

2013 Project Abstract

For the Period Ending June 30, 2017

PROJECT TITLE: Assessment of Natural Copper-Nickel Bedrocks on Water Quality

PROJECT MANAGER: Stephen Monson Geerts

AFFILIATION: Natural Resources Research Institute (NRRI), University of Minnesota Duluth

MAILING ADDRESS: 5013 Miller Trunk Highway

CITY/STATE/ZIP: Duluth, MN 55811

PHONE: (218) 720-4294

E-MAIL: sgeerts@nrri.umn.edu

WEBSITE: <http://www.nrri.umn.edu/strategic-research/minerals-metallurgy-mining>

FUNDING SOURCE: Environment and Natural Resources Trust Fund

LEGAL CITATION: M.L. 2013, Chp. 52, Sec. 2, Subd. 05b

APPROPRIATION AMOUNT: \$585,000.00

Overall Project Outcomes and Results

The Natural Resources Research Institute, the U. S. Geological Survey, and the Minnesota Department of Natural Resources conducted a three-year study to 1) assess copper, nickel, and other metal concentrations in surface water, bedrock, streambed sediments, and soils in watersheds where the basal part of the Duluth Complex is exposed or near the land surface; and 2) determine if these concentrations, and metal-bearing deposits, are currently influencing regional water quality in areas of potential base-metal mining. The data will be used by Federal, State, local, and tribal entities to better assess background water-quality in watersheds with existing mineralization and where mining could occur. Surface-water, streambed sediment, soil, and bedrock samples were collected and analyzed in three largely undisturbed watersheds with different mineral-deposit settings: (1) copper-nickel-platinum group metal mineralization (Spruce Road deposit - Filson Creek watershed), (2) iron-titanium-oxide mineralization (Skibo deposit – upper part of the St. Louis River watershed), and (3) no identified mineralization (Keeley Creek watershed). Streamflow also was monitored in the three watersheds at continuous streamflow gages and through discharge measurements to determine estimates of trace metal and inorganic constituent loads.

The geochemistry of surface waters and streambed sediments reflects the geochemistry of underlying rock types and glacially transported unconsolidated material. Water-quality data also suggest that streamflow influences concentrations of major constituents, such as Ca, Mg, and K, with lower concentrations during high flow, but has little apparent influence on metal concentrations. Copper-nickel mineralization in the northern Filson Creek watershed contributes both metals to stream waters and streambed sediment. All trace metals concentrations in all surface-water samples were below human-health guidelines and aquatic life standards established by the state of Minnesota and the U.S. Environmental Protection Agency. Dissolved and total organic carbon (DOC and TOC) concentrations in surface waters are very high compared to most surface waters in Minnesota, ranging from 13.7 to 41.4 milligrams per liter (mg/L) in all watersheds. Results from biotic-ligand modeling suggest that the high DOC content may exert some control on copper concentrations in water, such that complexation with DOC may reduce the bioaccessibility of copper.

Project Results Use and Dissemination

A U.S. Geological Survey Scientific Investigations Report (SIR) is being completed for colleague and USGS review that will summarize analytical results, present interpretations of bedrock, soil, streambed sediment, and water-quality data, and describe conceptual hydrology for the three watersheds (once published, the report will be available through the USGS Publication Warehouse at <https://pubs.er.usgs.gov/>). A draft of the report will be

completed for review by June 30, 2017, and an on-line version of the report will be completed by December 31, 2017. At that time, a pdf version of the report will be sent to LCCMR staff.

Numerous oral and poster presentations were given at geologic, water-quality, and hydrologic conferences in the State outlining project results. These presentations also were given at meetings with federal (U.S. Forest Service, U.S. Environmental Protection Agency), state (Minnesota Department of Natural Resources, Minnesota Pollution Control Agency, Minnesota Department of Health), local, and tribal agencies, mining companies, and university researchers. These meetings included the following:

- U.S. Environmental Protection Agency (EPA) Lake Superior Cooperative Science and Monitoring Workshop, Duluth, MN, September 25, 2013.
- Minnesota Lake Superior Stream Science Symposium, Duluth, MN, January 7-8, 2014. (Poster presentation can be found at <http://www.lrcd.org/uploads/1/6/4/0/16405852/mnlsstreamconf172013-2.pdf>).
- U.S. Environmental Protection Agency (EPA) National Conference on Mining-Influenced Waters in Albuquerque, NM, August 12-14, 2014 (participation in the conference was funded by U.S. Geological Survey Midwest Region Mining Initiative) (abstract can be found at <https://clu-in.org/download/issues/mining/mining-influencedwater/Mining-600-R-15-088.pdf>).
- U.S. Environmental Protection Agency (EPA) Lake Superior Cooperative Science and Monitoring Workshop, Duluth, MN, November 19-20, 2014.
- East Range Water Resources Data Collaboration Meeting, Duluth, MN, January 29, 2015.
- University of Minnesota – Duluth, Natural Resources Research Institute, Duluth, MN, March 18, 2015.
- 61st Annual Institute on Lake Superior Geology, Dryden, Ontario, May 20-24, 2015. (participation in the conference was funded by U.S. Geological Survey, Eastern Minerals Research Funds) (abstract can be found at <http://www.d.umn.edu/prc/lakesuperiorgeology/Volumes/2015%20Abstracts%20and%20Proceedings%20Volume%20sm.pdf>)
- 2015 Healthy Watershed Conference: Water and Forest, Cohasset, MN, July 31, 2015. (presentation can be found at <https://mavenperspectives.com/wp-content/uploads/2015/02/Assessing-the-Influence-of-Copper-Nickel-Bearing-Bedrocks-on-Baseline-Water-Quality-in-Three-Northeastern-Minnesota-Watersheds.pdf>)
- USGS Monitoring Trace Metals in the Lake Superior Basin Meeting, Ashland, WI, November 12, 2015 (gave presentation via web)
- Minnesota Geological Survey, Minneapolis, MN, March 7, 2016
- 2016 International Rainy-Lake of the Woods Watershed Forum, International Falls, MN, March 10, 2016.
- White Iron Chain of Lakes Lake Association's Annual Meeting, Ely, MN, August 4, 2016

