglacial settings by gravity, water, and wind. The layers above subglacial till (for example, those layers interpreted as representing moraine-forming processes and ice retreat) are commonly much more bouldery and more variable in texture and appear vaguely to well-stratified in places.

Surficial landforms of the St. Louis River watershed are mainly the product of Rainy lobe glaciation (fig. 4). The most prominent glacial landscape features in the watershed are drumlins that are part of the much larger Toimi drumlin field (Lehr and Hobbs, 1992). Drumlins are made up of gray, sandy, stony till with little clay and silt, typically rich in fragments of the Duluth Complex (Wright, 1972). Much of the circuitous course of the St. Louis River in the western part of the study area is controlled by topography and orientation of the drumlins.

In the western part of the St. Louis River watershed, deposits of the Winnipeg-provenance St. Louis sublobe of the Koochiching lobe (Aitkin Formation; Knaeble, 2016) cover Rainy lobe deposits but do not completely obscure Rainy lobe landforms. A reddish, clayey till with rare clasts exposed in the St. Louis River watershed diverges from the typical yellow brown to gray, calcareous and fine-grained till containing limestone and shale fragments of other Winnipeg-provenance glacial sediment because of incorporation of Superior-provenance red, clayey lake sediment (Wright, 1972).

Hydrology/Hydrogeology

Wetlands are important hydrologic features in all three watersheds. We calculated the percent of area in each watershed that is covered by wetlands using the National Wetland Inventory dataset (U.S. Fish and Wildlife Service, 2009). Groundwater is not a substantial contributor to base flow; rather base flow is potentially from metered discharge from upstream storage in wetlands and lakes.

Filson Creek

The Filson Creek watershed encompasses about 10.2 square miles (mi^2). The watershed includes two main tributaries (Filson Creek and the Filson Creek South Fork, fig. 2) and is approximately 24 percent wetlands. The watershed is mostly underlain by northeast-southwest trending bedrock highlands of the Duluth Complex with adjacent lowlands and wetlands. Total relief in the watershed is about 328 ft. Two small, shallow lakes, Omaday and Bogberry, are part of the main-stem Filson Creek System; Bogberry Lake drains northward through a perennial stream into Omaday Lake. The generally north-northeast course of the main-stem Filson Creek turns abruptly southwest along the basal contact between the Mesoproterozoic Duluth Complex and granitic rocks of the Archean Giants Range batholith. Filson Creek South Fork flows mainly north along a prominent northeast-southwest lineament in underlying bedrock before joining the main-stem Filson Creek about 1.2 mi upstream from the confluence of Filson Creek with the South Kawishiwi River. Streamflow often is affected by beaver activity (inactive and active dams and lodges are present in all three watersheds).

Base flow in Filson Creek mainly is sustained by discharge from lakes and wetlands, with minimal groundwater discharge (Siegel and Pfannkuch, 1984). Groundwater in the Filson Creek watershed primarily moves through fractures in granitic rocks of the Giants Range batholith and mafic rocks of the Duluth Complex. The few domestic water wells in the area are mainly along the south shoreline of Birch Lake, are generally less than about 328 ft deep, and obtain water from fractured rocks.

Keeley Creek

The Keeley Creek watershed is about 24 mi^2. Keeley Creek flows northwest from Heart Lake, a small lake in the upper part of the watershed, for about 0.12 mi and then turns southwest for about 4.6 mi where it drains into Birch Lake (fig. 2). Approximately 23 percent of the watershed is covered by wetlands. A small unnamed tributary enters Keeley Creek from the north about 1.2 mi from its connection with Birch Lake. The Keeley Creek watershed is entirely underlain by bedrock of the Duluth Complex.

Like Filson Creek, base flow in Keeley Creek mainly is supported by discharge from lakes and wetlands, with minimal groundwater discharge. No wells used for domestic water supplies are known to exist in the watershed.

Headwaters of the St. Louis River

The portion of the St. Louis River watershed included in this study encompasses an area of about 135 mi^2. The study area includes the upper headwaters that flow into Seven Beaver Lake down to its confluence with the Partridge River, about 1.1 mi west of Whitewater Lake (fig. 3). Approximately 52 percent of the watershed is covered by wetlands. This part of the St. Louis River is variable in gradient; the section from Seven Beaver Lake to the confluence with the Partridge River drops almost 295 ft in about 21 mi. The course of the river is, in part, controlled by the underlying glacial structure, which is dominated by the northeast-southwest trending Toimi drumlin field of the Rainy lobe (Wright, 1972). Small sections of the river between Seven Beaver Lake and Whitewater Lake are characterized by abundant large rounded boulders that appear to restrict the river during low flow. These areas can be as much as 0.62 mi in length. Typically, the river spreads out into a broader wetland setting upstream from the boulder trains.

Base flow in the St. Louis River is sustained mainly through discharge from wetlands, with minimal groundwater discharge. There are some domestic wells scattered throughout the watershed that were completed in bedrock and are generally <328 ft deep.

Methods of Study

Sampling methods for collecting solid-media and surface-water samples and analytical methods for determination of selected analytes are described below.

Solid Media

Baseline concentrations of trace elements, carbon, and metals were determined for bedrock, soil, and streambed sediments in the three study watersheds. Sample site locations are shown in figures 5 and 6, and concentrations are provided in a U.S. Geological Survey (USGS) data release (Woodruff, 2019). A total of 42 bedrock, 106 soil, and 42 streambed sediment samples were collected during 2013 to 2015.

Bedrock

The distribution of bedrock units across the study areas was from Miller and others (2001), Peterson (2008), and Jirsa and others (2012). Some bedrock sample sites were selected to be near soil and water-quality sample sites where outcrop was present (fig. 5). Samples in the Filson and Keeley Creek watersheds, where outcrops are abundant, are representative of the varied exposed bedrock types and mineralization styles (figs. 2 and 5). In the Filson Creek watershed, bedrock samples included (1) granite from the Archean Giants Range batholith, (2) metamorphosed basalt of the North Shore Volcanic Group, (3) anorthosite and augite troctolite of the South Kawishiwi intrusion (Duluth Complex), (4) gabbroic and troctolitic anorthosite of the anorthosite series (Duluth Complex), (5) sulfide-bearing mineralized gabbro and melatroctolite from the mapped outline of the Spruce Road deposit, and (6) sulfide-bearing altered troctolite near the South Filson deposit. Multiple bedrock samples of mineralized rock from the Spruce Road deposit were collected to document the heterogeneous nature of the mineralization.

Bedrock in the Keeley Creek watershed is generally monotonous anorthosite troctolite of the South Kiwishiwi intrusion. In addition to nine samples of troctolite, a sample of melatroctolite that crops out in the valley of Keeley Creek was provided by Dean Peterson, then of Duluth Metals.

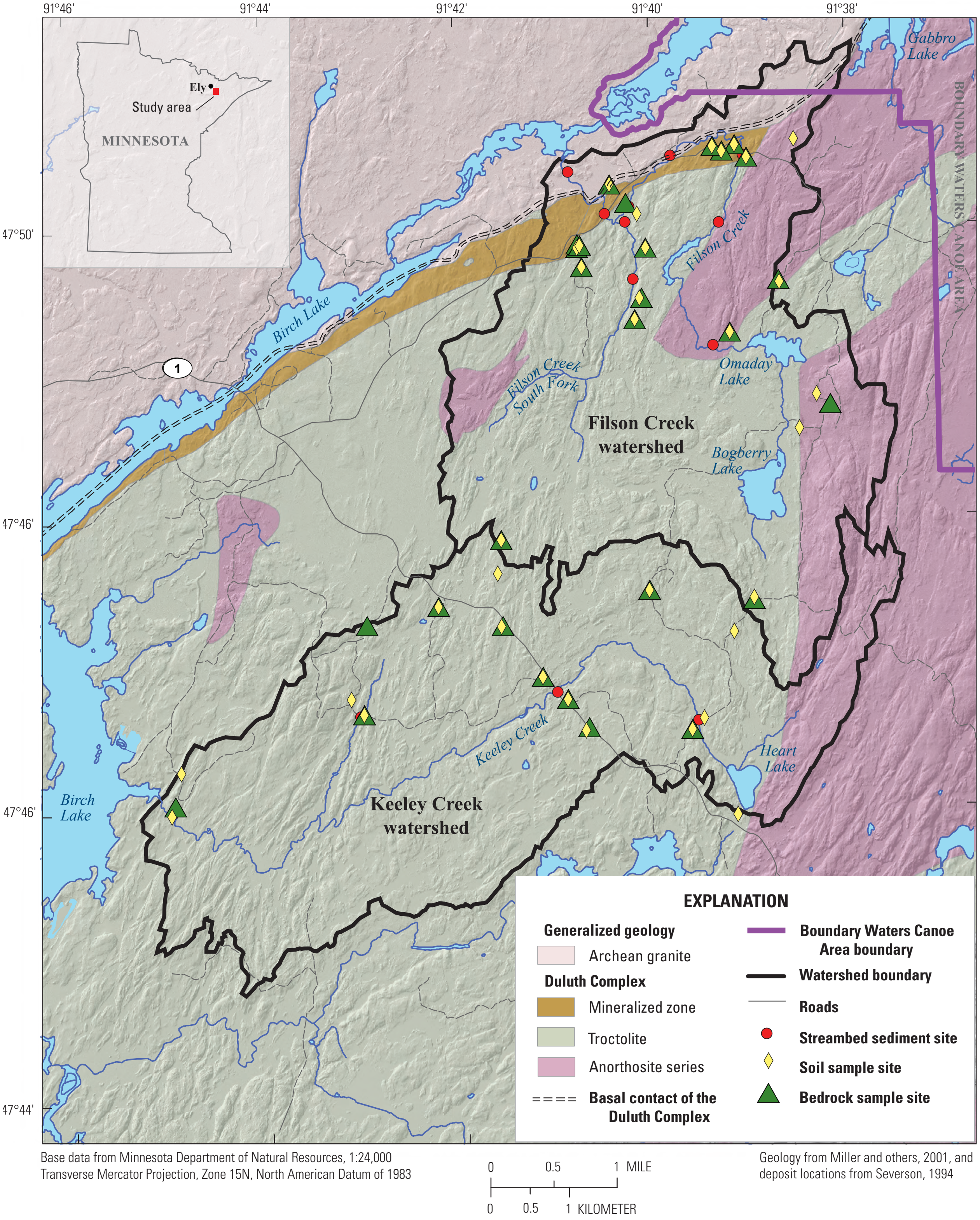
Outcrop in the St. Louis River watershed is sparse. Shale and argillite of unmetamorphosed Virginia Formation were collected along the river bed south of Whitewater Lake (fig. 6). Splits of troctolite from the Partridge River intrusion of the Duluth Complex that crop out along the banks of the St. Louis River were from archived samples at the Natural Resources Research Institute, where they were originally collected by Mark Severson during reconnaissance field work. Additional samples of troctolite and anorthosite were collected during the soil sampling effort. Bedrock samples from the metamorphosed contact between the Virginia Formation and the Duluth Complex exposed in the Water Hen Creek area were also submitted for analysis (fig. 6). All bedrock samples were processed into small chips in the field and samples with obvious surficial alteration were discarded. Fresh bedrock chips were collected into cloth sample bags.

Soil

Soil was collected from multiple sites within the three watersheds (figs. 5 and 6). At the time of sampling, no soil maps or data were available from the Natural Resources Conservation Service for Lake or St. Louis Counties; thus, sampling was based on known geologic criteria.

In the Filson and Keeley Creek watersheds, glacial materials are very thin, and topography is controlled by underlying bedrock (Olcott and Siegel, 1978). Soil was collected only on dry, typically upland sites, often in proximity to bedrock outcrops. Soil sample sites in the Filson Creek watershed were selected to represent the wide variety of bedrock types. Access to the interior of the watershed is somewhat problematic so soil sampling sites were mainly located along two broad transects that cut across the general trend of the major bedrock types, including granite of the Giants Range batholith and differing rock types of the Duluth Complex. Soil was also collected from sites along a short east-west transect within the mapped area of the Spruce Road deposit (fig. 2). In the Keeley Creek watershed, access is even more problematic; however, the very homogeneous nature of the bedrock made site selection relatively straightforward. Fifteen soil sites are near the four water-quality sites and along the limited access ways. In contrast to the other two watersheds, the St. Louis River watershed has thick glacial cover. The 15 soil sites were selected based on the diverse glacial features visible in the publicly available 3.3-ft lidar hillshade coverage and the newly completed glacial map for the region interpreted from Hobbs and Goebel (1982), Lehr and Hobbs (1992), Lehr (2000), and Jennings and Reynolds (2005) (fig. 4). Soil samples were collected from modern landscape features including esker, draped drumlin, ground till, terminal moraine, ice-walled lake, tunnel valley, and alluvial plain.

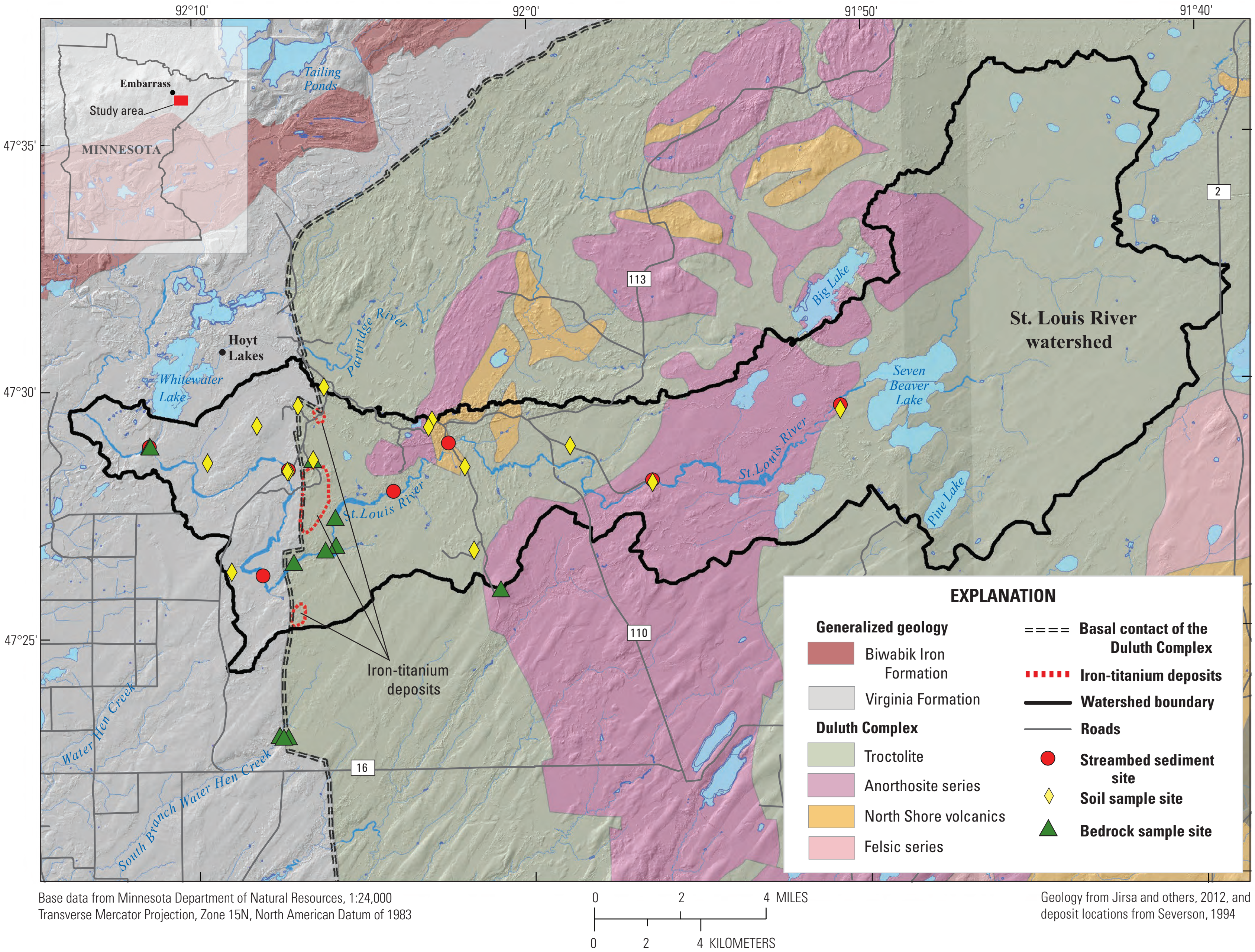
All soil samples were collected using hand tools. The target samples from each site were (1) the soil O horizon, consisting of the decomposing organic material at the surface but not including leaf litter or living plants; (2) the soil A horizon, defined as an organic mineral soil; and (3) a deeper sample representing the soil B or C horizon, assumed to best approximate the soil parent material. Mineral soil was collected into plastic bags and organic soil was collected into cloth bags. Soil O horizon samples were collected at about 30 percent of all sites. Where a soil O horizon is missing, it is assumed to have been consumed by worms, and the soil A horizon is



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Miller and others, 2001, and deposit locations from Severson, 1994

Figure 5. Solid-media sample sites in the Filson and Keeley Creek watersheds, near Ely, Minnesota.



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Jirsa and others, 2012, and
deposit locations from Severson, 1994

Figure 6. Solid-media sample sites in the St. Louis River watershed, near Hoyt Lakes, Minnesota.

typically much thicker from the processing and mixing of organic material into the upper mineral soil from burrowing worms. At a few sites where a soil O horizon was present, the soil A horizon was too thin to collect.

Streambed Sediment

Streambed sediment represents a time-integrated composite of the solid material transported and deposited within a stream. The concentration of trace elements in streambed sediment generally increases as the size fraction decreases. Thus, two different streambed sediment size fractions [<2 millimeters (mm) and <63 microns (µm)] were collected for this study. Streambed sediments were hand-collected at the water-quality sites during low flow to maximize access to depositional areas. Three additional streambed sediment samples were collected from Filson Creek and a small tributary within the mapped area of the Spruce Road deposit.

For the clastic <2-mm size fraction, samples were collected from depositional areas within an approximately 164-ft reach using a stainless-steel scoop, and wet-sieved in the field with native water to <2 mm using a stainless-steel sieve. Within each sampling area, about 500 grams of sieved material was composited and placed into acid-rinsed polyethylene bottles. Samples were air-dried prior to submittal for analysis.

Thirteen fine-grained streambed sediment samples were collected using the method for flexible 63-µm nylon-cloth sieve bags described in Shelton and Capel (1994). Streambed sediment was collected with a stainless-steel scoop placed onto a 63-µm nylon-cloth sieve, which was then rinsed in a glass beaker containing native water, with the intent of washing the <63-µm material into the beaker. Multiple composites of material were collected along a 164-ft reach. At the end of the sampling period, all native water and suspended material in the receiving container were transferred to an acid-rinsed polyethylene bottle. After sitting for more than 2 weeks, the bottles were decanted, and the solid material allowed to air dry.