All of the data collected and compiled during this study is too large to be included in the appendix tables of the final LCCMR report, however the data is available in several databases. Geochemical data for bedrock, soils, and streambed samples were entered and stored in the USGS National Geochemical Database (http://minerals.cr.usgs.gov/projects/geochem_database/index.html). Metal and major constituent concentrations for water samples collected in the project were entered and stored in the USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). All continuous streamflow data and streamflow measurements were entered and are available in USGS National Water Information System (NWIS) at <http://waterdata.usgs.gov/nwis>.

Table 4. Median concentrations of measured physical parameters, organic carbon, trace metals, and elements in surface-water samples collected in Filson, Keeley, and St. Louis watersheds during September 2013 to October 2015 and northeastern Minnesota during 1976-1977.

µS/cm, microsiemens per centimeter; --, no data; mg/L, milligram per liter; CaCO ₃ , calcium carbonate; µg/L, micrograms per liter										
Parameter	Filson		Keeley		StLouis		Northeastern Minnesota ¹	Minnesota water quality chronic standard for aquatic life in class 2 waters of Lake Superior Basin ³	Minnesota human health-based water guidance - chronic ^{3,4}	U.S. federal drinking water standards ⁴
	Total	Dissolved	Total	Dissolved	Total	Dissolved	Dissolved	Total	Total	Total
Physical Parameters										
Specific conductance (µS/cm)	30	--	47	--	48	--	55	--	--	--
Dissolved oxygen (mg/L)	7.6	--	6.8	--	8.3	--	--	--	--	--
pH	6.1	--	6.2	--	6.9	--	6.9	--	--	--
Alkalinity (mg/L as CaCO ₃)	--	7.1	--	8.1	--	16	19	--	--	--
Organic Carbon (mg/L)	29	26	27	25	28	26	15 ²	--	--	--
Major Ions (mg/L)										
Calcium	--	2.9	--	3.2	--	4.8	6	--	--	--
Magnesium	--	2.1	--	2.3	--	3.6	3	--	--	--
Sodium	--	1.1	--	2.4	--	1.5	1.6	--	--	--
Potassium	--	0.18	--	0.17	--	0.31	0.6	--	--	--
Chloride	--	0.26	--	1.6	--	0.44	1.6	--	--	--
Sulfate	--	0.84	--	1.2	--	1.3	--	--	--	--
Fluoride	--	0.03	--	0.03	--	0.07	0.18	--	--	4,000 ⁵
Silica	--	5.3	--	5.5	--	4	--	--	--	--
Trace Metals (µg/L)										
Aluminum	--	205	--	240	--	100	90	--	--	--
Chromium	0.59	<0.6	0.66	<0.6	0.4	<0.6	--	11 ⁶	100 ⁶	--
Cobalt	--	0.68	--	0.59	--	0.33	0.4	--	--	--
Copper	4.4	3.65	1.4	1.1	0.83	<0.8	1.3	52 ⁷	--	1,300 ⁸
Iron	1200	770	985	760	1300	915	560	--	--	--
Lead	0.29	0.21	0.24	0.19	0.39	0.28	0.5	--	--	15 ⁸
Nickel	3.4	3.2	2.3	2.2	1.1	1.1	1	29 ⁷	100	--
Strontium	--	13	--	14	--	20	--	--	--	4,000 ¹⁰
Titanium	2.1	1.7	2	1.6	2.8	1.8	--	--	--	--
Zinc	2.6	2.4	2.5	2.4	2.8	<2	2	67 ⁷	2,000	2,000 ¹⁰
Trace Elements (µg/L)										
Arsenic	0.53	0.47	0.51	0.41	0.82	0.82	0.8	148	2	10 ⁵
Barium	--	5.05	--	4.5	--	5.1	--	--	2,000	2,000 ⁵
Beryllium	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	--	--	0.08 ⁹	4 ⁵
Boron	--	4	--	4	--	7.9	--	--	1,000	--
Manganese	47	33	30	30	84	50	35	--	100	--
Lithium	--	0.33	--	0.27	--	0.58	--	--	--	--
Selenium	<0.1	0.11	<0.1	0.11	<0.1	0.13	--	--	30	50 ⁵
Vanadium	<0.6	0.43	<0.6	0.43	0.9	0.58	--	--	50	--
1 - Median concentration reported from Thingvold and others (1979).										
2 - Median concentration reported is total organic carbon.										
3 - Minnesota Office of the Revisor of Statutes, 2017 (https://www.revisor.lg.state.mn.us/rules/?id=7052.0100)										
4 - Minnesota Department of Health, 2017 (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										
5 - U.S. Environmental Protection Agency (EPA) Maximum Contaminant Level (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										
6 - Standard for Chromium VI										
7 - standard for total hardness of 50 mg/L as calcium carbonate (standards vary with total hardness (total calcium and magnesium concentration)).										
8 - U.S. Environmental Protection Agency (EPA) Maximum Contaminant Level - action level at tap (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										
9 - standard for cancer										
10 - U.S. Environmental Protection Agency (EPA) Lowest Health Advisory (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										