Analytical Methods

Mineral soil samples were air-dried at ambient temperature, disaggregated, and sieved to <2 mm. The <2-mm sieved mineral soil, <2-mm streambed sediment, and fresh bedrock chips were sent to the USGS Geochemistry Group in Denver, Colorado, for further processing. In Denver, each sample was crushed to <150 µm prior to chemical analysis. The <63-µm streambed sediment samples were not further processed prior to analysis.

All samples were submitted to the USGS geochemistry contract laboratory, SGS Laboratories, for analysis. Concentrations of 42 elements were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES) and by inductively coupled plasma–mass spectrometry (ICP–MS). For this combined analytical method, all samples were decomposed using a near-total four-acid (hydrochloric, nitric, hydrofluoric, and perchloric) digestion at a temperature between 257 and 302 °F.

Additional analyses were completed for all samples, except for <63-µm streambed sediment (because of small quantities). Mercury (Hg) was determined by cold-vapor atomic absorption spectrometry after dissolution in a mixture of nitric and hydrochloric acids. Arsenic (As) was determined by hydride generation atomic absorption spectrometry after samples were fused in a mixture of sodium peroxide and sodium hydroxide at 1,382 °F and dissolved in hydrochloric acid. Selenium (Se) was determined by hydride generation atomic absorption spectrometry after dissolution in a mixture of nitric, hydrofluoric, and perchloric acids.

Soil was also analyzed for total carbon (C) and carbonate C. Total C was determined using an automated carbon analyzer. Each sample was combusted in an oxygen atmosphere at 2,498 °F to oxidize C to carbon dioxide (CO_2), which was measured by a solid-state infrared detector. Carbonate C was determined as CO_2 by coulometric titration after treatment with hot 2 normal perchloric acid. The concentration of organic C is calculated by subtracting the amount of inorganic (carbonate) C from the total C concentration.

Samples of the soil O horizon were air-dried, sieved to <2 mm, and sent to the USGS Denver Geochemistry Group, where they were milled and split. One portion was set aside and the remainder of the sample ashed at 932 °C for 13 hours at the USGS analytical laboratory to combust organic materials and leave a residue of inorganic materials. Both the unashed and ashed portions were sent to SGS Laboratories. The unashed split was analyzed for As, Hg, and Se; the ashed portion was analyzed by the 42-element ICP–MS/AES methods.

In addition to the near-total four-acid digestion technique, the <2-mm streambed sediments were analyzed using a weak partial extraction method. For this method, a hydrochloric acid/hydrogen peroxide solution solubilizes metals loosely bound in a mineral silicate lattice. Ten metals are extracted by a 10-percent aliquot 336-disobutylketone solution as organic halides. It is important to note that this procedure is a partial digestion and, depending on an element’s availability, results may be biased low when compared to other methods of analyses. This method was not available when additional samples were collected from the Filson Creek watershed in 2015. More detail for all analytical methods is provided in Woodruff (2019).

Quality Assurance/Quality Control

Solid-media samples analyzed for inorganic constituents received quality control (QC) checks on three separate levels to measure the accuracy and precision of data provided, based on analysis of reference materials and sample replicates, respectively. The first-level QC assessment was performed by the USGS contract laboratory, SGS Laboratories. The second-level QC assessment was performed by the USGS Mineral Resource Team QC officer, followed by a third-level assessment by the USGS principal investigator.

The laboratory includes a reagent blank and reference sample with every batch of 20 environmental samples to measure analytical accuracy. All samples submitted to SGS Laboratories were accompanied by a set of USGS in-house reference samples submitted at the rate of 10 percent. Data for the reference samples were evaluated by comparing the “obtained” analytical value to the “expected” value for each element. The values must fall within the range of acceptance, which varies from plus or minus (±) 5 percent to ±20 percent depending on the analytical method. The accuracy of elements determined by the ICP–MS/AES method were considered acceptable if recovery for all 42 elements was ±15 percent at five times the lower limit of determination (LLD) and the calculated relative standard deviation (RSD) of duplicate samples was no greater than (>) 15 percent. The accuracy for As, Hg, and Se single element analyses were considered acceptable if recovery was ±20 percent at five times the LLD and the calculated percent RSD of duplicate samples was no >20 percent. Total and carbonate C were deemed acceptable if recovery was ±15 percent at five times the LLD and the calculated percent RSD of duplicate samples was not >15 percent. Blind duplicates were included by the principal investigator with all analytical jobs at a rate of 10 percent of total samples. Quality control determinations at all levels identified no substantial quality problems with the dataset.

Surface-Water Quality

A total of 141 water-quality samples were collected from surface waters in the three study watersheds during September 2013 to July 2015. Physical and chemical water-quality characteristics were measured to assess water-quality differences in the three different mineral-deposit settings. All water-quality samples were collected following USGS protocols outlined in the USGS “National Field Manual for the Collection of Water-Quality Data” (U.S. Geological Survey, variously dated).

Site Selection

Water-quality sites were selected (1) to capture conditions upstream, within, and downstream from known mineral deposits, if present; (2) to coincide with current U.S. Forest Service water-quality sites; and (3) based on accessibility. Nine water-quality sites were sampled along Filson Creek (fig. 7, table 1): three sites upstream from the mineralized area of the Spruce Road deposit, four sites within the mineralized area, two sites on the south fork of Filson Creek, and one site downstream from the mineralized area. Four water-quality sites were sampled along Keeley Creek (fig. 7, table 1). Because there are no known mineral deposits in the Keeley Creek watershed, sites were selected along the creek and on one tributary to represent conditions spanning the entire watershed. Seven water-quality sites were sampled along the St. Louis River (fig. 8, table 1): four sites upstream and three sites downstream from the basal contact of the Duluth Complex.

Sample Collection

Surface-water samples were collected once during September 2013 and four times during April through October in 2014 and 2015. Site access was seasonally restricted at some sites and therefore samples were not collected at every water-quality site on every sampling trip. Surface-water samples were analyzed for physical properties, dissolved and total trace metals, major ions, alkalinity, total organic carbon (TOC), and dissolved organic carbon (DOC) (table 2). Total metals were analyzed only at select sites in September 2013 because of funding constraints.

Physical water-quality properties were measured at the time of sampling using a Yellow Springs Instrument Company data sonde. Upon arrival at each site, the Yellow Springs Instrument Company data sonde was completely submerged underwater downstream from sample collection, where it was left to stabilize to ambient environmental conditions. Temperature, specific conductance, pH, and dissolved oxygen were recorded after the readings stabilized.

Surface-water grab samples were collected for total metals, pH, and specific conductance by dipping a polyethylene bottle directly into the stream. Bottles were rinsed three times with native water prior to sample collection. This same method was used to collect surface-water grab samples for TOC, only using a 125-milliliter (mL) baked, amber glass bottle. Glass bottles were not rinsed with native water prior to sample collection. Surface-water grab samples were collected for dissolved metals, alkalinity, and DOC by directly pumping stream water through a prerinsed 0.45-µm pore-size disposable capsule filter fitted onto Teflon® tubing using a peristaltic pump. Sample bottles were rinsed three times with native water prior to sample collection.

To verify representative samples were being collected with the grab method, composite samples were collected at select sites during five sampling trips for comparison. Composite samples were collected using a DH-81 wading rod fitted with a Teflon® collar and 1-liter Teflon® bottle. Samples were collected at equally spaced points across the stream channel at similar transit rates. Samples from each sample point were composited into a Teflon® churn where they were homogenized prior to dispensing into sample bottles. Composite samples were collected at St. Louis River sites SLR1 and SLR6 in April 2014 from a bridge using a DH-95 water-quality sampler because of high streamflow, which limited access for grab sampling. There are no associated grab samples for comparison for these two samples.

All equipment used for water sample collection was made of inert materials, such as Teflon®, to reduce the potential for chemicals leaching from sample equipment. Tubing used to collect samples for metal and ion analyses, churns, and sample

Table 1. Water-quality sample sites for Filson Creek, Keeley Creek, and the St. Louis River, northeastern Minnesota.

[USGS, U.S. Geological Survey; MN, Minnesota]

Map identifier	USGS station number	USGS station name	Latitude, decimal degrees	Longitude, decimal degrees
FC1	05124970	Filson Creek below Omaday Lake near Isabella, MN	47.81961	−91.65645
FC2	05124974	Filson Creek in Southeast Southwest Section 19 near Winton, MN	47.83367	−91.65509
FC3	05124977	Filson Creek in Southwest Northeast Section 19 near Winton, MN	47.84131	−91.65083
FC4	05124980	Filson Creek in Southeast Northeast Section 24 near Winton, MN	47.84138	−91.66318
FC5	05124982	Filson Creek in Southwest Southeast Section 24 near Winton, MN	47.83562	−91.67040
FC6	05124985	Filson Creek Tributary in Southwest Northeast Section 25 near Winton, MN	47.82730	−91.66985
FC7	05124988	Filson Creek Tributary in Northwest Northeast Section 25 near Winton, MN	47.83384	−91.67105
FC8	05124990	Filson Creek in Southeast Southwest Section 24 near Winton, MN	47.83480	−91.67455
FC9	05124992	Filson Creek above Mouth near Winton, MN	47.83965	−91.68063
KC1	05125033	Keeley Creek below Heart Lake near Babbitt, MN	47.77671	−91.65995
KC2	05125035	Keeley Creek at State Highway 1 near Babbitt, MN	47.78016	−91.68385
KC3	05125037	Keeley Creek Tributary below State Highway 1 near Babbitt, MN	47.77769	−91.71734
KC4	05125039	Keeley Creek above mouth near Babbitt, MN	47.76687	−91.74954
SLR1	04015430	St. Louis River below Seven Beaver Lake near Fairbanks, MN	47.49204	−91.84562
SLR2	04015439	St. Louis River above County Highway 110 near Skibo, MN	47.46746	−91.94016
SLR3	04015438	St. Louis River near Skibo, MN	47.48085	−92.04058
SLR4	04015441	St. Louis River below County Highway 110 near Hoyt Lakes, MN	47.46508	−92.06908
SLR5	04015443	St. Louis River above River Bend Road near Hoyt Lakes, MN	47.43705	−92.13450
SLR6	04015444	St. Louis River at Moose Line Road near Hoyt Lakes, MN	47.47263	−92.12122
SLR7	04015445	St. Louis River above Whitewater Lake confluence near Hoyt Lakes, MN	47.48136	−92.18889

collection bottles were cleaned according to USGS protocols (Wilde, 2004) between sites with a succession of soapy water, tap water, deionized water, 5-percent hydrochloric acid, and organic-free blank water. Tubing used for collection of TOC and DOC was rinsed between sites with only organic-free blank water purchased from the USGS National Water Quality Laboratory (NWQL). Capsule filters used to filter sample water for inorganic chemicals and organic carbon were rinsed with 1 liter of deionized water or organic-free water, respectively, no more than 12 hours prior to sample collection.

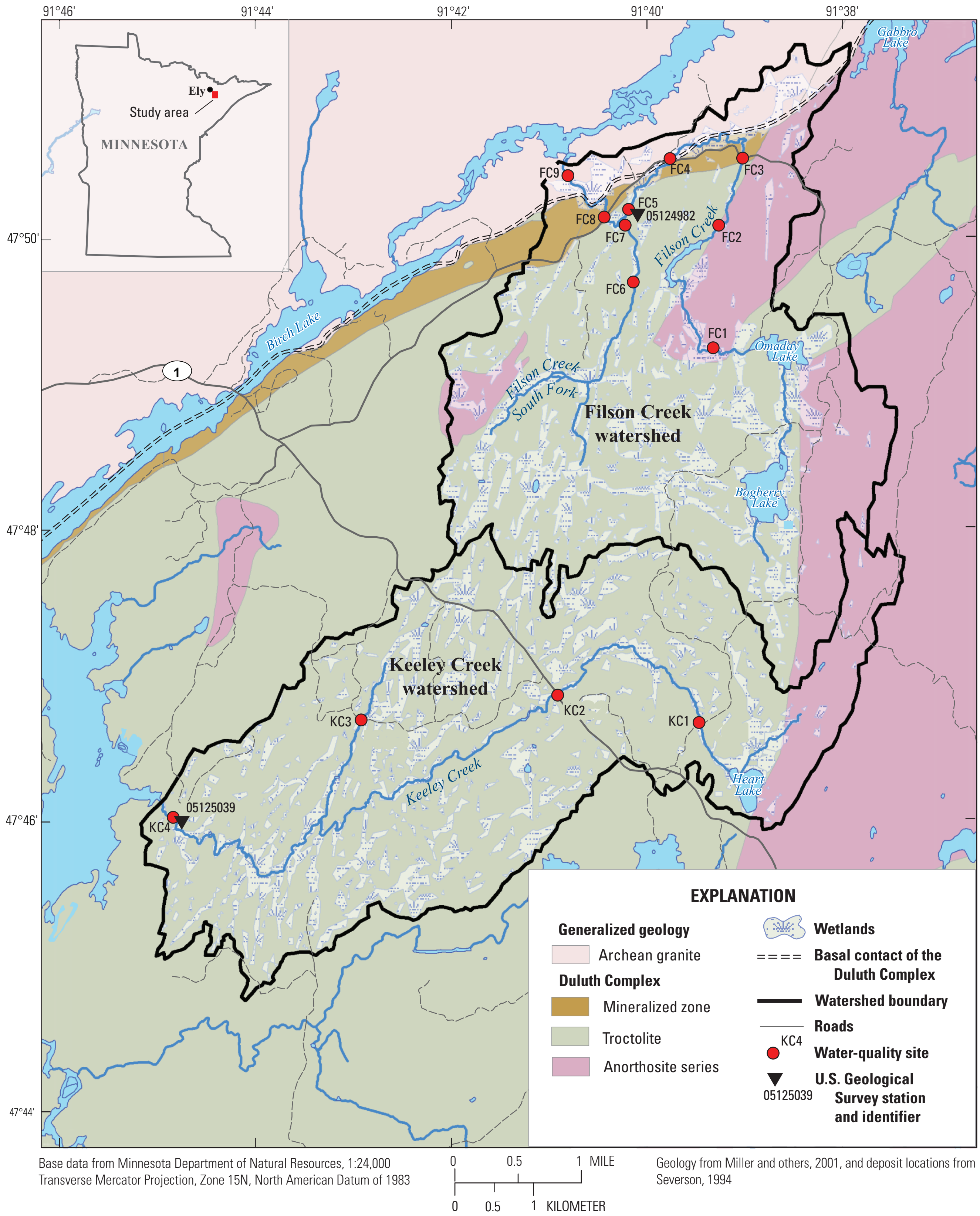
Sample Handling and Analysis

Filtered water samples collected for analysis of dissolved cations and unfiltered samples collected for total trace metals were preserved with 2 mL of 7.5 normal nitric acid immediately following sample collection. Filtered water samples collected for analysis of DOC were preserved with 1 mL 4.5 normal sulfuric acid immediately following sample collection. All samples were stored on ice and shipped to the NWQL within 24 hours.

Cation and anion concentrations were determined at the NWQL according to methods described in Fishman (1993). Dissolved trace metal concentrations were determined at the NWQL according to methods described in Fishman and Friedman (1989), Struzeski, and others (1996), Garbarino (1999), and Garbarino and others (2006). Total trace metals were determined at the NWQL according to methods described by Fishman and Friedman (1989), Hoffman and others (1996), and Garbarino and others (2006). Concentrations of TOC and DOC were determined at the NWQL according to methods described by Brenton and Arnett (1993). Alkalinity and bicarbonate were determined by USGS field personnel through inflection-point titrations performed within 24 hours after sample collection (Rounds, 2006). Alkalinity and bicarbonate were also measured by NWQL laboratory technicians using similar methods, although holding times were often exceeded.

Quality Assurance/Quality Control

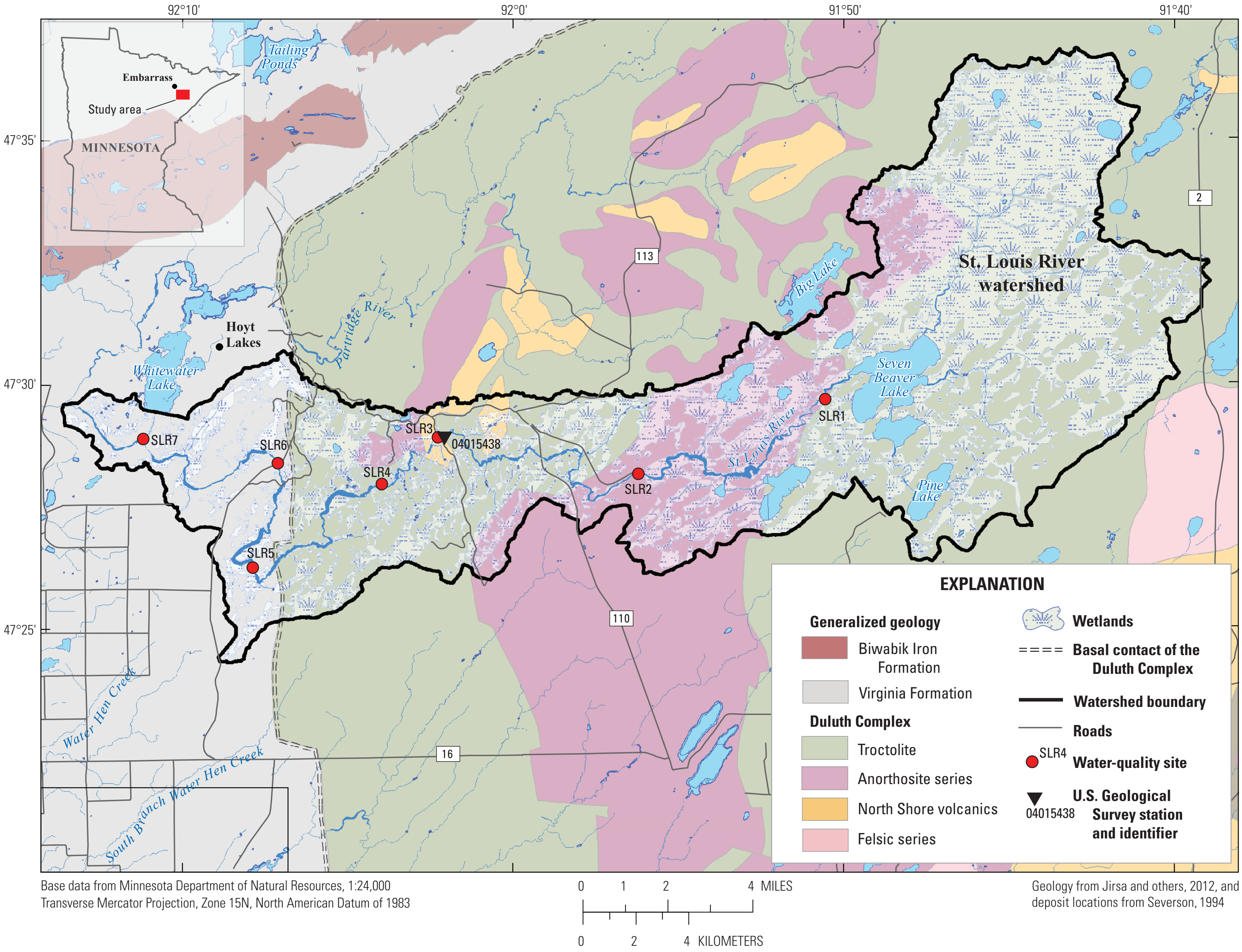
The NWQL has a rigorous set of procedures for ensuring and controlling the quality of received water samples and analytical results determined by the laboratory (Pirkey and Glodt, 1998). All the water-quality data and sampling-site information, including quality-assurance and control-sample



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Miller and others, 2001, and deposit locations from Severson, 1994

Figure 7. Water-quality stream sites with bedrock geology, wetlands, and watershed boundaries, Filson Creek and Keeley Creek watersheds, near Ely, Minnesota.