Environment and Natural Resources Trust Fund (ENRTF) M.L. 2013 Work Plan Final Report

Date of Status Update Report: December 31, 2016

Final Report

Date of Work Plan Approval: June 11, 2013

Project Completion Date: June 30, 2017

PROJECT TITLE: Assessment of Natural Copper-Nickel Bedrocks on Water Quality

Project Manager: Stephen Monson Geerts

Affiliation: Natural Resources Research Institute (NRRI), University of Minnesota Duluth

Mailing Address: 5013 Miller Trunk Highway

City/State/Zip Code: Duluth, MN 55811

Telephone Number: (218) 788-2694, Stephen Monson Geerts (218) 788-2608

Email Address: sgeerts@nrri.umn.edu

Web Address: <http://www.nrri.umn.edu/strategic-research/minerals-metallurgy-mining>

Location: St. Louis and Lake Counties

Total ENRTF Project Budget:	ENRTF Appropriation:	\$585,000.00
	Amount Spent:	\$585,000.00
	Balance:	\$0.00

Legal Citation: M.L. 2013, Chp. 52, Sec. 2, Subd. 05b

Appropriation Language:

\$585,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota in cooperation with the United States Geological Survey to assess impacts of existing mineralization and potential mining on northeastern Minnesota regional water quality, including impacts from copper, nickel, and other metal concentrations in rocks, streambed sediments, and soils in areas of potential base-metal mining. This appropriation is available until June 30, 2016, by which time the project must be completed and final products delivered.

Carryforward: (a) The availability of the appropriations for the following projects are extended to June 30, 2017: (4) Laws 2013, chapter 52, section 2, subdivision 5, paragraph (b), Assessment of Natural Copper-Nickel Bedrocks on Water Quality.

I. PROJECT TITLE: How Do Natural Copper-Nickel Concentrations in Bedrock Influence Water Quality?

II. PROJECT STATEMENT: The large deposits of copper, nickel, cobalt, and platinum-group-elements, and titanium oxide minerals occurring in the Duluth Complex of northeast Minnesota could provide huge economic and employment benefits to the State and provide critical metals to the Nation. The complicated geologic setting of the mineral deposits within the Duluth Complex and the complex glacial history of the region make assessment of any potential water-quality impacts from future metal mining challenging. Streams and rivers that flow over mineralized rocks discharge into the Boundary Waters Canoe Area Wilderness as well as other environmentally sensitive watersheds. Federal, State, local, and tribal entities, mining companies, and environmental groups need up-to-date and accurate geochemical data to assess and predict water-quality impacts of existing mineralization and potential impacts from future mining. This study will determine if copper, nickel, and other metal concentrations in bedrock, streambed sediments, and soils are currently influencing regional water quality in areas of potential base-metal mining. The geochemical and water quality data and accompanying hydrologic analysis will be used by Federal, State, local, and tribal entities to better assess water-quality impacts of existing mineralization and any future mining.

Water-quality, streambed sediment, soil, and rock samples will be collected and analyzed in three watersheds with differing mineral potential: (1) Filson and South Filson Creeks with known copper, nickel, cobalt, and platinum group-element mineralization, (2) St. Louis River with titanium-oxide potential, and (3) Keeley Creek, with no known mineralization. In each of these three watersheds, water samples will be collected 4 times a year for two years (total of a maximum of 96 samples). Water samples will be analyzed for 18 metals, 12 major constituents (ions) and dissolved organic carbon. Up to 20 soil samples, 10 streambed sediment samples, and 10 bedrock samples will be collected in each of the three watersheds. All solid media samples will be analyzed for 46 major and trace elements. In addition, streambed sediment and soil samples will be analyzed for 10 metals by a weak-leach method. Streamflow data from 2 installed stream gages and one existing stream gage will be combined with existing and new water-quality data to develop conceptual hydrologic models for each watershed. Water-quality and modeling results will be compared to data available in the 1979 *Minnesota Regional Copper-Nickel Study* to assess long-term trends in water quality.

III. PROJECT STATUS UPDATES:

Project status reports will be submitted not later than December 31, 2013, June 30, 2014, December 31, 2014, June 30 2015, December 31, 2015, and June 30, 2016. A final work program report and associated products will be submitted between June 30 and December 31, 2016 as requested by the LCCMR.

Project Status as of December 31, 2013:

A cooperative agreement between USGS and University of Minnesota for the flow of LCCMR funding was completed in December.

A first round of water quality and stream bed sediment sampling was completed in September 11-13, 2013. A second round of sampling was delayed because of the federal government shut down.

Streamflow was measured and water-quality samples were collected during September 11-13 in three northeastern Minnesota watersheds. Sample sites are located along, upgradient, or downgradient of the basal contact of the Duluth Complex. Water-quality samples were collected at 5 sites on Filson Creek, 4 sites on Keeley Creek, and 4 sites on the headwaters of the St. Louis River. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). Solid media samples were dried, but have not been submitted for chemistry until LCCMR funding is available.

Permits were submitted to the U.S. Forest Service, Superior National Forest to install continuous streamflow gages on Filson and Keeley Creek. These permits have yet to be approved, with final approval delayed in part by the federal government shutdown and retirements in the U.S. Forest Service. Continuous streamflow data were collected at the St. Louis River near Skibo, MN gage between July 1, 2013 and December 31, 2013. Streamflow measurements were measured at the gage on July 30, September 10, September 12, and October 22.

Geographic Information System (GIS) coverages outlining hydrologic, geologic, and other physical characteristics for the three watersheds (Filson Creek, Keeley Creek, headwaters of the St. Louis River) were constructed in ArcMap 10. Data interpretation and hydrologic models will be developed using these coverages.

An abstract for a poster presentation was submitted to the upcoming Minnesota Lake Superior Stream Science Symposium, to be held in Duluth, January, 2014. The poster will summarize project objectives and activities to be done in the study.

Project Status as of June 30, 2014:

A second and third round of water quality sampling was completed in April 28-May 1, 2014 and June 16-20, 2014, respectively. Streamflow was measured and water-quality samples were collected during both sampling trips in three northeastern Minnesota watersheds. Sample sites are located along, upgradient, or downgradient of the basal contact of the Duluth Complex. Water-quality samples were collected during the second round of water quality sampling at 5 sites on Filson Creek, 3 sites on Keeley Creek, and 4 sites on the headwaters of the St. Louis River. During the third round of water quality sampling, water-quality samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 4 sites on the headwaters of the St. Louis River. During both sampling trips, poor road access and high water levels prevented access to collecting water samples at some sites on Keeley Creek and on the headwaters of the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during both trips at one site on Filson Creek and one site on Keeley Creek. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>).

Permits were approved by the U.S. Forest Service, Superior National Forest to install continuous streamflow gages on Filson and Keeley Creek in February 12, 2014. The streamflow gages were installed on the south fork of Filson Creek (USGS station number 05124982) on March 13 and on Keeley Creek above its confluence with Birch Lake (USGS station number 05125039) on February 19. Streamflows were measured at the south fork of Filson Creek gage on March 18, April 28, May 13, June 19, and June 23. Streamflows were measured at the Keeley Creek gage on March 18, April 28, April 29, and June 18. Gage height is measured at each gage at 15-minute intervals, and the real-time data are available on the USGS National Water Information System web site (<http://waterdata.usgs.gov/mn/nwis/rt>). Continuous streamflow values will be available once a stream discharge/gage height rating curve is established with additional stream discharge measurements.

Continuous streamflow data were collected at the St. Louis River near Skibo, MN gage between January 1, 2014 and June 30, 2014. Streamflows were measured at the gage on January 28, March 10, April 15, April 23, and June 16.

A GIS with the distribution of bedrock units within each of the watersheds and all known outcrop locations was completed. Some bedrock samples in the Filson watershed were collected in May, 2014. Bedrock in outcrop in the Filson and Keeley Creek watersheds is abundant and representative samples easily accessible in the field. Some bedrock samples the St. Louis watershed were selected by Mark Severson (formerly NRRI) from the NRRI bedrock archive. Samples have been crushed and are ready for submittal for chemistry. Bedrock in the St. Louis watershed is sparse; possible sites have been located. Sampling trips for all watersheds have been planned.

Amendment Request of December 31, 2014

We are requesting to shift funds between budget categories under Activities 1 and 2. Under Activity 1, we are requesting to shift funds from Natural Resources Research Institute Personnel (Mark Severson) to USGS Personnel. Mark Severson, a geologist assigned to work on Activity 1, has recently taken a permanent position with Teck American on their Mesaba Copper-Nickel deposit near Babbitt, and therefore will no longer be working on the project. The Natural Resources Research Institute does not currently have a qualified geologist to replace his position on the project. However, the USGS geologist already assigned to the project will be able to complete the work assigned to Mark with some of the ENRTF funds budgeted to Natural Resources Research Institute for the work. We are requesting \$13,800 be shifted from Natural Resources Research Institute Personnel to USGS Personnel to complete the work.

Under Activity 2 we are requesting to shift funds within USGS Contract to account for increases in USGS shipping costs and USGS water-quality sampling supplies costs, and a decrease in USGS travel costs. Additional USGS water quality assurance and quality control requirements for water-quality sampling have resulted in higher shipping and supplies costs. Travel costs (less vehicles, fewer overnight stays) have been reduced to compensate for these additional costs. We are requesting \$9,358 be shifted from USGS travel category to USGS water-quality sampling supplies category (\$9358) and \$3,897 be shifted from USGS travel category to USGS shipping category.