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Jirsa and others, 2012, and
deposit locations from Severson, 1994

Figure 8. Water-quality stream sites with bedrock geology, wetlands, and watershed boundary, St. Louis River watershed, near Hoyt Lakes, Minnesota.

Table 2. Selected physical and chemical properties analyzed in surface-water samples collected from Filson Creek, Keeley Creek, and St. Louis River watersheds, northeastern Minnesota, September 2013–July 2015.

[CASRN, Chemical Abstract Service Registry Number; USGS, U.S. Geological Survey; mg/L, milligram per liter; ltmdl, long-term method detection level; µg/L, microgram per liter; --, not applicable; mrl, minimum reporting level; µS/cm, microsiemen per centimeter]

Chemical	Parameter number	CASRN[1]	Reporting limit	Units	Reporting level type
Custom schedule 2574 for analysis of major ions and trace metals in filtered water at USGS National Water Quality Laboratory					
Alkalinity	29801	471-34-1	4.6	mg/L	ltmdl
Aluminum	1106	7429-90-5	3	µg/L	ltmdl
Arsenic	1000	7440-38-2	0.1	µg/L	ltmdl
Barium	1005	7440-39-3	0.25	µg/L	ltmdl
Beryllium	1010	7440-41-7	0.02	µg/L	ltmdl
Boron	1020	7440-42-8	2	µg/L	ltmdl
Calcium	915	7440-70-2	0.022	mg/L	ltmdl
Chloride	940	16887-00-6	0.02	mg/L	ltmdl
Chromium	1030	7440-47-3	0.6	µg/L	ltmdl
Cobalt	1035	7440-48-4	0.05	µg/L	ltmdl
Copper	1040	7440-50-8	0.8	µg/L	ltmdl
Fluoride	950	16984-48-8	0.01	mg/L	ltmdl
Iron	1046	7439-89-6	4	µg/L	ltmdl
Lead	1049	7439-92-1	0.04	µg/L	ltmdl
Lithium	1130	7439-93-2	0.22	µg/L	ltmdl
Magnesium	925	7439-95-4	0.011	mg/L	ltmdl
Manganese	1056	7439-96-5	0.4	µg/L	ltmdl
Nickel	1065	7440-02-0	0.2	µg/L	ltmdl
pH	403	--	0.1	standard units	mrl
Potassium	935	9/7/7440	0.03	mg/L	ltmdl
Selenium	1145	7782-49-2	0.05	µg/L	ltmdl
Silica	955	7631-86-9	0.018	mg/L	ltmdl
Sodium	930	7440-23-5	0.06	mg/L	ltmdl
Specific conductance	90095	--	5	µS/cm	mrl
Strontium	1080	7440-24-6	0.8	µg/L	ltmdl
Sulfate	945	14808-79-8	0.02	mg/L	ltmdl
Titanium	1150	7440-32-6	0.5	µg/L	mrl
Vanadium	1085	7440-62-2	0.1	µg/L	ltmdl
Zinc	1090	7440-66-6	2	µg/L	ltmdl
Custom schedule 2575 for analysis of trace metals in unfiltered water at USGS National Water Quality Laboratory					
Arsenic	1002	7440-38-2	0.2	µg/L	ltmdl
Beryllium	1012	7440-41-7	0.02	µg/L	ltmdl
Chromium	1034	7440-47-3	0.4	µg/L	ltmdl
Copper	1042	7440-50-8	0.8	µg/L	ltmdl
Iron	1045	7439-89-6	4.6	µg/L	ltmdl
Lead	1051	7439-92-1	0.04	µg/L	ltmdl
Manganese	1055	7439-96-5	0.4	µg/L	ltmdl
Nickel	1067	7440-02-0	0.2	µg/L	ltmdl
Selenium	1147	7782-49-2	0.1	µg/L	ltmdl
Specific conductance	90095	--	5	µS/cm	mrl

Table 2. Selected physical and chemical properties analyzed in surface-water samples collected from Filson Creek, Keeley Creek, and St. Louis River watersheds, northeastern Minnesota, September 2013–July 2015.—Continued

[CASRN, Chemical Abstract Service Registry Number; USGS, U.S. Geological Survey; mg/L, milligram per liter; ltmdl, long-term method detection level; µg/L, microgram per liter; --, not applicable; mrl, minimum reporting level; µS/cm, microsiemen per centimeter]

Chemical	Parameter number	CASRN[1]	Reporting limit	Units	Reporting level type
Custom schedule 2575 for analysis of trace metals in unfiltered water at USGS National Water Quality Laboratory—Continued					
Titanium	1152	7440-32-6	0.1	µg/L	mrl
Vanadium	1087	7440-62-2	0.6	µg/L	ltmdl
Zinc	1092	7440-66-6	2	µg/L	ltmdl
Custom schedule 2576 for analysis of organic carbon in filtered and unfiltered water at USGS National Water Quality Laboratory					
Organic carbon, filtered	681	--	0.23	mg/L	ltmdl
Organic carbon, unfiltered	680	--	0.7	mg/L	ltmdl

[1] This report contains CAS Registry Numbers®, which is a Registered Trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client Services℠.

information, are stored and can be accessed in the USGS National Water Information System database (U.S. Geological Survey, 2016) using the USGS station numbers in table 1.

Concentrations of several dissolved elements exceeded total element concentrations. Because the total concentration includes the dissolved concentration, the former can never be greater than the latter. Samples in which dissolved concentrations were more than 10 percent greater than total concentrations were reanalyzed by the NWQL, upon request. At this stage, a threshold of 10 percent was used because this margin of error allows room for analytical variability and uncertainty. Reanalysis corrected the issue in several instances; however, several results were not reconciled (for example, the relative percent difference [RPD] between the dissolved and total fractions was still >10 percent). For samples in which the dissolved fraction was more than 20 percent greater than the total, concentrations greater than the third quartile plus one and a half times the interquartile range [$Q3+1.5(IQR)$] were excluded from the dataset. This analysis led to the exclusion of two dissolved Cu, one dissolved manganese (Mn), one dissolved Ti, and one dissolved zinc (Zn) data points. Additionally, all total Se values were excluded from the dataset because of consistent low recovery rates at the NWQL during the period in which our samples were analyzed.

A field-blank sample is collected to measure the magnitude of contaminant concentrations that be introduced into the sample because of the sampling process (U.S. Geological Survey, 2006). Eight field-blank samples (one per sampling trip) were collected throughout the study. Inorganic blank water purchased from the NWQL was pumped through clean tubing and prerinsed filters into bottles for trace metal and ion analyses; organic-free blank water was used for TOC and DOC analyses.

Concentrations of total chromium (Cr), total lead (Pb), dissolved Mn, TOC, and DOC were detected above the laboratory reporting level in at least one blank sample. If the blank-sample detection was greater than the reporting level, environmental samples were determined to be affected by contamination if the concentration was <10 percent higher than the blank-sample concentration. Field blank concentrations of total Fe, dissolved Mn, TOC, and DOC were not high enough to affect environmental sample concentrations. Total Cr data collected during September 2014 were considered affected by contamination and not used in analyses because the field blank concentration was greater than all environmental sample concentrations.

Twelve sequential-replicate sample pairs were collected at randomly selected sites throughout the study. A sequential-replicate sample is collected consecutively following that of the environmental sample to assess variability among samples resulting from sample collection, processing, shipping, and laboratory procedures performed at different sampling times (U.S. Geological Survey, 2006). Replicate sample pairs in which detectable concentrations were present in both samples were assessed to determine the extent that the concentrations varied between the two samples using the absolute RPD (absolute difference in concentrations between environmental and replicate samples divided by the mean and multiplied by 100). The RPD of replicate sample pairs ranged from 0 to 148, with an overall mean of 10 (±20) (table 3). Consistent concentrations (RPD <1) of numerous elements were observed in multiple replicate pairs.

In addition to grab samples, two composite samples were collected at select sites in June 2014, three in September 2014, and one in April, June, and July 2015. A composite sample integrates the water of the entire channel cross-section into one sample. The RPD was calculated to determine the extent that concentrations varied between composite and grab sample pairs. The RPD was only calculated when detectable concentrations of analytes were reported in corresponding samples. The RPD between analytes detected in composite and grab samples ranged from 0 to 111, with an overall mean of 7

Table 3. Summary statistics of relative percent differences between replicate pairs for trace elements and metals measured in surface-water samples collected from Filson Creek, Keeley Creek, and the St. Louis River watersheds, northeastern Minnesota, 2013–15.

[USGS, U.S. Geological Survey; na, not applicable]

USGS parameter code	Trace element/metal	Number of replicate pairs with detections in both samples	Number of replicate pairs with detections in one sample	Number of replicate pairs with no detections in both samples	Number of sample pairs analyzed	Relative percent difference			
						Minimum	Mean	Standard deviation	Maximum
00915	Calcium, filtered	12	0	0	12	0	2	2	5
00925	Magnesium, filtered	12	0	0	12	0	1	1	5
00935	Potassium, filtered	12	0	0	12	0	6	6	22
00930	Sodium, filtered	12	0	0	12	0	3	2	7
29801	Alkalinity, laboratory	12	0	0	12	0	1	1	3
39086	Alkalinity, field	10	0	0	10	0	10	9	24
00940	Chloride, filtered	12	0	0	12	0	3	5	18
00950	Fluoride, filtered	12	0	0	12	0	1	3	11
00955	Silica, filtered	12	0	0	12	0	1	1	2
00945	Sulfate, filtered	12	0	0	12	0	1	1	3
01106	Aluminum, filtered	12	0	0	12	0	4	5	15
01005	Barium, filtered	12	0	0	12	0	2	1	4
01010	Beryllium, filtered	2	0	10	12	10	13	5	17
01012	Beryllium, unfiltered	1	0	9	10	na	na	na	86
01030	Chromium, filtered	0	2	10	12	na	na	na	na
01034	Chromium, unfiltered	6	1	3	10	2	38	39	100
01035	Cobalt, filtered	12	0	0	12	1	11	11	36
01040	Copper, filtered	8	0	4	12	0	3	3	6
01042	Copper, unfiltered	7	1	2	10	0	22	27	61
01046	Iron, filtered	12	0	0	12	0	11	17	51
01045	Iron, unfiltered	10	0	0	10	0	13	31	100
01049	Lead, filtered	12	0	0	12	0	20	26	79
01051	Lead, unfiltered	10	0	0	10	0	18	31	100
01130	Lithium, filtered	11	0	1	12	0	2	3	8
01056	Manganese, filtered	12	0	0	12	0	3	3	8
01055	Manganese, unfiltered	10	0	0	10	0	17	33	100
01065	Nickel, filtered	12	0	0	12	0	3	7	24
01067	Nickel, unfiltered	10	0	0	10	0	40	56	148

Table 3. Summary statistics of relative percent differences between replicate pairs for trace elements and metals measured in surface-water samples collected from Filson Creek, Keeley Creek, and the St. Louis River watersheds, northeastern Minnesota, 2013–15.—Continued

[USGS, U.S. Geological Survey; na, not applicable]

USGS parameter code	Trace element/metal	Number of replicate pairs with detections in both samples	Number of replicate pairs with detections in one sample	Number of replicate pairs with no detections in both samples	Number of sample pairs analyzed	Relative percent difference			
						Minimum	Mean	Standard deviation	Maximum
01080	Strontium, filtered	12	0	0	12	0	1	1	2
01150	Titanium, filtered	11	0	0	11	0	19	29	100
01152	Titanium, unfiltered	10	0	0	10	0	26	39	101
01085	Vanadium, filtered	12	0	0	12	0	12	17	55
01087	Vanadium, unfiltered	6	0	4	10	0	26	37	100
01090	Zinc, filtered	8	4	0	12	4	14	12	37
01092	Zinc, unfiltered	8	1	1	10	3	22	19	59
01000	Arsenic, filtered	11	0	0	11	0	4	4	13
01002	Arsenic, unfiltered	8	1	0	9	0	24	29	100
01020	Boron, filtered	12	0	0	12	0	4	3	8
01145	Selenium, filtered	12	0	0	12	0	6	5	17
01147	Selenium, unfiltered	5	0	5	10	2	24	37	100
00681	Organic carbon, filtered	12	0	0	12	0	1	1	3
00680	Organic carbon, unfiltered	11	0	0	11	0	5	6	16

(±14). No consistent patterns in concentration differences (for example, consistently greater concentrations in composite samples compared to grabs) were observed for most elements and therefore it is assumed that grab samples are representative of the sampled streams. Dissolved Cu was one exception; concentrations in composite samples tended to be higher (17 to 100 percent), though concentrations were all <5 micrograms per liter (µg/L).

Streamflow

To estimate baseline streamflow conditions, streamflow was monitored at 15-minute intervals by a continuous streamgage in each of the three watersheds. These three streamgages were located at water-quality sites FC5, KC4, and SLR3 (figs. 7, 8; tables 1, 4). Streamflow was also measured at an existing Minnesota Department of Natural Resources streamgage (Minnesota Department of Natural Resources, 2016, site ID 72032001) located at water-quality site FC8, downgradient from the confluence of the south and main branches of Filson Creek (fig. 7).

Installation and maintenance of the streamgages, and stream stage, level, and streamflow measurements were completed following USGS protocols outlined in Rantz and others (1982), Sauer and Turnipseed (2010), Kenney (2010), and Turnipseed and Sauer (2010). The locations of the streamgages were based on different flow and constituent load considerations for the three watersheds. The Filson Creek streamgage (USGS station number 05124982, Filson Creek in Southwest Southeast Sec. 24, near Winton, Minnesota) was placed at water-quality site FC5 to estimate the flow and load contribution of the south branch of the creek to the main branch. The Keeley Creek streamgage (USGS station number 05125039; Keeley Creek above mouth near Babbitt, Minnesota) was placed at water-quality site KC4 to estimate total streamflow for the watershed. The St. Louis River streamgage (USGS station number 04015438, St. Louis River near Skibo, Minnesota) was placed at water-quality site SLR3; this site was optimal because few boulders and logs were present, adjacent wetlands were absent, and a narrow, relatively straight stream channel is present.

In addition to the continuous streamflow data collected at the three USGS streamgages, a total of 201 instantaneous streamflow measurements were collected at surface-water-quality sample sites coincident with water-quality sample collection or during periodic maintenance trips for the streamgage. All continuous streamflow data for USGS streamgages and instantaneous streamflow measurements are available in the USGS National Water Information System database at https://waterdata.usgs.gov/nwis (U.S. Geological Survey, 2016) using the station numbers provided in the previous paragraph.

Synthetic Hydrographs

Synthetic hydrographs were produced to estimate daily mean streamflow values for the 17 unregulated, ungaged water-quality sites in the three watersheds from March 18, 2014, through December 31, 2015. Production of synthetic hydrographs was completed using drainage-area ratios between gaged and ungaged sites and continuous daily mean streamflows from USGS streamgages. These mean streamflows were used in conjunction with water-quality data to estimate instantaneous constituent loads.

One hydrograph parameter can be used to derive hydrographs at ungaged sites if other physical parameters are hydrologically like the gaged basin for which the estimated streamflow values are developed (Melching and Marquardt, 1997). These physical parameters include topography, geomorphology, soil types, land cover, land use, and climate (Melching and Marquardt, 1997). Errors occur if there are hydrologic differences resulting from differences in physical parameters between the ungaged site and the gaged site that are not accounted for in the analysis. Drainage-area ratios of gaged and ungaged sites between 0.25 and 4 typically work well for estimating streamflow (Lorenz and Ziegeweid, 2016). In our study, drainage-area ratios for all but two of the ungaged sites (KC1 and KC3) were between 0.25 and 4 (table 4).

The estimated streamflow values were computed using the following equation:

$$Q_0 = (A_0 * Q_G)/ A_G \tag{1}$$

where

Q_0 is estimated streamflow value at the ungaged site, in cubic feet per second;

A_0 is drainage basin area of the ungaged site, in square feet;

Q_G is streamflow value at the gaged site, in cubic feet per second; and

A_G is drainage basin area of the gaged site, in square feet.

Estimating daily mean streamflows at ungaged sites using one parameter, the drainage basin area, simplifies underlying hydrologic transport processes. Resulting models are useful for this study because the ungaged sites within each of the three watersheds are hydrologically similar and close (<17 mi) to the gaged site within its watershed. Drainage basin areas for all 20 sites were estimated using StreamStats, a USGS web-based mapping tool (U.S. Geological Survey, 2015).

Unregulated, daily mean streamflows were estimated at eight ungaged water-quality sampling sites in the Filson Creek watershed, three in the Keeley Creek Watershed, and six in the St. Louis River watershed. The USGS station 05124982 (FC5, fig. 7) was the reference streamgage used to estimate streamflow at ungaged Filson Creek sites. Four (FC1–FC4, fig. 7) ungaged sites are upstream from the reference gage and four (FC6–FC9, fig. 7) are downstream. Two of the downstream sites (FC6 and FC7) are on a tributary of Filson Creek.

Table 4. Watershed characteristics and comparison of daily mean and estimated (synthetic) streamflows in Filson Creek, Keeley Creek, and the St. Louis River watersheds, northeastern Minnesota, 2014–15.

[USGS, U.S. Geological Survey; <, less than; *, indicates site with a USGS streamgage (U.S. Geological Survey, 2016); --, no data; **, indicates site with a Minnesota Department of Natural Resources streamgage, site ID 72032001 (Minnesota Department of Natural Resources, 2016)]

Map identifier	USGS station number	Drainage area, square miles	Drainage area ratio (gaged/ungaged)	Distance to gage site, stream miles	Comparison of measured and estimated streamflow			
					Spearman's rho	*p*-value	Number of streamflow measurements	Nash-Sutcliffe efficiency coefficient
FC1	05124970	3.5	1.7	3.8	0.80	0.13	5	0.43
FC2	05124974	4.1	1.4	2.2	1.00	0.02	5	0.94
FC3	05124977	4.5	1.3	1.6	0.98	<0.001	10	0.76
FC4	05124980	5.6	1.0	0.61	0.99	<0.001	8	0.38
FC5*	05124982	5.8	1.0	0.00	--	--	--	--
FC6	05124985	3.1	1.9	0.70	0.80	0.33	4	−0.12
FC7	05124988	3.3	1.7	0.19	0.82	0.03	7	0.83
FC8**	05124990	9.5	0.6	0.32	0.96	0.003	7	0.84
FC8**	05124990	9.5	1.0	0.00	[1]0.93	[1]0.007	[1]7	[1]0.71
FC9	05124992	10	0.6	0.97	0.96	0.003	7	0.67
KC1	05125033	1.6	6.9	7.0	0.90	0.08	5	0.95
KC2	05125035	3.5	3.1	5.2	0.94	0.02	6	0.99
KC3	05125037	1.2	8.8	3.1	0.94	0.02	6	0.66
KC4*	05125039	11	1.0	0.00	--	--	--	--
SLR1	04015430	68	1.5	14	1.00	0.02	5	1.00
SLR2	04015439	86	1.2	7.6	--	--	0	--
SLR3*	04015438	101	1.0	0.00	--	--	--	--
SLR4	04015441	106	0.9	2.5	--	--	1	--
SLR5	04015443	119	0.8	7.7	--	--	2	0.99
SLR6	04015444	122	0.8	11	0.97	0.00	13	0.98
SLR7	04015445	133	0.8	16	1.00	0.08	4	0.93

[1] Comparison of measured streamflows at Minnesota Department of Natural Resources streamgage to estimated (synthetic) streamflows.

Distances from ungaged sites to the reference site range from 0.19 (FC7) to 3.8 (FC1) stream miles and gaged-to-ungaged drainage-area ratios range from 0.6 (FC8) to 1.9 (FC6, table 4). The USGS station 05125039 (KC4, fig. 7) was the reference streamflow gage for ungaged Keeley Creek sites. All three ungaged sites (KC1, KC2, and KC3, fig. 7) are upstream from the gage. One of the sites (KC3) is on a tributary of Keeley Creek. Distances from ungaged sites to the reference site range from 3.1 (KC3) to 7.0 (KC1) stream miles and gaged-to-ungaged drainage-area ratios for the Keeley Creek sites range from 3.1 (KC2) to 8.8 (KC3, table 4). The USGS station 04015438 (SLR3, fig. 8) was the reference streamflow gage for ungaged St. Louis River sites. Two of the ungaged sites (SLR1 and SLR2, fig. 8) are upstream from the gage and four (SLR4, SLR5, SLR6, and SLR7, fig. 8) are downstream. Distances from ungaged sites to the reference site range from 2.5 (SLR5) to 16 (SLR1) stream miles and gaged-to-ungaged drainage-area ratios for the St. Louis River sites range from 0.8 (SLR5, SLR6, SLR7) to 1.5 (SLR1, table 4).

Statistical comparisons between measured streamflow and estimated daily mean streamflow were completed for each of the ungaged sites to assess how representative estimated streamflow is of real flow. Streamflow was periodically measured at each of the ungaged sites using a FlowTracker in 2014 and 2015, often during days when water-quality samples were collected. The number of observed streamflow measurements was dependent on flow conditions, so varied between sites. Often a streamflow measurement could not be made because streamflow was too high, which frequently occurred on the St. Louis River. Thus, Spearman’s rho was computed for 14 of the 17 ungaged sites to evaluate the estimated streamflows at these sites using the cor.all() function in the smwrStats package (version 0.7.5; Lorenz, 2016) within R software (R Core Team, 2019). The Nash-Sutcliffe efficiency (NSE) coefficient was computed for 15 of the ungaged sites to evaluate the accuracy of the estimated streamflow using the NSE coefficient function in the hydroGOF package (version 0.3-8; Zambrano-Bigiarini, 2014). Measurements of streamflow collected by the Minnesota Department of Natural Resources streamgage (site ID 72032001; Minnesota Department of Natural Resources, 2016) were also used to compare against estimated streamflows at site FC8 using Spearman’s rho and the NSE coefficient.

Daily Constituent Loads

Daily loads for each constituent were estimated using dissolved concentrations detected in each sample and daily synthetic hydrograph streamflow data (described in the “Synthetic Hydrographs” section of this report) from the date on which the sample was collected. Streamflow from synthetic hydrographs was used instead of measured streamflow because the quality of the streamflow measurements was generally rated fair to poor. Stream cross-sections were often filled with boulders and logs, making good streamflow measurements difficult to obtain. Only loads for constituents of environmental concern (Cu, Ni, and SO_4^{-2}) are presented in this report.

Loads were only determined for the farthest downstream water-quality sampling site for Filson and Keeley Creeks (sites FC9 and KC4, table 1, fig. 7) to estimate the total amount of Cu, Ni, and SO_4^{-2} being transported by the creeks out of their watersheds. For the St. Louis River, the farthest downstream water-quality sampling site (site SLR7, table 1, fig. 8) was often not accessible during high flows, so loads were determined for the second farthest downstream water-quality site (site SLR6, table 1, fig. 8) to allow loads to be determined at low, medium, and high flows. Water-quality samples with concentrations below detection levels were considered unknown, and loads were not calculated.

Solid Media Geochemistry and Water Quality near the Basal Part of the Duluth Complex

The following sections report the results of geochemical analysis of solid-media samples, chemical analysis of surface-water-quality samples, estimates of streamflow, and daily metal loads.

Solid Media

Complete geochemical data and descriptions of analytical methods for all solid-media samples are provided in Woodruff (2019). Summary tables for each media type are provided in this report.

Bedrock

A total of 42 bedrock samples were analyzed for their geochemical content (table 5). The three major rock types within the study areas, granite of the Archean Giants Range batholith, sedimentary rocks of the Paleoproterozoic Virginian Formation, and igneous rocks of the Mesoproterozoic Duluth Complex have element concentrations distinct from one another because of the different minerals that make up the bulk of the rock units. Granite of the Archean Giants Range batholith consists of potassium (K) feldspar, plagioclase, and quartz with small percentages of other minerals (Boerboom and Zartman, 1993). The Paleoproterozoic Virginia Formation is variably argillite, siltstone, and graywacke, sedimentary rocks consisting of clay, silt, and fine sand; identified framework minerals include quartz and feldspar (Lucente and Morey, 1983). The Mesoproterozoic Duluth Complex rocks are dominated by gabbro, troctolite, and anorthosite; primary minerals are plagioclase, pyroxene, and olivine (Miller and others, 2002).

Major element concentrations in each of these broad rock groups in the study area reflect the varying mineralogy. Duluth Complex bedrock has comparatively high concentrations of aluminum (Al), calcium (Ca), Fe, and magnesium (Mg), consistent with the presence of pyroxene, olivine, and plagioclase. Granite of the Giants Range batholith has relatively low concentrations of these four major elements, and higher K and sodium (Na) compared to rocks of the Duluth Complex because of the presence of K- and Na-rich feldspar. The geochemical composition of sedimentary rocks is variable because it is dependent on the mineralogy of original sediment sources and subsequent sorting and alteration (McLennan and Taylor, 1991). Within the St. Louis River watershed, bedrock of the Virginia Formation has relatively low Al, Ca, and Na concentrations, but high K values compared to Duluth Complex bedrock (table 5).

Trace element concentrations in bedrock samples follow tendencies of major elements. For example, the granite of the Archean Giants Range batholith has high concentrations of barium (Ba) (2,050 milligrams per kilogram [mg/kg]) and strontium (Sr) (1,130 mg/kg). Both Ba and Sr are preferentially incorporated into K-feldspar from a crystallizing magma, as indicated by their high (>1) partition coefficients for K-feldspar (Henderson, 1982). Compared to the granite of the Archean Giants Range batholith, unmineralized rocks of the Duluth Complex have high concentrations of cobalt (Co), Cr, Cu, Mn, and Ni because these elements preferentially partition into olivine and pyroxene from basaltic magma (Henderson, 1982). Sulfide mineralized rock of the Spruce Road deposit can have high Ni (as much as 1,967 mg/kg) and Cu (as much as 7,722 mg/kg). Nickel and Cu are chalcophile elements, meaning that they easily combine with sulfur (S). Thus, mineralized rocks that have a discrete sulfide phase will also have higher values of Ni, Cu, and Co, because these elements are incorporated into an immiscible sulfide liquid from silicate magma. Not all bedrock samples collected within the mapped area of the Spruce Road deposit, and therefore labeled as "mineralized" in table 5, have high Ni and Cu concentrations. The lack of consistently high Ni and Cu concentrations is an indication of the heterogeneous nature of sulfide mineralization along the basal section of the Duluth Complex. Trace elements that distinguish bedrock of the Virginia Formation from the Duluth Complex include relatively high concentrations of cerium (Ce), lanthanum (La), lithium (Li), niobium (Nb), Pb, rubidium (Rb), thorium (Th), uranium (U), and Zn (see Woodruff, 2019).

Soil

A total of 106 soil samples from all three watersheds were analyzed for their geochemical content (table 6). Soil is a heterogeneous mixture of organic and organo-mineral substances; silicate minerals; oxyhydroxides of Al, Fe, and Mn; and other mineral forms, as well as a variety of soluble substances, all existing in a microbial bath. With time, soil parent materials are modified by soil forming factors, creating a vertical soil profile. Soil chemistry within a soil profile is complex, and the distribution of different elements varies with the composition of the soil parent material, soil age, landscape topography, vegetation cover, and climate. The three watersheds in this study all have soils of similar age (post-glaciation), with little regional variation in topography or climate. Thus, the most critical factors controlling soil geochemistry are parent materials and soil-forming processes, such as leaching, oxidation, and addition of organic material, acting over the last approximately 10,000 years, as well as more recent anthropogenic impacts. Because soil properties and chemistry change with depth in a soil profile, multiple samples were collected at each site (as described previously in the "Soil" subsection of "Methods of Study").

Soil O Horizon

A soil O horizon is defined as a surface accumulation of decomposing organic materials with little mineral matter (Schoeneberger and others, 2012). Seven soil O horizon samples were collected in the Filson Creek watershed, five from the Keeley Creek watershed, and one from the St. Louis River watershed. As discussed in the Methods of Study section, the soil O horizon in many places was lacking, likely because of invasive worm activity.

The percent organic matter (OM) in each sample is measured by subtracting measured percent ash (table 6) from 100. Using this calculation, OM of the soil O horizon ranged from about 35 to 85 weight percent. Analyses of the residual material remaining after ashing are given in Woodruff (2019) and summarized in table 6. Organic matter in the soil O horizon effectively binds many metals (Sposito and Weber, 1986), which, because of the relatively low temperature of combustion (500 °C), remain in the analyzed residual ash fraction. Elements with positive Spearman correlations with OM (>0.5) include Ca, Cu, Mn, molybdenum (Mo), phosphorus (P), S, antimony (Sb), tungsten (W), and Zn. Aluminum has the highest negative Spearman correlation coefficient with OM (−0.821). Some higher individual element concentrations for samples in the Keeley Creek and Filson Creek watersheds include S >0.85 weight percent (3 sites); Mn >6,000 mg/kg (2 sites); Pb >100 mg/kg (3 sites); and Zn >400 mg/kg (2 sites) (Woodruff, 2019). For this overall small dataset, however, there are no significant differences among the three watersheds in the chemistry of the soil O horizon.

Soil A Horizon

A soil A horizon is defined as a mineral soil formed at the surface, typically below an O horizon, with no remnant rock structure (Schoeneberger and others, 2012). Forty soil A horizon samples were collected in the three watersheds. Because of subtle gradations between soil O and A horizons, six of the soil A horizon samples have analyzed organic C concentrations >20 weight percent, a characteristic more typical of a soil O horizon.

Soil A horizon samples are transitional between the soil O and C horizons in space and in chemistry. In many cases where aggressive worm activity has likely affected the soil O horizon, organic material (and its element load) has been incorporated into a thick mineral soil A horizon. Concentrations of many elements in the soil A horizon are highly dependent on organic C concentrations (Sposito and Weber, 1986; table 6). The concentration of elements contributed by silicate minerals (for example, Al, K, and Na from feldspar) are lowered by higher organic C concentrations because of a dilution effect. Mercury and Pb have positive Spearman correlation coefficients with organic C in soil A horizon samples (0.852 and 0.759, respectively). These two element's affinities for organic C and relatively higher concentrations, compared to corresponding underlying soil C horizon concentrations, are attributed to atmospheric deposition and soil retention by organic materials (for example, Lindberg and Turner, 1988; Grigal, 2003).

Our limited soil A horizon chemistry cannot be directly related to parent material compositions, but more likely reflects other soil forming/soil modifying factors. Differences in element concentrations among the three watersheds related to soil parent materials are much more distinct for the soil C horizon, as discussed below.

Soil C Horizon

A soil C horizon is defined as a mineral soil that is little affected by soil forming factors and that may or may not be related to underlying unweathered parent material (Schoeneberger and others, 2012). Forty-eight soil C horizon samples were collected in the three watersheds. It is assumed that these samples most closely approximate the non-organic mineral components that constitute each sample's parent materials. In the Filson and Keeley Creek watersheds, some elements closely reflect regional bedrock. For example, soil developed on weathered Mesoproterozoic Duluth Complex bedrock has relatively high concentrations of the major elements Al, Ca, Fe, and Mg, which are the principal constituents of plagioclase, olivine, and pyroxene. A sample of the soil C horizon collected from the area underlain by granite of the Archean Giants Range batholith has the highest measured concentrations of K, Na, Ba, and Sr among all soil C horizon samples, because of the persistence of K-feldspar and plagioclase in weathered granitic parent materials. Soil C horizon samples in the St. Louis River watershed also have relatively high K, Ba, beryllium (Be), bismuth (Bi), Ce, La, scandium (Sc), Th, and U, compared to soil C horizon samples from the Filson and Keeley Creek watersheds, perhaps reflecting a diverse glacial origin from a variety of mixed glacial parent materials. In the St. Louis River watershed, there is little difference in element concentrations in the soil C horizon among the varying glacial landforms that were the basis of sample site selection within the watershed.

The spatial distribution of different elements and scatter plots clearly reveal the influence of local bedrock to soil parent materials (figs. 9, 10, 11). For example, Paleoproterozoic Virginia Formation bedrock is high in Rb and Ba (fig. 9), whereas granitic bedrock of the Archean Giants Range batholith is high in Ba, but not Rb (fig. 9). This is because the partition coefficient for Ba into K-feldspar is much greater than 1, whereas the partition coefficient for Rb is <1 (Henderson, 1982). All lithologies of Duluth Complex bedrock (fig. 9) have low concentrations of Ba and Rb. In figure 9, soil C horizon samples from the St. Louis River watershed trend towards the polygon that encompasses Virginia Formation bedrock. Those soil samples with the highest Ba and Rb values are from the western end of the watershed study area, where glacial movement would have incorporated Virginia Formation bedrock. Soil C horizon samples collected in the Keeley Creek watershed, and many collected in the Filson Creek watershed, plot close to Duluth Complex bedrock. Those soils within the Filson Creek watershed that trend towards the single point representing granitic Ba concentrations are from the northern part of the watershed, where the Duluth Complex is in contact with the granite of the Archean Giants Range batholith. This trend for some of the soil C horizon samples in the Filson Creek watershed is likely the result of down-ice movement of granitic materials onto the footprint of the Duluth Complex.

Concentrations of Ni and Cu (fig. 10) in soil C horizon samples collected within the mapped mineralized area of the Spruce Road deposit are higher because of Cu-Ni sulfide mineralization in soil parent material. Silicate mineralogy, however, can also influence metal distribution in soil. In magma containing an immiscible sulfide liquid and a silicate liquid, Ni and Cu will partition into the sulfide liquid in favor of the silicate liquid (Peach and others, 1990). But if a magma has not reached sulfur saturation, Ni will selectively substitute into olivine's silicate lattice structure because of partition coefficients much greater than 1 between basaltic silicate melt and olivine (Henderson, 1982). In contrast, partition coefficients for Cu between silicate liquid and olivine are <1 (Paster and others, 1974). Thus, in a sulfide-undersaturated mafic magma, Cu is increasingly concentrated in the melt fraction as Ni is incorporated into crystallizing olivine.

The influence of both sulfide mineralization and the presence of abundant olivine can be seen in soil C horizon samples (fig. 10). Most soil C horizon samples from the Filson Creek and Keeley Creek watersheds fall within the Duluth Complex bedrock. Bedrock from the Filson Creek watershed that contains disseminated sulfides have Ni and Cu mostly >1,000 mg/kg (fig. 10). We interpret the trend of some soil C horizon samples from the Filson Creek watershed towards the Spruce Road mineralized bedrock as denoting a component of mineralized bedrock in soil parent materials. An unmineralized olivine-rich rock identified as a melatroctolite from the Keeley Creek watershed has high Ni (705 mg/kg) but very low Cu (5.6 mg/kg) because of the presence of abundant olivine and a lack of sulfide mineral phases. Soil C horizon samples from the Keeley Creek watershed that trend towards higher

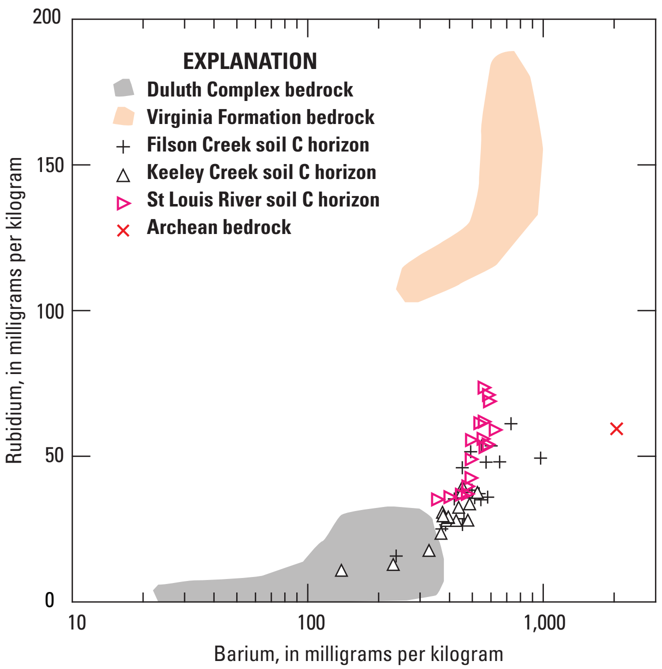


Figure 9. Comparison of rubidium and barium concentrations for all bedrock and soil C horizon samples collected throughout Filson Creek, Keeley Creek, and St. Louis River watersheds, northeastern Minnesota, 2014–15. The shaded areas represent the distribution of values associated with Duluth Complex and Virginia Formation bedrock.