Project Status as of December 31, 2014:

A first round of solid media sampling is complete. In August, samples of the basal contact of the Duluth Complex with the older Virginia Formation were collected from outcrop. These samples along with several samples collected in June were submitted for geochemical analysis in August using expiring USGS funds in Woodruff's geochemistry contract (no charge to LCCMR). Woodruff and Jennings collected both bedrock and soil samples from the three watersheds in September-October. Twenty-five additional bedrock samples were collected: 13 additional samples from the Filson watershed (for a total of 15 samples); 10 samples from the Keeley watershed, and 2 additional samples from the St. Louis watershed (for a total of 8 samples). Soils were collected from selected sites within watershed – up to 3 samples/site (an organic O horizon, and the soil A and C horizon, if all samples present – note: the activity of invasive earthworms often destroys the O horizon, so that sample is not always available). For the Filson (15 sites) and Keeley (14 sites) watersheds, sample sites were selected along transects that crossed most major rocks units. The glacial cover in this area is very thin, and typically rock clasts in the till reflect local bedrock. Where possible, soil samples were paired with bedrock samples. In the St. Louis watershed (13 sites), sample sites were selected based on the glacial deposit type. In this area the glacial cover is thick, and the depositional style controls soil parent material.

Soil samples were dried and sieved to < 2mm. All soil and bedrock samples have been submitted for analysis to the USGS geochemistry contract lab SGS for the following constituents: total C, carbonate C, Al, Ca, Fe, K, Mg, Na, S, Ti, Ag, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Ga, Hg, In, La, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, Sb, Sc, Se, Sn, Sr, Te, Th, Tl, U, V, W, Y, and Zn. Data should be back by late winter, 2015.

Streamflow was measured and a fourth and fifth rounds of water-quality sampling were completed in August 4-8, 2014 and September 29 – October 3, 2014, respectively, in the three study watersheds. During the fourth and fifth rounds of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 7 sites on the headwaters of the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during both trips at one site on Filson Creek and one site on Keeley Creek. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes.

Continuous gage height data were collected and streamflows were determined between July 1, 2014 and December 31, 2014 at the south fork of Filson Creek (USGS station number 05124982) and Keeley Creek above

its confluence with Birch Lake (USGS station number 05125039), and between September 10 and December 31, 2014 at the St. Louis River near Skibo, MN gage (USGS station number 04015438). Continuous data at the St. Louis River near Skibo, MN gage were lost between April 22 and September 10 due to an inability to download the data from the data logger and pressure transducer present at the site. Continuous streamflow will be estimated for this data gap from streamflow measured at nearby stream gages.

Water-quality data were examined to determine trends within and across the three watersheds. Dissolved ion concentrations generally were low in all of the water-quality samples collected in the three watersheds, with specific conductance values for the all of the samples less than 110 $\mu\text{s}/\text{cm}$. Waters generally were neutral to slightly acidic, with pH values ranging from 5.0 to 8.3. The lower pH values were likely related to stream water interactions with acidic waters in attached or nearby wetlands and bogs or more mineralized parts of local bedrock. Sulfate concentrations in all of the water samples were relatively low, less than 3.0 mg/L. The range of sulfate concentrations varied little with flow conditions and among the three watersheds. Concentrations for the major cations (calcium, magnesium, sodium, iron, manganese, and dissolved organic carbon) were higher during periods of lower flows. Dissolved copper and nickel concentrations in all of the water samples were less than 10 and 6 $\mu\text{g}/\text{L}$, respectively, with the highest mean concentrations of both copper and nickel present in waters sampled from Filson Creek. Dissolved organic carbon concentrations were high in all three watersheds, with concentrations ranging from 17 to 46 mg/L. The streams and river likely obtain much of their dissolved organic carbon from interaction with waters from attached or nearby wetlands, which are abundant in all three watersheds.

Water-quality data were examined to assess stream water interactions with wetlands and groundwater. Dissolved organic carbon concentrations were compared to the percentage and topographic location of wetlands in the three watersheds to determine the relations between wetlands and water quality. Geographic Information System (GIS) coverages outlining hydrologic, geologic, and other physical characteristics for the three watersheds (Filson Creek, Keeley Creek, headwaters of the St. Louis River) were updated with lineament assessments in ArcMap 10. The lineament assessment identified possible structural features in the shallow bedrock in Filson and Keeley Creek watersheds that may influence water flow, and will be used with water-quality data to identify where groundwater flow may be prevalent in these two watersheds. Data interpretation and hydrologic models will be developed using these coverages. Base maps have been compiled into a GIS in ArcMap. These coverages include surficial and bedrock geology, hydrology, LiDAR, and historic geochemical data from MGS, DNR, and USGS data bases.

Amendment Request of June 30, 2015

We are requesting to shift funds between budget categories under Activity 1. In our previous amendment (December 31, 2014) we requested a shift funds from Natural Resources Research Institute Personnel (Mark Severson) to USGS Personnel. Recent discussions between USGS and Minnesota Department of Natural Resources (MDNR) geologists have determined that the MDNR geologist has the time and expertise to do the additional geologic work need for the project. However, the MDNR geologist will require some of the ENRTF funds budgeted to Natural Resources Research Institute for the work. We are requesting \$13,800 that was previously amended for USGS Personnel, be shifted from Natural Resources Research Institute Personnel to MDNR Personnel to complete the work.

We would also like to request to change the date of submission of associated documents (U.S. Geological Survey Scientific Investigations Report) from June 30, 2016 to December 31, 2016. Water-quality sampling will continue until September 2015. Analysis and review of the water-quality samples has taken approximately five months to complete (completion date: February 2016). Interpretation of all of the water-quality data and incorporation of the final water-quality data into hydrologic models and a draft copy of the final report will require five months to complete (completion date: July, 2016) . The USGS report review will require six months (completion date: December 2016). Changing the date of submission of associated documents (U.S. Geological Survey Scientific Investigations Report) from June 30, 2016 to December 31, 2016 will allow for all of the water-quality data to be

included in the final report. This change in the project completion date will not require any additional funding for the project. All of the project funding will be spent by June 30, 2016, and any additional support to produce the USGS report after June 30, 2016 will be the responsibility of NRRI, the United States Geological Survey, and the Minnesota Department of Natural Resources.

We would also like to request that Stephen Monson Geerts from NRRI be added to the project in June 2015 as a co-manager for the project. Steve Hauck, the current manager for the project, will be retiring in summer 2016, and Mr. Monson Geerts would be replacing Steve Hauck's position.

Project Status as of June 30, 2015:

Streamflow was measured and a sixth and seventh rounds of water-quality sampling were completed in April 20-24 and June 8-12, 2015, respectively, in the three study watersheds. During the sixth round of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 7 sites on the headwaters of the St. Louis River. During the seventh round of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 5 sites on the headwaters of the St. Louis River. High water levels and limited access to the sites during the week of June 8-12 prevented the collection of samples at 2 sites on the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during both trips at one site on Filson Creek and one site on Keeley Creek. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>).

Continuous gage height data were collected and streamflows determined between Jan 1, 2015 and June 30, 2015 at the south fork of Filson Creek (USGS station number 05124982), Keeley Creek above its confluence with Birch Lake (USGS station number 05125039), and at the St. Louis River near Skibo, MN gage (USGS station number 04015438). On-site streamflow measurements were done at the Keeley Creek gage on four days (March 5, April 15, April 20, and May 19), at the Filson Creek gage on four days (March 5, April 16, April 21, and May 27), and at the St. Louis River near Skibo, MN gage on seven days (January 6, March 2, April 1, April 17, April 23, May 12, and June 22) between January 1 and June 30, 2015. These measurements were used to determine continuous stream discharge from continuous gage heights. Gage height is measured at each gage at 15-minute intervals, and the real-time streamflow and gage height data are available on the USGS National Water Information System web site (<http://waterdata.usgs.gov/mn/nwis/rt>).

Hydrologic data were used to estimate annual water balances for Filson Creek, Keeley Creek, and headwaters of the St. Louis River watersheds. Historical and recent streamflow records were analyzed to determine total annual runoff and estimate groundwater recharge to the three project watersheds. Annual and 30-year normal precipitation data were compiled for precipitation stations located in Tower, Embarrass, Isabella, and Babbitt, MN and used with the total annual runoff and groundwater recharge estimates to produce estimates of annual evapotranspiration. These annual evapotranspiration estimates were similar to estimates determined in other USGS and other water-balance studies for these and nearby watersheds.

Water-quality model simulations for parts of the Filson Creek watershed where the Spruce Road copper-nickel deposits is exposed at or near the land surface were constructed and run to assess water-quality conditions and chemical processes that may be controlling trace metal transport occurring in the creek. Equilibrium water-quality models (PHREEQC and Visual MINTEQ) were used to evaluate equilibrium chemistry at water-quality sampling sites in Filson Creek, assessing the effects of dissolved iron and organic carbon concentrations on trace metal concentrations. Chemical transport simulations using a USGS water-quality transport model (OTIS) were constructed and will be used with results from the equilibrium water-quality simulations to assess transport of metals between water-quality sampling sites.

Amendment Request of November 30, 2015

We would like to request to extend the availability of the funds until December 3, 2016 because the U.S. Geological Survey Scientific Investigations Report with interpretation of all water-quality data would not be completed until December 3, 2016. Analyses of water-quality samples collected in September 2015 and review of the analysis will not be completed until February 2016. Incorporation of the final water-quality data into hydrologic models and a draft copy of the final report will not be completed until July, 2016. The USGS report review process will require six months (December 2016).

Process seeking legislative approval is underway. – 2/10/2016

Project Status as of December 31, 2015:

In September 2015, Laurel Woodruff and Carrie Jennings, Minnesota Department of Natural Resources, completed field-checking of the digital glacial map that Dr. Jennings is constructing for the St. Louis watershed area. During additional field work in September, soil samples were collected from the St. Louis River watershed (3 sites), the Keeley watershed (1 site) and the Filson watershed (4 sites). At each site, 2 soil samples were collected – a surface mineral soil (A horizon) and a deeper soil (C horizon). At the Keeley and Filson sites, nearby bedrock samples were also collected. The additional sites in the Filson watershed were concentrated along the mineralized horizon of the Spruce Road deposit, proximal to the area of the tracer test. Three new clastic streambed sediment samples were also collected in the Filson watershed, two upstream from the tracer input site and one from a tributary draining the Spruce Road deposit footprint into Filson Creek. Soil, bedrock, and streambed samples were dried and sieved. These samples and thirteen <63 micron streambed sediment samples (collected in 2014) were submitted for analysis to the USGS geochemistry contract lab SGS for carbon, trace metal and major constituent concentrations, listed above in the December 2014 report. Two samples of manganese oxide coatings scrapped from boulders in the St. Louis River at the Moose Line Road were collected but have not been submitted for analyses as these sample require special handling not currently available through the USGS contract.