Ni values without higher Cu values are more indicative of the presence of olivine rather than sulfide in soil parent materials (fig. 10). A conclusion from this interpretation of these patterns is that weathering and breakdown of olivine in bedrock will release Ni but not Cu into soil and waters, whereas alteration of sulfide minerals will release both metals into the environment.

Even though glacial transport distances are short, and many soil samples were collected near bedrock outcrops, some major and trace elements in the soil C horizon from the Filson Creek and Keeley Creek watersheds do not track well with concentrations of Duluth Complex bedrock, the assumed common soil parent material. Soil C horizon samples and bedrock have comparable Al concentrations, but most soils also have higher concentrations of K than Duluth Complex bedrock, with samples trending toward the high K value of the Archean Giants Range batholith (fig. 11). Trace elements similarly enriched in these soil C horizon samples, when compared to Duluth Complex bedrock, include Ba, Be, Ce, La, Pb, Rb, Th, and U. It is hypothesized that this suite of elements is variably sourced from geologic materials combined with weathered Duluth Complex bedrock.

A silty texture was noted at many sites during soil collection in the Keeley Creek and Filson Creek watersheds, indicating the possible presence of wind-blown silt on the recently glaciated landscape. Silty areas may be remnants of a loess cap on bedrock uplands. A source for such an eolian component could be weathered materials derived from Archean and Paleoproterozoic bedrock north and west of the two watersheds. If weathered granite of the Archean Giants Range batholith was one of those possible sources, it could explain the higher K and suite of trace element concentrations in soil C horizon sample from the Filson Creek and Keeley Creek watersheds.

Streambed Sediments

Two different size fractions of streambed sediment were collected from the three study watersheds. Clastic sediment sieved to <2 mm was collected at all water-quality sites, along with additional samples within the mapped area of the Spruce Road deposit along Filson Creek and a small tributary. A second set of streambed sediment, sieved to <63 µm, was collected at water-quality sites where finer sediment was present.

Less Than 2-Millimeter Fraction

Fourteen clastic streambed sediment samples were collected from Filson Creek; five of these samples were collected from stretches of the creek and a tributary within the

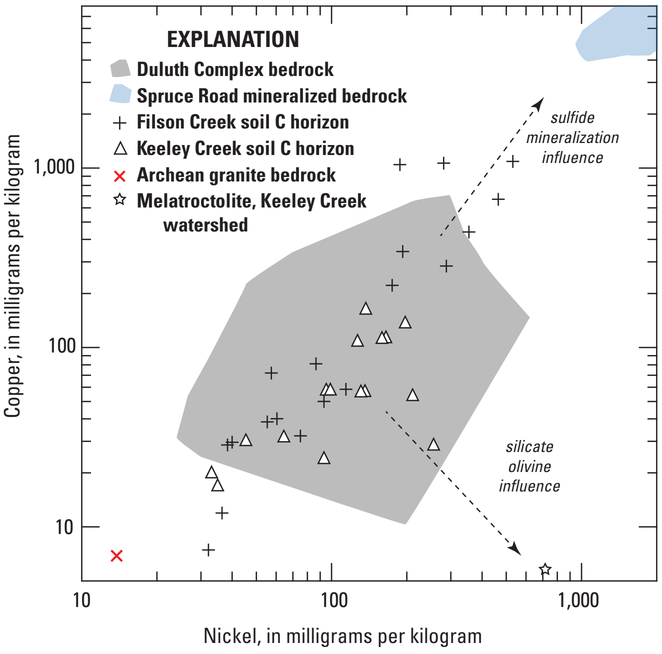


Figure 10. Comparison of nickel and copper concentrations for all bedrock and soil C horizon samples collected throughout Filson Creek and Keeley Creek watersheds, northeastern Minnesota, 2014–15. The shaded areas represent the distribution of values associated with Duluth Complex bedrock and Spruce Road mineralized bedrock.

mapped area of exposed sulfide mineralization of the Spruce Road deposit. Five samples were collected from Keeley Creek, and seven samples were collected from the St. Louis River.

Streambed sediment samples collected within the area of known sulfide mineralization in the Filson Creek watershed have Cu concentrations that range from 108 to 404 mg/kg, with corresponding Ni values ranging from 104 to 586 mg/kg, much higher than comparable ranges for sediment outside of the area of mineralization (table 7). There is no difference in median S concentrations between mineralized and unmineralized sites, with identical median values of 0.02 weight percent S, which indicates that Ni and Cu in streambed sediments within the mineralized zone are not part of a sulfide mineral phase. At Filson Creek water-quality site FC9, where the stream is cutting through granite of the Archean Giants Range batholith, streambed sediment has high K (1.81 weight percent), Na (4.39 weight percent), and Ba (1,070 mg/kg), reflecting local granitic influence. The median concentrations of elements other than those related to sulfide mineralization from each watershed show no consistent patterns of enrichments or depletions based on watershed, except for Zn (table 7). The median Zn concentrations for Filson and Keeley Creeks are 43 and 54 mg/kg, respectively, whereas the median concentration for the St. Louis River is 82 mg/kg.

Seven of the 10 metals analyzed by a weak partial leach method can be compared to the equivalent metals analyzed by the near-total digestion methods. Spearman correlation coefficients comparing concentrations from the weak partial leach method versus concentrations from the four-acid near-total extraction are As=0.936, Cd=0.945, Cu=0.979, Mo=0.918, Pb=0.975, Sb=0.200; Zn=0.988. The relation between the two methods for Zn is shown in figure 12. Antimony consistently has much higher concentrations in the weak partial leach compared to the near-total analyses, which indicates that one or both analytical methods may have interference issues that may make the Sb data suspect.

The weak partial leach method would not liberate these seven elements (As, Cd, Cu, Mo, Pb, Sb, and Zn) from silicate or sulfide mineral structures. Because there is little or no carbonate in these samples, and organic C concentrations are relatively low, with median values ranging from 0.38 to 0.43 weight percent (table 7), it is indicated that most metals released by the partial weak leach were initially bound to Fe-Mn oxyhydroxides or clays in streambed sediment (Piatak and others, 2015). Thus, more than 90 percent of the total concentration of these metals could be mobilized by redox reactions or changes in pH and potentially be bioavailable to aquatic species (Piatak and others, 2015).

Less Than 63-Micrometer Fraction

As streambed sediment grain size decreases, surface area increases, as do concentrations of trace elements that may be bound to Fe-Mn oxyhydroxides, clay minerals, and (or) organic C (Horowitz and Elrick, 1987). To understand the effect of grain size for streambed sediments within the study watersheds, streambed sediment samples sieved to <63 µm were collected at 13 water-quality sites: 5 in Filson Creek, 4 in Keeley Creek, and 4 in the St. Louis River. The small quantity of the <63-µm samples precluded obtaining a fully comparable geochemical dataset to the <2-mm size fraction.

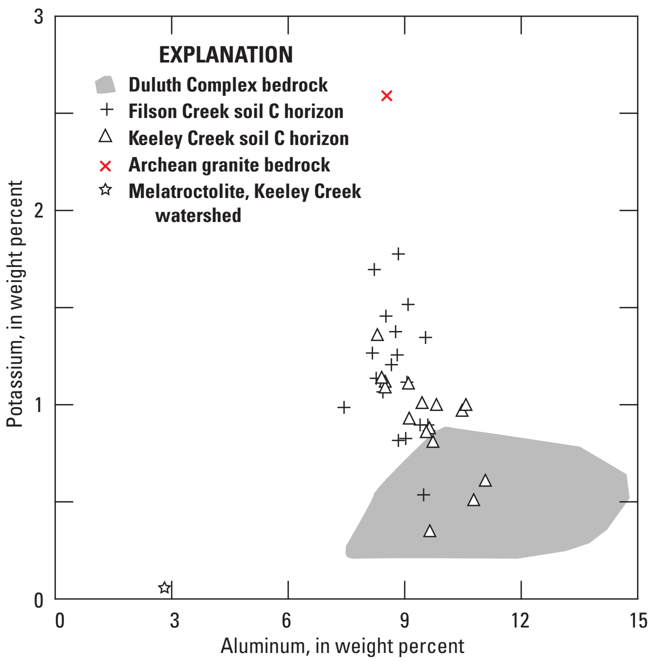


Figure 11. Comparison of aluminum and potassium concentrations for all bedrock and soil C horizon samples collected throughout Filson Creek and Keeley Creek watersheds, northeastern Minnesota, 2014–15. The shaded area represents the distribution of values associated with Duluth Complex bedrock.

In general, when element concentrations of the <63-µm fraction are compared to the concentrations of the <2-mm fraction from the same sampling reach, the finer fraction has lower values for the major elements Al, Ca, K, Mg, Na, and Ti (table 7). This likely is because of a higher abundance of mineral fragments, such as feldspar, olivine, pyroxene, and Fe-Ti-oxides, in the <2-mm fraction. Trace elements with the same pattern include Ba, Sc, Sr, and vanadium (V), which all partition into one or several of these minerals. Median P concentrations are consistently two to three times higher in the <63-µm fraction than the equivalent <2-mm fraction (table 7). In the <63-µm fraction, P has positive Spearman correlation coefficients (>0.5) with As, Fe, Co, Mo, and Pb.

In Filson Creek, a <63-µm sample collected near water-quality site FC5, which is within the mapped area of the Spruce Road deposit, had 4,864 mg/kg Cu and 1,876 mg/kg Ni, compared to 179 mg/kg Cu and 127 mg/kg Ni for the <2-mm sample from the same stream reach (Woodruff, 2019). Similarly, the <63-µm fraction had 0.12 weight percent S, compared to 0.03 weight percent S in the <2-mm fraction. The higher Ni, Cu, and S values in the finer fraction are the

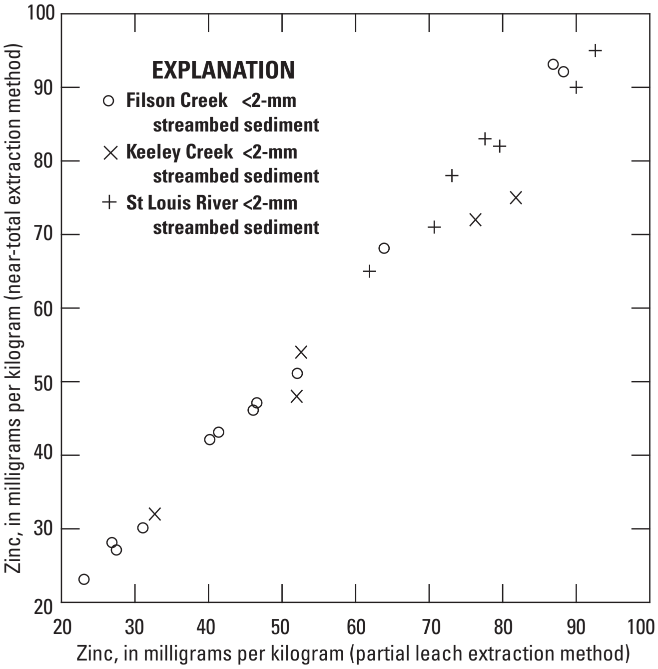


Figure 12. Comparison of zinc partial leach extraction method results versus zinc near-total extraction method results for less than (<) 2-millimeter (mm) streambed sediment collected from Filson Creek, Keeley Creek, and St. Louis River watersheds, northeastern Minnesota, 2013–15.

probable result of sulfide mineral breakdown within the mineralized zone, and possible retention of S and metals in clays, oxyhydroxide coatings, or OM.

Median Fe and Mn concentrations are also higher in the fine fraction, indicating the presence of Fe-Mn oxyhydroxide coatings on grains. Because Fe-Mn oxyhydroxides can scavenge metals by adsorption, coprecipitation, and other processes (Nowlan, 1976; Hem, 1978), a higher percentage of Fe-Mn oxyhydroxides in the fine fraction is consistent with higher metal concentrations, such as Pb, Sb, W, and Zn.

In Filson and Keeley Creeks, Mn concentrations in the <63 µm fraction are 2 to 10 times higher than in the coarser fraction, but not close to Mn values for the St. Louis River. Manganese concentrations in <63-µm streambed sediments from the St. Louis River watershed are strikingly high, with values ranging from 12,451 to 22,280 mg/kg (table 7). The highest values were found near the west end of the study area where the Virginia Formation crops out or is commonly present as cobbles in the river bed. One of the notable features of the boulders and cobbles that clog many parts of the St. Louis River is a black coating. Based on these high Mn values, this coating is very likely a Mn-rich oxide. The proposed abundance of Mn oxides on the boulder/cobble substrate in the St. Louis River is a possible explanation of why Zn values also are higher in the St. Louis River watershed than in the other two watersheds, because Mn oxides strongly sorb Zn (Nowlan, 1976).

Synthetic Hydrographs

Estimated daily mean streamflows for each of the ungaged, water-quality sampling sites mimic measured streamflows at the reference streamgages (fig. 13). Estimated flow generally was higher for downstream ungaged sites and lower in upstream ungaged sites (appendix table 1.1). Estimated daily mean streamflows may be less representative of actual flows at ungaged sites on small tributaries to the main channels of the creeks (sites FC6, FC7, and KC3, fig. 7) because the physical parameters controlling general flow characteristics in the tributaries might be different than those on the main channel, where the reference streamgage is located.

Strong, positive correlations (p-value <0.05) between estimated and measured streamflow values were observed at 12 of the 17 ungaged sites (table 4). Sites SLR2, SLR3, and SLR4 were excluded from correlation analysis because of inadequate numbers of streamflow measurements. Estimated and measured streamflow were not correlated at two sites (FC6 and FC1; p-values >0.1; table 4). FC6 is located on a tributary of Filson Creek where the reference streamgage (FC5) is located (fig. 7, table 1), likely resulting in larger differences between the measured and estimated flows in median streamflows. Estimated streamflows may poorly represent the measured streamflows at FC1 because (1) it is the farthest from the reference streamgage (3.8 mi), and (2) several wetlands adjacent to Filson Creek are present between FC1 and the reference streamgage (fig. 7).

Generally, good estimates of streamflow were obtained, as evidenced by the NSE coefficients (−0.12 to 1.00; table 4). NSE coefficients could not be determined for water-quality sites SLR2, SLR3, and SLR4 because there were too few streamflow measurements at these sites. NSE coefficients <0 indicate the mean observation is a better predictor than the estimated values, and therefore the estimated values are unacceptable (Moriasi and others, 2007). Using this criterion, estimated values are acceptable for all but one of the ungaged sites (FC6). As mentioned earlier, the poor agreement between estimated and measured streamflow values may be a result of the site being located on a tributary, and not the main channel, of Filson Creek (fig. 7).

Estimated streamflows at water-quality site FC8 tend to underestimate peak flows in the spring measured by the Minnesota Department of Natural Resources streamgage at the site and overestimate measured peak flows in early to mid-summer (fig. 13). Despite these inconsistencies, estimated streamflow and measured streamflow were positively correlated with acceptable estimations (table 4).

Surface-Water Quality

A total of 141 stream samples were collected from Filson Creek, Keeley Creek, and the St. Louis River during September 2013 to July 2015. The resultant dataset was used to compare patterns in water quality across watersheds, flow conditions, seasons, and along stream reaches. Although dissolved and total fractions were measured, the discussion that follows is focused on dissolved concentrations because this is the fraction that is more bioavailable to organisms. Concentrations of all measured elements in surface waters are provided in appendix table 1.2.

Major Constituents, Trace Metals, and Organic Carbon

Following is a description of the chemical characterization of sampled surface waters in the Filson, Keeley, and St. Louis River watersheds.

Watershed Comparisons

Surface waters in the three sampled watersheds are relatively dilute. Specific conductance ranged from 24 to 110 microsiemens per centimeter (µS/cm) in all watersheds with median values of 30, 47, and 48 µS/cm in Filson Creek, Keeley Creek, and the St. Louis River, respectively (table 8). Specific conductance exceeded 100 µS/cm at KC3, a tributary site of Keeley Creek, most likely a signature of groundwater inputs. Although pH in all three watersheds ranged from 4.4 to 8.7, median pH values were relatively neutral (close to 7.0). Median pH in Filson and Keeley Creeks was slightly lower compared to the St. Louis (table 8). Waters in all three watersheds have a low buffering capacity, with alkalinity ranging from 3 to 40 mg/L as calcium carbonate.

Dissolved organic carbon was consistently high and similar across all three watersheds, with median concentrations around 26 mg/L. These high DOC concentrations are potentially important because the DOC can complex with metals, effectively making them unavailable for uptake by organisms. Using water-quality and streambed sediment data collected in the first study year, Piatak and others (2015) concluded that high dissolved organic matter resulted in formation of Cu-dissolved organic matter complexes that reduced the availability of Cu to aquatic organisms.

Major element concentrations followed the general pattern of Filson<Keeley<St. Louis, such as that seen for Ca and Mg (fig. 14). Chloride and Na are exceptions because of site KC3, which has higher concentrations compared to the other sample sites within Keeley Creek and the other watersheds. Site KC3 is hypothesized to be fed by a brackish groundwater source that has been previously documented in the study area (Thingvold and others, 1979). Sulfate concentrations are consistently low (<4 mg/L) across all three watersheds (fig. 14), with median concentrations of 0.84, 1.2, and 1.3 mg/L in Filson Creek, Keeley Creek, and the St. Louis River, respectively.

The surface waters of Filson Creek, Keeley Creek, and the St. Louis River are classified as calcium bicarbonate type waters because of the lack of a dominant cation and the dominance of bicarbonate (fig. 15; table 9; Manoj and others, 2013). Median ion concentrations at KC3, a tributary site of Keeley Creek, show Na/K as the dominant cation type and chloride as the dominant anion type, which classifies this site as a Na-chloride water (fig. 15; table 9; Manoj and others, 2013). Median ion concentrations at KC4, just downstream from KC3, do not show a dominant cation or anion type; water at KC4 is classified as a mixed Ca-Mg-chloride type water (fig. 15; table 9; Manoj and others, 2013).

Ionic balances of median concentrations at each site ranged from 10.78 to 48.82 percent difference (table 9). The relatively high positive ionic balances indicate that cations are more abundant than anions. It is hypothesized that the high content of OM from adjacent wetlands likely contributes to the excess cation to anion imbalance (Siegel and Pfannkuch, 1984).