Streamflow was measured and the eighth, and final, round of water-quality sampling was completed in July 27-30, 2015 in the three study watersheds. During the eighth round of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 7 sites on the headwaters of the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during the trip at one site on Filson Creek and one site on Keeley Creek. Continuous gage height data were collected and streamflows were determined between July 1 and December 31, 2015 at the south fork of Filson Creek, Keeley Creek above its confluence with Birch Lake, and at the St. Louis River near Skibo, MN gage. On-site streamflow measurements were done at the Keeley Creek gage on five days, at the Filson Creek gage on five days, and at the St. Louis River near Skibo, MN gage on seven days between July 1 and December 31, 2015.

Water-quality data from the first seven water-quality sampling trips were analyzed by Sarah Elliott and Perry Jones, and Daniel Morel reviewed water-quality data in the NWIS database. Water-quality model simulations for parts of the Filson Creek watershed where the Spruce Road copper-nickel deposits is exposed at or near the land surface were updated by Joshua Messenger and Sarah Elliott and run to assess water-quality conditions and chemical processes that may be controlling trace metal transport occurring in the creek. Equilibrium water-quality models (PHREEQC and Visual MINTEQ) were used to evaluate equilibrium chemistry at water-quality sampling sites in Filson Creek, assessing the effects of dissolved iron and organic carbon concentrations on trace metal concentrations. Chemical transport simulations using a USGS water-quality transport model (OTIS) were constructed and were used with results from the equilibrium water-quality simulations to assess transport of metals between water-quality sampling sites.

Synthetic hydrographs were developed by Aliasha Diekoff for each of the water-quality sampling sites in the three study watersheds using streamflow data collected at the three continuous stream gages operated in the

three study watersheds. Estimated streamflows from synthetic hydrographs in Filson Creek were used in the Visual MINTEQ simulations for evaluating equilibrium chemistry at water-quality sampling sites.

A potassium-bromide tracer test was conducted between September 11 and 17 in a part of Filson Creek where mineralized bedrock is exposed at the land surface. The objective of the tracer test was to determine stream storage and dissolved metal movement in the creek. Water-quality samples were collected by USGS and NRRI staff, and analyzed for bromide, trace metal, major constituent, iron species and dissolved organic carbon concentrations by USGS water-quality laboratories. Results from the tracer test are being used to calibrate the OTIS model simulations of Filson Creek.

Amendment Request of February 2, 2016

We would like to request the following shifting in Environmental and Natural Resources Trust Funding in the budget:

- 1) Transfer \$21,851.55 from Activity 1, Personnel (University of Minnesota, Natural Resources Research Institute) Budget to Activity 3, USGS Personnel Budget to cover additional USGS staff time for data analysis and report writing.
- 2) Transfer \$2,148.45 from Activity 1, Personnel (University of Minnesota, Natural Resources Research Institute) Budget to Activity 2, U.S. Geological Survey Water-Quality Laboratory Budget to cover additional USGS water-quality analytical costs occurred in the project.
- 3) Transfer \$6,500.00 from Activity 3, Personnel (University of Minnesota, Natural Resources Research Institute) Budget to Activity 3, USGS Personnel Budget to cover additional USGS staff time for data analysis and report writing.
- 4) Transfer \$2,500.00 from Activity 3, Natural Resources Research Institute Lodging/Meals/Vehicle Cost to Activity 3, USGS Personnel Budget to cover additional USGS staff time for data analysis and report writing.
- 5) Transfer \$500.00 from Activity 1, Natural Resources Research Institute Lodging/Meals/Vehicle Cost to Activity 3, USGS Personnel Budget to cover additional USGS staff time for data analysis and report writing.
- 6) Transfer \$13,180.24 from Activity 2, USGS Travel Budget to Activity 2, USGS Personnel Budget to cover additional time needed by USGS staff for database entry and data analysis.
- 7) Transfer \$11,944.55 from Activity 2, U.S. Geological Survey, Minnesota Water Science Center Data Section Budget to Activity 2, USGS Personnel Budget to cover USGS staff time for streamflow measurements.
- 8) Transfer \$34,169.19 from Activity 2, U.S. Geological Survey, Minnesota Water Science Center Data Section Budget to Activity 2, U.S. Geological Survey Water-Quality Laboratory Budget to cover additional USGS water-quality analytical costs occurred in the project.
- 9) Transfer \$1,187.41 from Activity 2, U.S. Geological Survey, Minnesota Water Science Center Water-Quality Sampling Supplies to Activity 2, USGS Personnel Budget to cover USGS staff time for water-quality data processing.
- 10) Transfer \$1,554.55 from Activity 2, U.S. Geological Survey Shipping Costs, Water-quality samples to Activity 2, USGS Personnel Budget to cover USGS staff time for water-quality data processing.

Budget transfers 1, 2, 3, and 4, will result in a total of \$33,500 of the budgeted funds for University of Minnesota, Natural Resources Research Institute moving to the U.S. Geological Survey needed to cover the cost of additional USGS staff time to complete data processing, analysis, and report writing. University of Minnesota, Natural Resources Research Institute staff time on data collection under Activity 1 and report writing under Activity 3 has been reduced from the original budget, allowing for the shifting of funding between the two organizations. The total Environmental and Natural Resources Trust Funding for the project (\$585,000) will not change from the original budget.