Trace metal and element concentrations are generally similar in surface water from Filson and Keeley Creeks; concentrations in the St. Louis River deviated slightly, depending on the constituent. For example, higher median concentrations of As, boron (B), Pb, and Sr were observed in the St. Louis River compared to Filson and Keeley Creeks, but lower concentrations of Al, Co, and Ni were observed in the St. Louis River. Furthermore, Filson Creek is listed as impaired for Al and Cu, and Keeley Creek is listed as impaired for Al. However, the impairments are designated as being the result of natural conditions, not anthropogenic (Minnesota Pollution Control Agency, 2019). Dissolved Cu and Ni concentrations have the most distinguishable differences in trace metal concentrations among the three watersheds. Concentrations were greater in Filson Creek compared to Keeley Creek and the St. Louis River (fig. 16), which will be described in more detail in the “Water-Quality Comparison with Bedrock, Soil, and Streambed Sediment Geochemistry” section that follows. In all watersheds, dissolved Co and Cr concentrations were low, with median Co concentrations <1 µg/L and most (92 percent) Cr concentrations less than the method detection limit (0.6 µg/L). Slightly higher concentrations of dissolved Fe and Mn were observed in the St. Louis River compared to Filson and Keeley Creeks. Concentrations of dissolved Ti were similar across watersheds with median concentrations ranging from 1.6 to 1.8 µg/L (fig. 16). Furthermore, dissolved Ti concentrations in the St. Louis River remained relatively constant throughout the sampled reach, despite the presence of Fe-Ti deposits within the watershed.

Element concentrations were compared to water-quality standards (WQSs) established by the Minnesota Pollution Control Agency (State of Minnesota, 2018) for class 2A

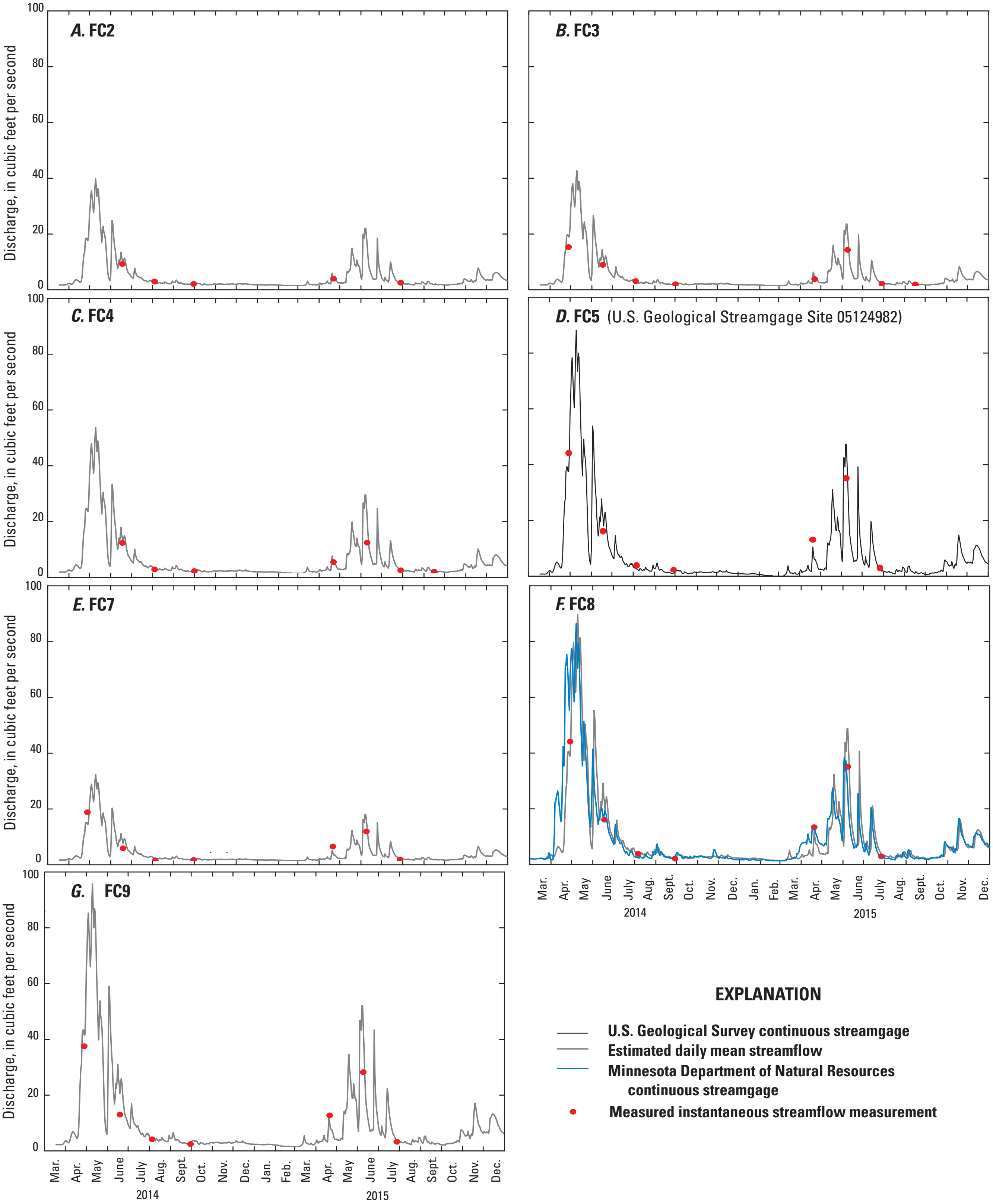


Figure 13. Synthetic hydrographs for six ungaged sites in the Filson Creek watershed, 2014–15. Hydrograph for FC5 includes continuous measured streamflow at U.S. Geological Survey streamgage 05124982. Hydrograph for FC8 includes continuous measured streamflow at Minnesota Department of Natural Resources streamgage 72032001.

waters for protection of aquatic life and recreation. Chronic WQSs represent the maximum concentration in water to which humans or wildlife can be exposed indefinitely without causing chronic toxicity. Maximum WQSs represent the maximum concentrations to which aquatic organisms can be exposed for a brief time with zero to slight mortality. Available WQSs applicable to this study are Al, As, chloride, Co, Cr, Cu, Ni, Pb, pH, and Zn. In general, water concentrations were at least an order of magnitude less than the chronic and maximum WQSs, with the exceptions of chloride and pH. Chloride concentrations at KC3, where brackish groundwater is believed to contribute to surface water, exceeded the chronic standard of 11 mg/L in 6 (of 7) samples and the maximum standard in 3 samples. The pH in Filson and Keeley Creeks was less than the minimum standard of 6.5 in 66 and 71 percent of samples, respectively. These low pH values were observed throughout the year and several times at each sample site within the creeks. The pH in the St. Louis River fell below the minimum pH standard in 20 percent of samples; all instances occurred during spring months and at least once at every sample site. The pH at FC9 also exceeded the maximum pH standard of 8.5 in August 2014. Although the pH of several samples fell outside the range of the pH WQSs, these values are believed to represent natural variation in the pH of these waters.

Flow Comparisons

Samples were qualitatively grouped according to streamflow based on the magnitude of the streamflow range across all sample sites in each watershed during every sampling event. Streamflows at Filson and Keeley Creeks were characterized the same because they are geographically adjacent and share similar climate, drainage areas, and streamflows. In Filson and Keeley Creeks, sampling events that occurred during streamflows ranging from 0.1 to 3 cubic feet per second (ft^3/s) were considered “low,” 1.8 to 21.2 ft^3/s were “medium,” and 10.8 to 51.0 ft^3/s were “high.” The St. Louis River watershed is 30 mi southwest of the Filson and Keeley Creek watersheds, and thus can be influenced by different precipitation patterns. Sampling events occurring during streamflows ranging from 1.3 to 12.8 ft^3/s were considered “low,” 18.1 to 56.6 ft^3/s were “medium,” and 98.7 to 445.6 ft^3/s were “high” for the St. Louis River.

The relations between ion concentrations and streamflow were largely dependent on the element and watershed. For example, Ca and Mg concentrations were significantly greater at low flow compared to medium and high flows (p-value<0.05) in Filson and Keeley Creeks (fig. 17). At high flows, ion concentrations were diluted by precipitation and runoff entering the streams. Similarly, in the St. Louis River, Ca and Mg concentrations significantly increased as flow decreased across all flow regimes (p-value<0.05). The reverse pattern was observed for SO_4^{-2} concentrations in Filson and Keeley Creeks, which were significantly lower at low flows compared to high (p-value<0.05). There was no difference in flow-related SO_4^{-2} concentrations in the St. Louis River.

Similar relations were observed between flow and trace metals and elements. For example, significantly greater concentrations of Fe and Sr occurred at low flows (p-value<0.05), compared to medium or high, in all watersheds. Manganese significantly increased with decreasing flow in all watersheds. These patterns may be an artifact of an Fe-Mn coating on rocks within the streambeds. At low flows, there is an increase in relative rock surface area in contact with the stream water, which allows for more contribution of Fe and Mn to the water. Although this mechanism may affect all three watersheds, there are more extensive boulder fields in sections of the St. Louis River, which may also explain the higher Fe and Mn concentrations compared to Filson and Keeley Creeks. Concentrations of Cu and Ni were not affected by streamflow in any of the watersheds (fig. 17).

Seasonal Comparisons

Generally, climate and season dictate streamflow, with higher flows in spring and early summer and lower flows in late summer and fall. Thus, patterns observed with relations between element concentrations and flow may be reflected in relations between element concentrations and season. However, streamflows in Filson and Keeley Creeks did not always follow typical patterns of high flow in spring and low flow in summer, which allowed for comparison among seasons. For this dataset, spring was defined as samples collected in April, early summer was defined as samples collected in June, late summer was defined as samples collected in late July/early August, and fall was defined as samples collected in late September/early October. Seasonal differences (independent of streamflow) were observed for B, K, pH, and SO_4^{-2}. Higher concentrations of B, K, and SO_4^{-2} were observed in spring compared to the other seasons, but streamflow did not affect concentrations (fig. 18). The increased SO_4^{-2} concentrations in spring can be attributed to atmospheric deposition during the fall and winter months (Siegel and Ericson, 1980), which would accumulate in the snowpack and be released during snowmelt. Median pH for all samples in spring was around 5, but closer to circumneutral during other seasons. This phenomena of low pH during spring mirrors historical observations by Thingvold and others (1979) and was largely attributed to snowmelt, which had a lower pH (>1 difference) compared to stream waters.

Loads

Copper, Ni, and SO_4^{-2} loads were generally highest in the St. Louis River and lowest in Keeley Creek (table 10). The median Cu load in Filson Creek (200 grams per day [g/d]) was more than three times that of Keeley Creek (66 g/d), and the maximum in Filson Creek (1,300 g/d) was more six times that of Keeley Creek (200 g/d). The St. Louis River has significantly higher discharge (a mean of 130 ft^3/s during our sampling trips, compared to about 17 ft^3/s at Filson and Keeley Creeks) because of a larger drainage area, and thus higher

Table 8. Median concentrations of measured physical properties, organic carbon, trace metals, and elements in surface-water samples collected in Filson Creek, Keeley Creek, and the St. Louis River watersheds, 2013–15, and northeastern Minnesota, 1976–77 (Thingvold and others, 1979).

[µS/cm, microsiemen per centimeter at 25 degrees Celsius; na, not applicable; mg/L, milligram per liter; --, no data; $CaCO_3$, calcium carbonate; µg/L, microgram per liter; <, less than]

Parameter	Filson Creek		Keeley Creek		St. Louis River		Northeastern Minnesota[1]
	Total	Dissolved	Total	Dissolved	Total	Dissolved	Dissolved
Physical parameters							
Specific conductance (µS/cm)	30	na	47	na	48	na	55
Dissolved oxygen (mg/L)	7.6	na	6.8	na	8.3	na	--
pH	6.05	na	6.2	na	6.9	na	6.9
Alkalinity (mg/L as $CaCO_3$)	na	7.1	na	8.1	na	16	19
Dissolved organic carbon (mg/L)	29	26	27	25	28	26	[2]15
Major ions (mg/L)							
Calcium	na	2.9	na	3.2	na	4.8	6
Magnesium	na	2.1	na	2.3	na	3.6	3
Sodium	na	1.1	na	2.4	na	1.5	1.6
Potassium	na	0.18	na	0.17	na	0.31	0.6
Chloride	na	0.26	na	1.6	na	0.44	1.6
Sulfate	na	0.84	na	1.2	na	1.3	na
Fluoride	na	0.03	na	0.03	na	0.07	0.18
Silica	na	5.3	na	5.5	na	4	na
Trace metals and elements (µg/L)							
Aluminum	na	205	na	240	na	100	90
Arsenic	0.53	0.47	0.51	0.41	0.82	0.82	0.8
Barium	na	5.05	na	4.5	na	5.1	na
Beryllium	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	na
Boron	na	4	na	4	na	7.9	na
Chromium	0.59	<0.6	0.66	<0.6	0.4	<0.6	na
Cobalt	na	0.68	na	0.59	na	0.33	0.4
Copper	4.35	3.65	1.4	1.1	0.83	<0.8	1.3
Iron	1,200	770	985	760	1,300	915	560
Lead	0.29	0.21	0.24	0.19	0.39	0.28	0.5
Lithium	na	0.33	na	0.27	na	0.58	na
Manganese	47	33	30	30	84	50	35
Nickel	3.4	3.2	2.3	2.2	1.1	1.1	1
Selenium	<0.1	0.11	<0.1	0.11	<0.1	0.13	na
Strontium	na	13	na	14	na	20	na
Titanium	2.1	1.7	2	1.6	2.8	1.8	na
Vanadium	<0.6	0.43	<0.6	0.43	0.9	0.58	na
Zinc	2.6	2.4	2.5	2.4	2.8	<2	2

[1] Median concentration reported from Thingvold and others (1979).

[2] Median concentration reported is total organic carbon.

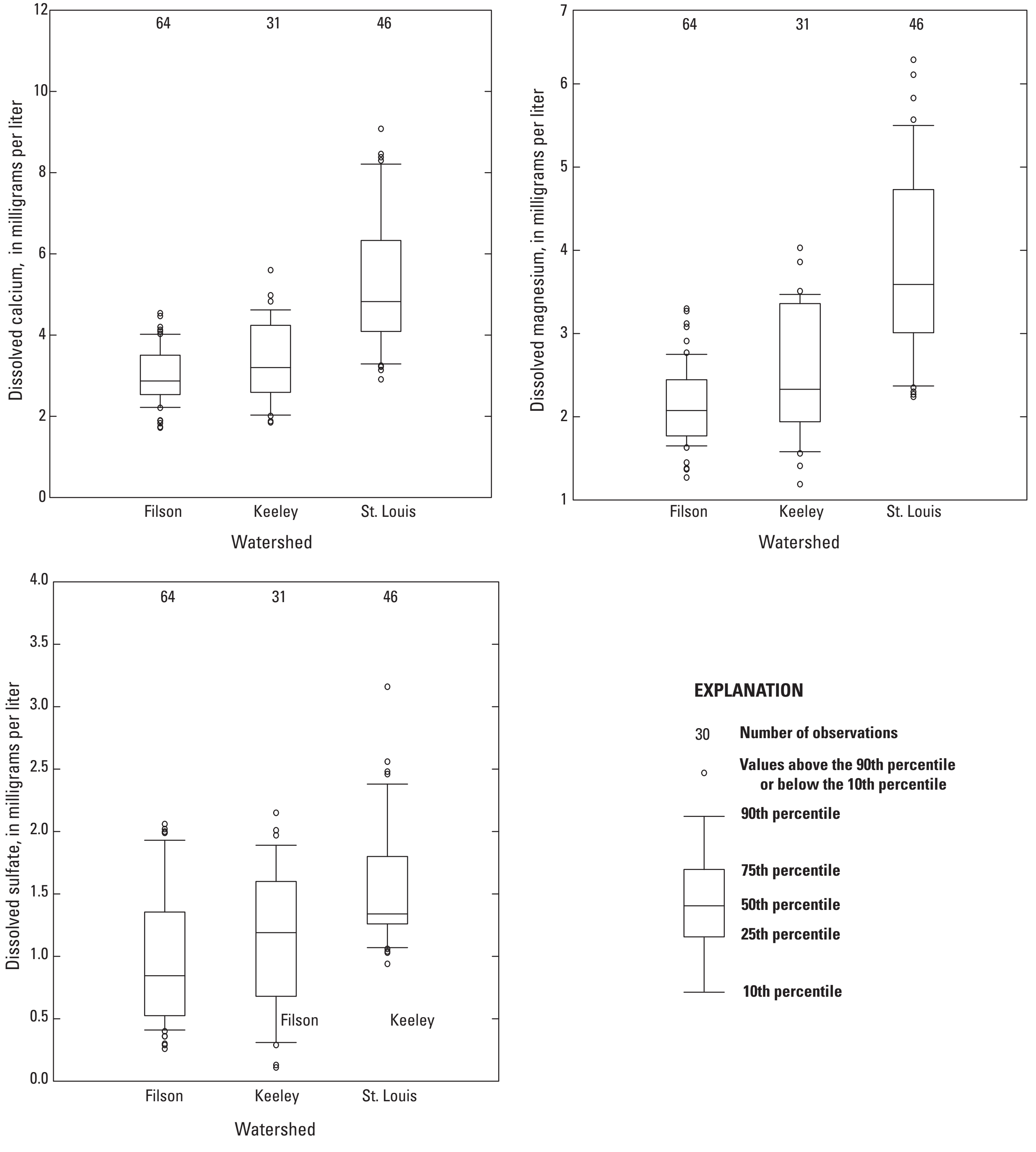


Figure 14. Boxplots of dissolved calcium, magnesium, and sulfate concentrations in Filson Creek, Keeley Creek, and St. Louis River watersheds, northeastern Minnesota, 2013–15.

Table 9. Median ion concentrations, specific conductance, pH, alkalinity, and ion balance for surface-water samples collected from Filson Creek, Keeley Creek, and the St. Louis River watersheds, northeastern Minnesota, 2013–15.

[mg/L, milligram per liter; µS/cm, microsiemen per centimeter; $CaCO_3$, calcium carbonate; <, less than]

Site	Carbonate (mg/L)	Bicarbonate (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Specific conductance (µS/cm)	pH	Alkalinity, mg/L as $CaCO_3$	Ion balance, percent difference
FC1	<0.1	9.10	2.43	1.86	1.01	0.245	0.245	1.08	28.0	5.75	7.40	28.2
FC2	<0.1	7.00	2.70	1.93	1.07	0.230	0.240	1.02	29.0	6.00	5.70	40.6
FC3	<0.1	6.00	2.87	1.90	1.05	0.250	0.230	1.18	30.0	6.00	4.90	45.1
FC4	<0.1	7.90	2.96	1.97	1.07	0.205	0.185	0.920	32.0	6.10	6.45	39.4
FC5	<0.1	8.10	2.78	1.93	1.08	0.190	0.210	1.14	31.0	5.80	6.60	35.6
FC6	<0.1	12.2	3.27	2.34	1.21	0.075	0.225	0.470	33.5	6.30	10.0	30.1
FC7	<0.1	10.9	3.00	2.15	1.23	0.100	0.260	0.570	30.0	6.50	8.90	31.1
FC8	<0.1	5.50	2.68	2.01	1.13	0.160	0.200	1.06	34.0	6.20	4.40	48.8
FC9	<0.1	12.0	2.88	1.98	1.17	0.170	0.290	1.17	30.0	5.80	9.90	21.8
KC1	<0.1	9.90	2.54	1.66	1.03	0.170	0.210	1.59	27.0	6.40	8.10	20.9
KC2	<0.1	9.90	2.63	2.13	1.36	0.210	0.700	1.29	32.0	6.50	8.10	27.2
KC3	<0.1	10.5	3.65	2.51	10.5	0.075	17.6	0.450	88.5	5.65	8.60	10.8
KC4	<0.1	9.10	2.75	2.26	4.16	0.160	5.84	0.990	42.0	6.00	7.40	20.1
SLR1	<0.1	19.9	4.49	3.37	1.44	0.275	0.360	1.26	43.5	6.85	16.3	21.9
SLR2	<0.1	17.4	4.27	2.95	1.29	0.275	0.340	1.20	41.5	6.45	14.3	23.2
SLR3	<0.1	17.5	4.26	3.17	1.52	0.305	0.400	1.46	46.0	7.10	14.5	24.4
SLR4	<0.1	20.7	4.95	3.63	1.65	0.435	0.730	1.80	49.5	7.05	17.0	22.1
SLR5	<0.1	22.8	5.54	3.96	1.47	0.250	0.470	1.31	52.0	6.50	18.7	23.4
SLR6	<0.1	21.0	4.55	3.20	1.38	0.300	0.530	1.37	46.0	7.40	17.2	17.6
SLR7	<0.1	29.7	6.17	4.58	1.47	0.345	0.305	1.45	61.5	7.10	24.4	17.8

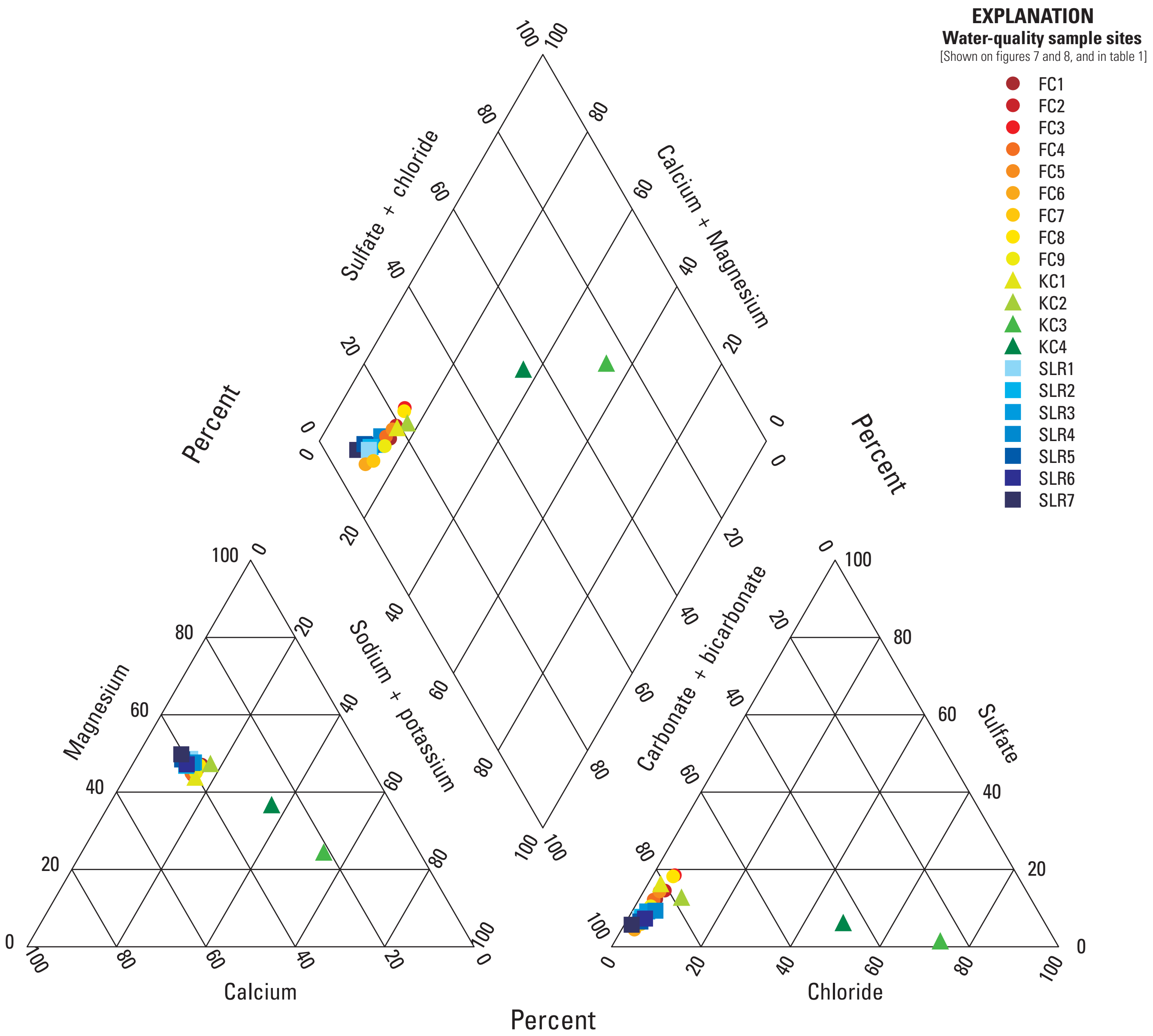


Figure 15. Piper diagram of median cation and anion concentrations, in milliequivalents per liter, in Filson Creek, Keeley Creek, and St. Louis River watersheds, northeastern Minnesota, 2013–15. Field names provided in explanation correspond to those in table 1.

stream loads for most analytes. However, Filson Creek has high Cu and Ni concentrations (despite smaller streamflows), resulting in comparable loads to the St. Louis River (table 11).

Water-Quality Comparison with Bedrock, Soil, and Streambed Sediment Geochemistry

The comparable water chemistry between Filson and Keeley Creeks can be attributed to the similar geology within the watersheds. Because the creeks have been scoured by glaciers, bedrock is at or near the surface throughout and covered by thin soil derived directly from the bedrock. Most water-quality differences between Filson and Keeley Creeks can be attributed to the mineralization in the Filson Creek watershed. In contrast to Filson and Keeley Creek watersheds, the St. Louis River watershed was influenced by depositional glaciation, resulting in a surface geology dominated by thick glacial sediment. This key difference in geology contributes to noticeable differences in St. Louis River water quality compared to Filson and Keeley Creeks.

Although solid-media geochemistry explains patterns of some metals in water, it does not explain patterns of major ions. For example, although Ca and Mg concentrations in Duluth Complex bedrock are similar across all watersheds, Ca and Mg concentrations in water were typically higher in the St. Louis River compared to Filson and Keeley Creeks, indicating water quality is influenced by other processes. In the

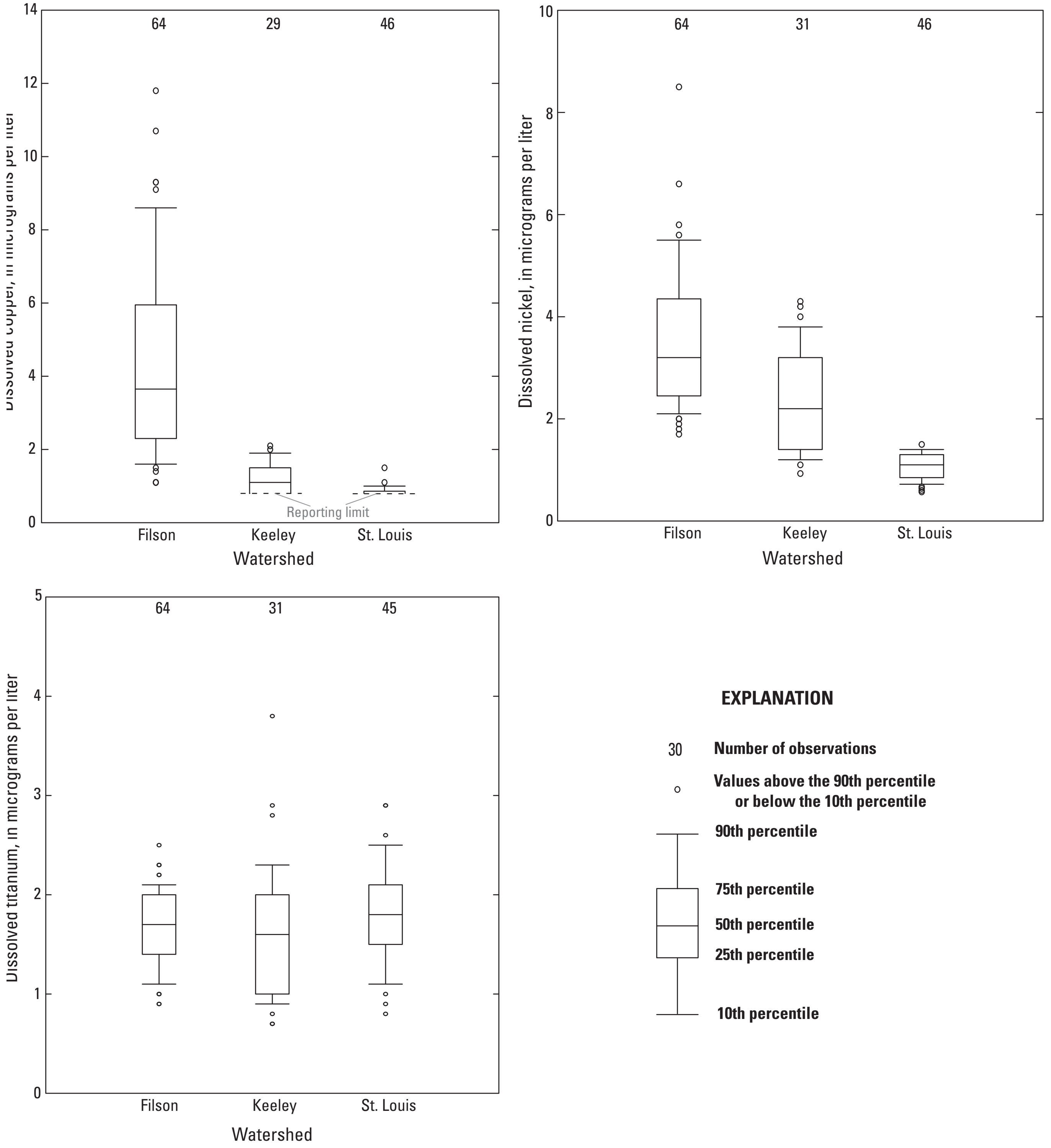


Figure 16. Boxplots of dissolved copper, nickel, and titanium concentrations in Filson Creek, Keeley Creek, and the St. Louis River, northeastern Minnesota, 2013–15.

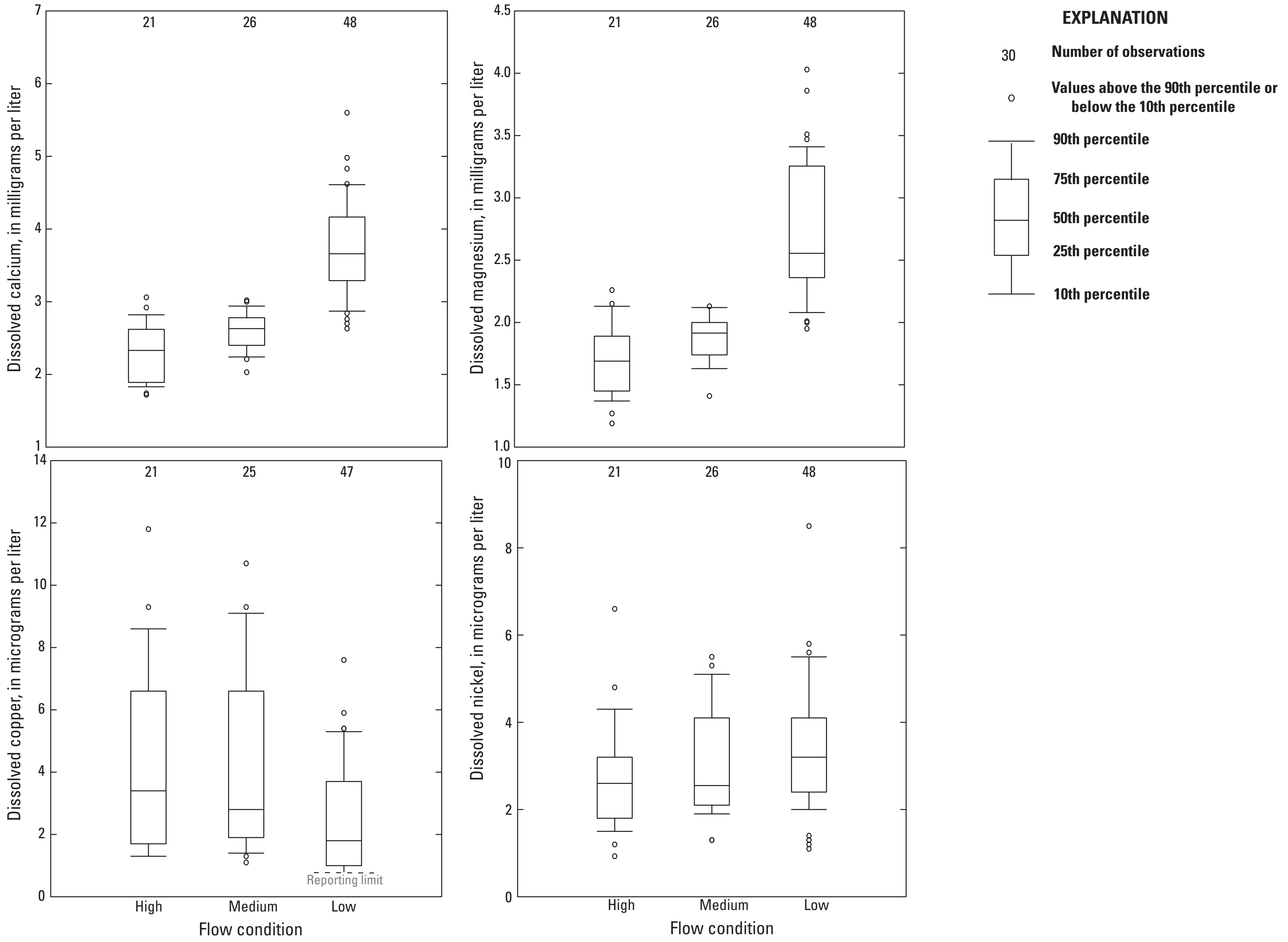


Figure 17. Boxplots of dissolved calcium, magnesium, copper, and nickel concentrations for different flow conditions in Filson Creek and Keeley Creek, northeastern Minnesota, 2013–15.

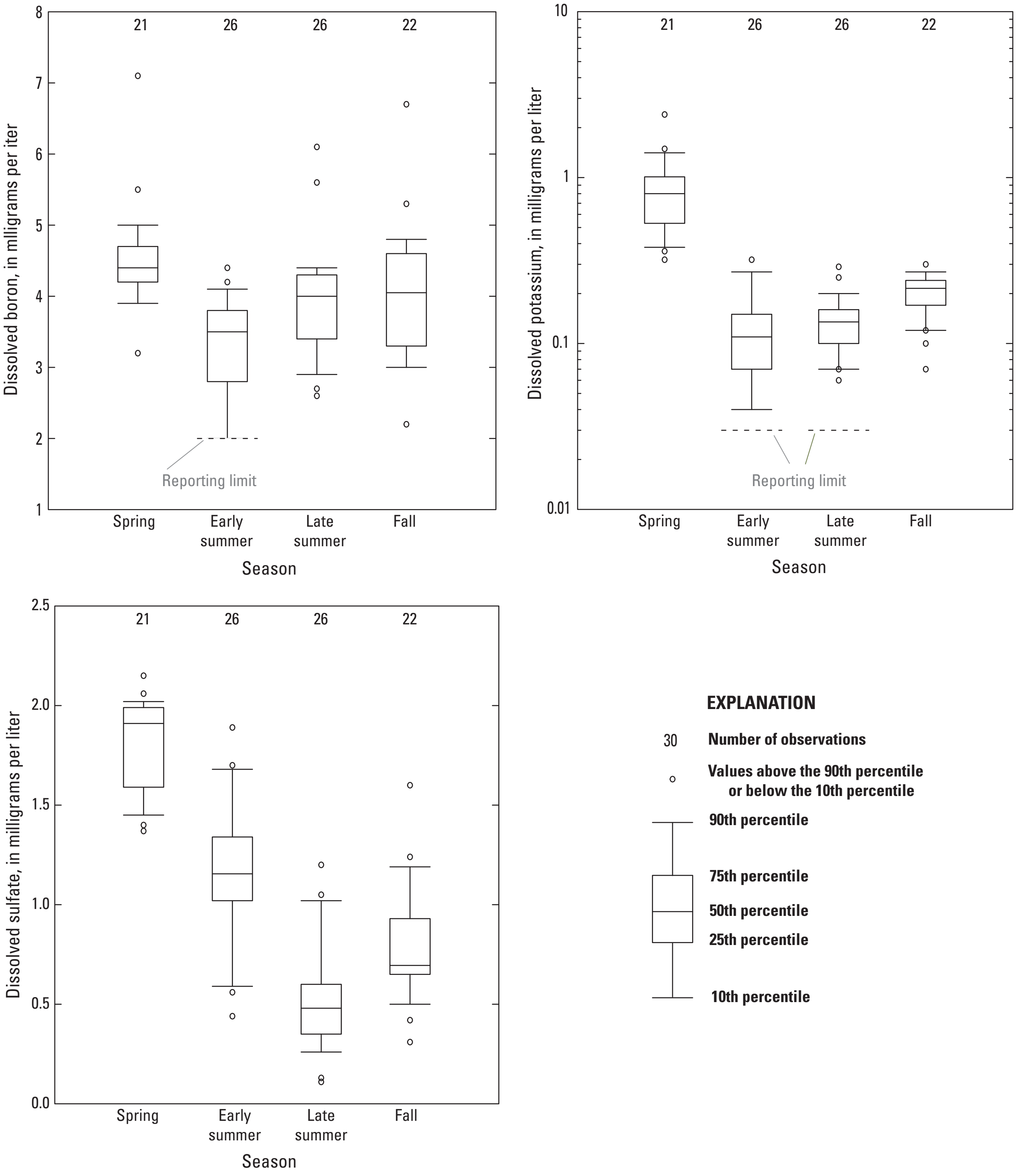


Figure 18. Boxplots of dissolved boron, potassium, and sulfate concentrations by season in Filson Creek and Keeley Creek, northeastern Minnesota, 2013–15.

St. Louis River watershed, which has more substantial glacial-sediment cover, the influence of groundwater on the river is a likely contributor of major ions to surface waters. Because of the larger glacial-sediment cover, groundwater must travel longer flowpaths, picking up ions along the way as it moves through the glacial overburden.

Although the Filson and Keeley Creek watersheds share similar bedrock geology, the Filson Creek watershed contains exposed Cu-Ni-sulfide mineralization along the basal contact of the Duluth Complex with older country rock, whereas the Keeley Creek watershed does not. The influence of this mineralization on water quality is evident in the higher Cu and Ni water concentrations in Filson Creek near the mineralized zone compared to upstream and within Keeley Creek. Concentrations of dissolved Ni in Keeley Creek do slightly increase in a downstream pattern, but dissolved Cu concentrations remain relatively low (from below detection limit to 1.6 µg/L) throughout. Similar patterns can be seen in soil and streambed sediment within the Keeley Creek watershed. The presence of abundant olivine in bedrock within the Keeley Creek watershed contributes Ni but not Cu to stream water. Although the St. Louis River is also underlain by Duluth Complex intrusions, water quality is not influenced by the bedrock geochemistry because of the thick glacial sediment (for example, surface water has low Cu and Ni concentrations). In fact, dissolved Cu concentrations were below the detection limit in 69 percent of all surface-water samples collected from the St. Louis River.

The spatial distribution of dissolved Cu and Ni concentrations in Filson Creek surface waters highlights the complex geology within the watershed. For example, dissolved Cu concentrations decrease at FC8, which is directly downstream from the confluence of the south fork tributary (fig 19*A*). Because this tributary has no evidence of mineralization, it effectively dilutes Cu concentrations in the main stem of Filson Creek. However, dissolved Ni concentrations do not decrease below this confluence (fig. 19*B*), indicating that the tributary is contributing Ni to the main stem. Like Keeley Creek, Ni contributions from the tributary are not from Ni-Cu mineralization but from the breakdown of olivine in the bedrock that underlies much of the Filson Creek watershed.

Element concentrations in the St. Louis River were relatively consistent with no obvious patterns along the sampled reach. Despite the three identified Fe-Ti deposits within the St. Louis River watershed (fig. 3), there were no apparent increases in Ti along the sampled reach. Furthermore, median Ti concentrations were similar among the three sampled watersheds. Again, it appears that the glacial overburden buffers the stream water from any direct influence from bedrock geochemistry. The patterns of Cu and Ni in Keeley Creek (Ni>Cu) are also apparent in the St. Louis River, although concentrations of both metals are much lower compared to Keeley Creek. This pattern is attributed to a lack of sulfide mineralization in the St. Louis River watershed, and a “diluting effect” of the thick glacial cover on the element contributions from Duluth Complex bedrock. Concentrations of K in the St. Louis River were significantly greater than those observed in Filson and Keeley Creeks (p-value<0.05). The high surface water K concentrations correspond to the higher K concentrations seen in soils collected from the St. Louis River watershed, attributed to contribution from Virginia Formation clasts in glacial deposits.

Water-Quality Comparison with Water-Quality Data from 1979 Copper-Nickel Study

A regional study conducted during 1975–77 measured major elements and trace metals in northeastern Minnesota surface and groundwaters (Thingvold and others, 1979), including one site each on Filson and Keeley Creeks. Median total concentrations of most major elements and trace metals determined from the current study were relatively similar to median concentrations determined for several undisturbed streams in northeastern Minnesota reported in Thingvold and others (1979) (table 8). Median Cu and Ni concentrations in Keeley Creek and the St. Louis River were similar to the regional median, whereas median concentrations in Filson Creek were higher, reflecting the influence of the mineralization in the watershed. Thingvold and others (1979) observed increasing Cu and Ni concentrations moving downstream in Filson Creek, similar to observations obtained during the present study. Furthermore, mean Ni concentrations near the mouth of Filson Creek were 3–5 µg/L, similar to those observed during the current study. Comparison of the data obtained from these two studies, separated by decades, indicates that the chemical composition of the surface waters in the three study watersheds (and specifically, Filson Creek) has not substantially changed under natural (for example, no active mining) conditions.

Table 10. Calculated instantaneous copper, nickel, and sulfate loads for Filson Creek, Keeley Creek, and the St. Louis River, northeastern Minnesota, 2013–15.

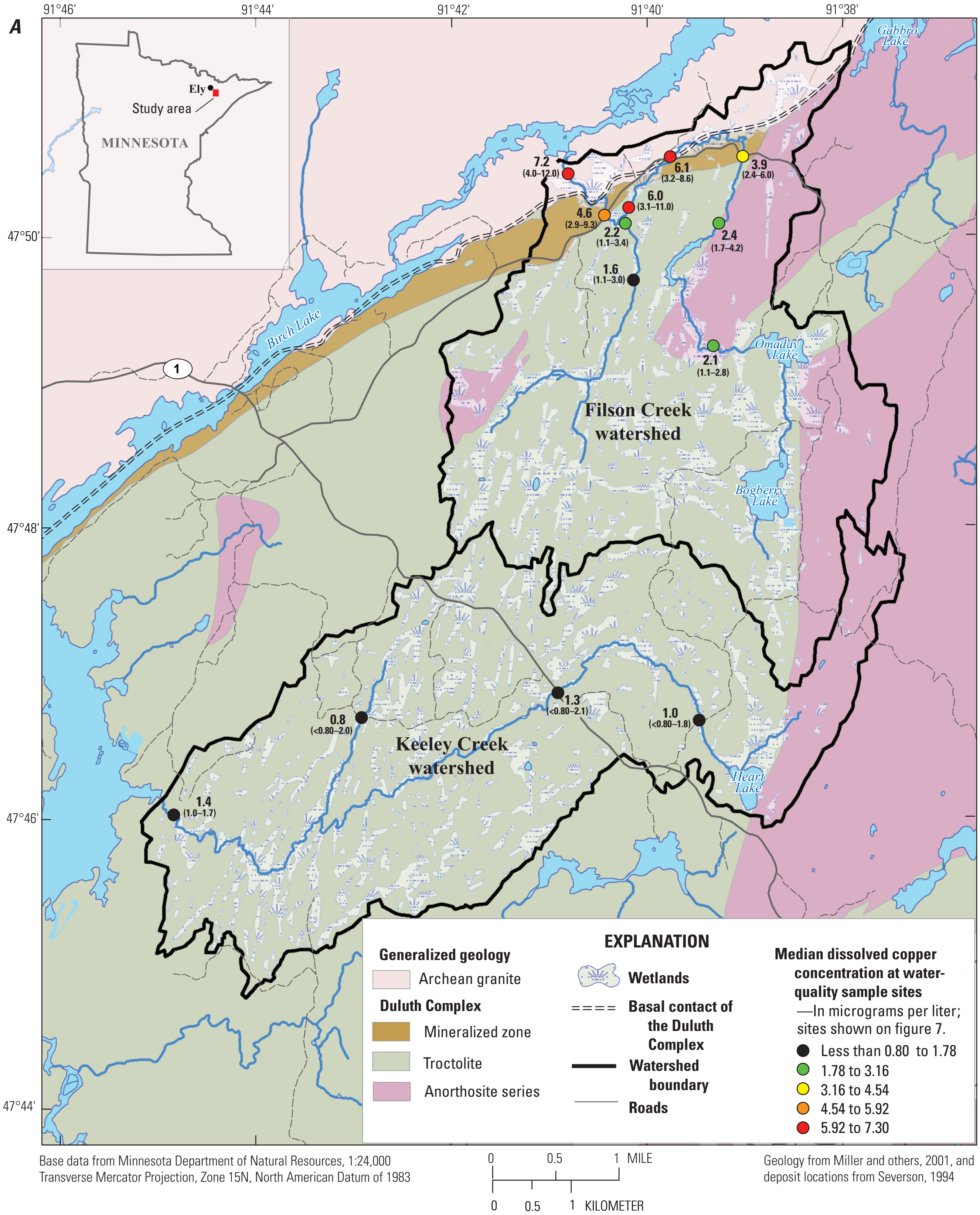
[USGS, U.S. Geological Survey; ft^3/s, cubic feet per second; g/d, gram per day; Min, minimum; Max, maximum; kg/day, kilogram per day; MN, Minnesota]

USGS station name	USGS station number	Mean streamflow (ft^3/s)	Copper (g/d)			Nickel (g/d)			Sulfate (kg/d)		
			Min	Median	Max	Min	Median	Max	Min	Median	Max
Filson Creek above Mouth near Winton, MN	05124992	17.0	20	200	1,300	18	120	700	3.1	44	187
Keeley Creek above mouth near Babbitt, MN	05125039	17.5	1.3	66	200	4.3	74	220	0.37	44	250
St. Louis River at Moose Line Road near Hoyt Lakes, MN	04015444	130	70	420	1,100	7.6	94	1,600	7.1	205	1,200

Table 11. Calculated copper, nickel, and sulfate loads per unit area for Filson Creek, Keeley Creek, and the St. Louis River, northeastern Minnesota, 2013–15

[USGS, U.S. Geological Survey; mi^2, square mile; g/d/mi^2, gram per day per square mile; kg/d/mi^2, kilogram per day per square mile; MN, Minnesota]

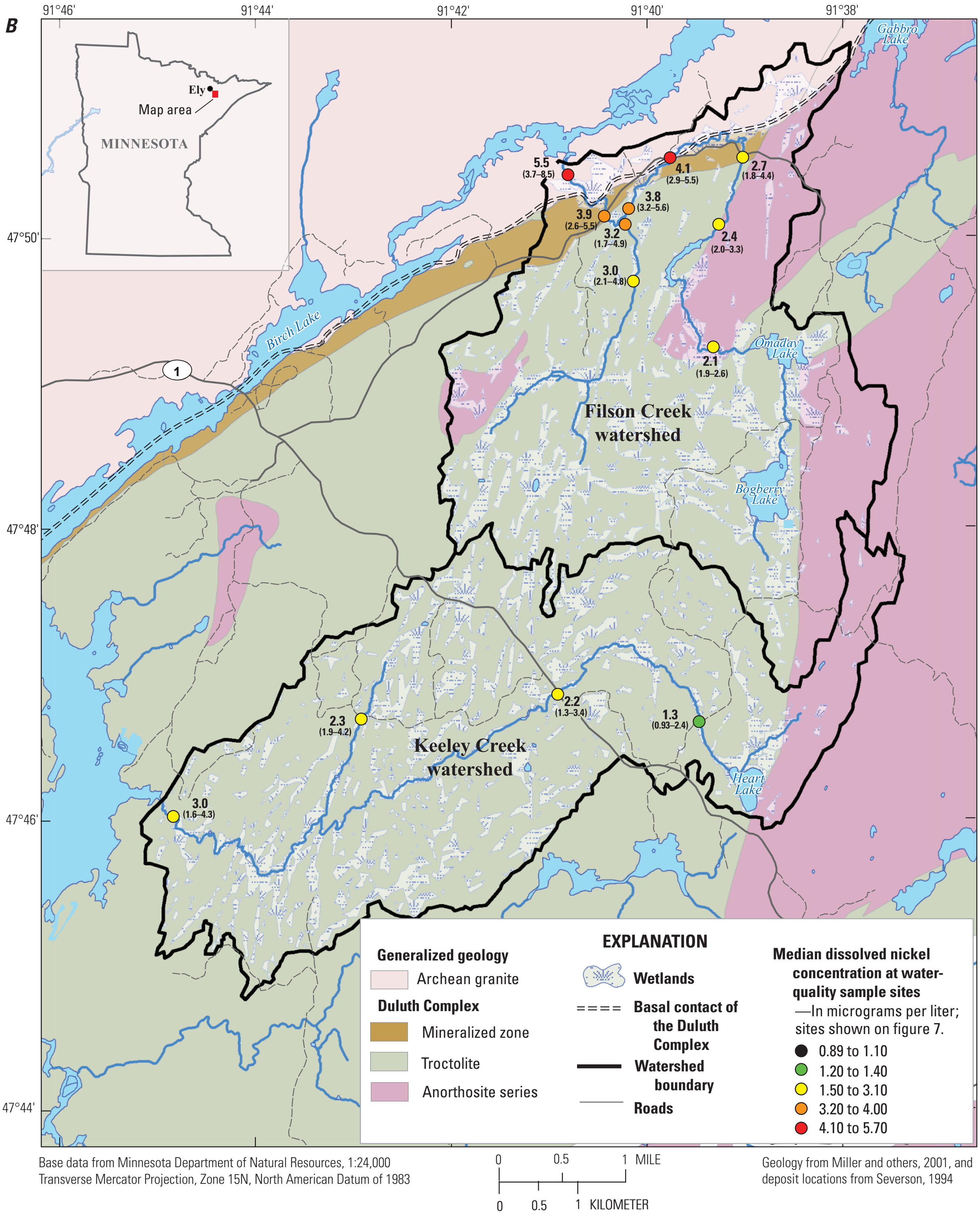
USGS station name	Drainage area (mi^2)	Copper (g/d/mi^2)			Nickel (g/day/mi^2)			Sulfate (kg/d/mi^2)		
		Min	Median	Max	Min	Median	Max	Min	Median	Max
Filson Creek above Mouth near Winton, MN	10	2.0	20	130	1.8	12	70	0.3	4.4	19
Keeley Creek above mouth near Babbitt, MN	24	0.05	2.8	8.3	0.18	3.1	9.2	0.02	1.8	10
St. Louis River at Moose Line Road near Hoyt Lakes, MN	135	0.52	3.1	8.1	0.06	0.70	12	0.05	1.5	8.9



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Miller and others, 2001, and
deposit locations from Severson, 1994

Figure 19. Dissolved surface-water concentrations in Filson Creek and Keeley Creek, northeastern Minnesota, 2013–15. *A*, Copper. *B*, Nickel.



Base data from Minnesota Department of Natural Resources, 1:24,000
Transverse Mercator Projection, Zone 15N, North American Datum of 1983

Geology from Miller and others, 2001, and deposit locations from Severson, 1994

Figure 19. —Continued

Summary

The U.S. Geological Survey, in cooperation with the University of Minnesota-Duluth Natural Resources Research Institute, completed an assessment of regional water quality in areas of potential base-metal mining. Bedrock, soil, streambed sediment, and surface-water samples were collected in three watersheds that cross the basal part of the Duluth Complex with different mineral-deposit settings: (1) copper-nickel-platinum group element mineralization (Filson Creek), (2) no identified mineralization (Keeley Creek), and (3) iron-titanium-oxide mineralization (headwaters of the St. Louis River). Data from this study provide a baseline of metal concentrations and general water quality within an area of active mineral exploration.

In the Filson Creek and Keeley Creek watersheds, the thin glacial cover causes most subsoil samples and streambed sediments in the study watersheds to largely reflect local bedrock sources. For example, sulfide-mineralized bedrock of the Spruce Road deposit in the Filson Creek watershed contributes copper (Cu) and nickel (Ni) to local soil and streambed sediment, but only within and or immediately down-ice to the mapped area of exposed mineralization. Nickel in soil from non-mineralized areas can be derived from weathering of olivine-rich bedrock of the Duluth Complex. Subsoil in the Filson and Keeley Creeks watershed may also contain a non-local eolian silt component.

In contrast to the Filson and Keeley Creek watersheds, the St. Louis River watershed is strongly influenced by a thick glacial cover. The circuitous trace of the river is controlled by the orientation of the drumlins that are part of the Toimi drumlin field. In places where the river cuts drumlinized till, numerous boulders and large cobbles with black, presumed manganese-rich coatings, clog the river. Release or absorption of metals from these coating may create variable water quality, depending on redox conditions.

Stream waters in the three sampled watersheds are dilute, have relatively neutral pH, high dissolved organic carbon, and low buffering capacity. Major element concentrations followed the general pattern of Filson Creek<Keeley Creek, and Keeley Creek<the St. Louis River. Trace metal and element concentrations were generally similar in Filson and Keeley Creek watersheds, with concentrations in the St. Louis River deviating slightly, depending on the constituent. The most distinguishable chemical difference is apparent in dissolved Cu and Ni, which are elevated in Filson Creek compared to the other watersheds. The comparable water chemistry between Filson and Keeley Creeks can be attributed to the similar geology within the watersheds, whereas most differences can be attributed to the mineralization in the Filson Creek watershed. In contrast to Filson and Keeley Creeks, the St. Louis River was influenced by depositional glaciation, resulting in a surface geology dominated by thick glacial sediment. This key difference in geology contributes to noticeable differences in St. Louis River water quality compared to Filson and Keeley Creek water quality, similar to patterns in the solid-media geochemistry.

Concentrations of some elements were influenced by streamflow. Calcium, magnesium, iron, and strontium concentrations were greater during low flow conditions in all three watersheds. Sulfate concentrations were lower during low flows in Filson and Keeley Creeks only. Manganese increased with decreasing flow in Filson and Keeley Creeks but was greatest during low flow conditions in the St. Louis River.

Compared to State of Minnesota water-quality standards, water concentrations were generally at least an order of magnitude lower, with few exceptions. Chloride concentrations at KC3, where brackish groundwater is believed to contribute to surface water, exceeded the chronic standard of 11 milligrams per liter in six of seven samples and the maximum standard in three of seven samples. The pH in Filson and Keeley Creeks often (greater than 50 percent) fell below the minimum standard; however, these values are believed to represent natural variation in the pH of these waters.

Solid-media geochemistry explained patterns of some metals in water, but not of major ions. The influence of the mineralized zone on water quality is evident in the higher Cu and Ni water concentrations in Filson Creek near the mineralized zone compared to upstream and in Keeley Creek. Similar to soil and streambed sediment in the Keeley Creek watershed, surface water Ni concentrations slightly increase in a downstream pattern in Keeley Creek; however, dissolved Cu concentrations remain relatively low (from below detection limit to 1.6 micrograms per liter) throughout. The presence of the abundant olivine in bedrock underlying the Keeley Creek watershed contributes Ni to the stream water, but Cu is not present in large quantities. Although the St. Louis River watershed is also underlain by Duluth Complex bedrock, water quality is not influenced (for example, surface water has low Cu and Ni concentrations) by the geochemistry because of the thick glacial sediment cover above the bedrock.

Median concentrations of most major elements and trace metals determined from the current study are relatively similar to historical median concentrations determined for several undisturbed streams in northeastern Minnesota. Comparison of the data obtained from these two studies, separated by decades, indicates that the chemical composition of the surface waters in the three study watersheds has not changed substantially under natural (for example, no active mining) conditions.

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Appendix 1

The appendix consists of one table that provides estimated daily mean streamflow data for 17 ungaged sites in the Filson Creek, Keeley Creek, and St. Louis River watersheds, March 18, 2014 through December 31, 2015 (table 1.1) and one table that provides all water-quality data collected from Filson Creek, Keeley Creek, and the St. Louis River in northeastern Minnesota, 2013-2015 (table 1.2).

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