Amendment approved by LCCMR, February 10, 2016

Amendment Request of June 30, 2016

We would like to request the following change from the current Project Manager Steven Hauck to Stephen Monson Geerts, effective on Steven Hauck's retirement July 22, 2016. Mr. Monson Geerts is a research fellow and has been an employee of the Natural Resources Research Institute since 1988. His qualifications include a M.S. in geology and minor in hydrogeology and has been a working colleague with Steven Hauck, specializing in the intrusive rocks and mineralogy of the Duluth Complex in northeastern Minnesota.

Approved by LCCMR, July 20, 2016

Project Status as of June 30, 2016:

Major constituent and trace-element analyses of bedrock, soil, and streambed-sediment sample analyses and interpretations were completed. Baseline major constituent and trace element concentrations were determined for a total of 38 bedrock samples, 102 soil samples, and 45 streambed sediment samples that were collected from the study watersheds. Geochemical data for bedrock, soils, and streambed samples were entered and stored in the USGS National Geochemical Database (http://minerals.cr.usgs.gov/projects/geochem_database/index.html).

One streamflow gage was maintained in each of the three watersheds between January 1 and June 30, 2016 to continuously monitor stream stage at 15-minute intervals. These 15-minute stage measurements were used with stage-streamflow relations developed from instantaneous streamflow measurements taken at the gages to determine 15-minute streamflow. A total of 201 instantaneous streamflow measurements were taken during the study at surface-water-quality sample sites coincident with water-quality sample collection or during periodic maintenance trips for the streamflow gage. All continuous stream stage and flow data, and streamflow measurements were entered and are available in USGS National Water Information System (NWIS) at <http://waterdata.usgs.gov/nwis>.

Water-quality analyses were completed and data was interpreted. A total of 141 stream (river) samples and eight precipitation samples were collected from a total of 21 sites in the three watersheds from September 2013 to July 2015. Metal and major constituent concentrations for water samples collected in the project were entered and stored in the USGS NWIS (<http://waterdata.usgs.gov/nwis>). Water qualities in the streams were found to be reflective of the bedrock and glacial geology.

The conceptual hydrology of the three watersheds was completed, producing annual evapotranspiration and groundwater recharge estimates for the study period (2014-15) using streamflow and precipitation data. Synthetic hydrographs for each of the unaged, water-quality sampling sites were developed and used to estimate instantaneous constituent loads at the water-quality sampling sites.

Water-quality analyses of water samples collected during the potassium-bromide (KBr) tracer test conducted in Filson Creek in September 2015 was completed. This water-quality data was interpreted to gain a better understanding of stream channel morphology streamflow dynamics, and water-quality over sulfide-bearing bedrock (the mineralized zone). Water-quality results from the tracer test and synthetic hydrographs are being used in water-quality models to assess factors controlling stream water-quality, under present conditions and higher metal concentrations that might be associated with potential mining in the watershed.

A draft of the U.S. Geological Survey Scientific Investigations Report is almost completed for colleague and USGS review that will 1) summarize analytical results; 2) present interpretations of bedrock, soil, streambed sediment, and water-quality data; and 3) describe conceptual hydrology for the three watersheds. It will be completed for review by July 31, 2016, with an on-line version of the report completed by December 31, 2016.

Overall Project Outcomes and Results

The Natural Resources Research Institute, the U. S. Geological Survey, and the Minnesota Department of Natural Resources conducted a three-year study to 1) assess copper, nickel, and other metal concentrations in surface water, bedrock, streambed sediments, and soils in watersheds where the basal part of the Duluth Complex is exposed or near the land surface; and 2) determine if these concentrations, and metal-bearing deposits, are currently influencing regional water quality in areas of potential base-metal mining. The new data will be used by Federal, State, local, and tribal entities to better assess water-quality impacts of existing mineralization and potential mining. Surface-water, streambed sediment, soil, and bedrock samples were collected and analyzed in three largely undisturbed watersheds with different mineral-deposit settings: (1) copper-nickel-platinum group metal mineralization (Spruce Road deposit - Filson Creek watershed), (2) iron-titanium-oxide mineralization (Skibo deposit – upper part of the St. Louis River watershed), and (3) no identified mineralization (Keeley Creek watershed).

Within each watershed, surface-water samples were collected from multiple sites at 10 different sampling times over a three-year span. Surface-water samples were analyzed for 12 trace metals (dissolved and total concentrations), 14 inorganic constituents (dissolved concentrations), alkalinity, and total and dissolved organic carbon. Streambed-sediment samples were collected at each water-quality site, and 10 to 15 bedrock samples and 15 nearby soils samples were collected per watershed and analyzed for 47 major and trace elements. Streamflow was monitored in the three watersheds at continuous streamflow gages and through discharge measurements conducted at all sites during each water-quality sampling event. A tracer test was conducted in Filson Creek watershed where copper concentrations in stream waters were relatively high, ranging from 4 to 12 micrograms per liter ($\mu\text{g/L}$), to determine streamflow characteristics.

The geochemistry of surface waters and streambed sediments reflects the geochemistry of underlying rock types and glacially transported unconsolidated material. Water-quality data also suggest that streamflow influences concentrations of major constituents, such as Ca, Mg, and K, with lower concentrations during high flow, but has little apparent influence on metal concentrations. Copper-nickel mineralization in the northern Filson Creek watershed contributes both metals to stream waters and streambed sediment. Dissolved and total organic carbon (DOC and TOC) concentrations in surface waters are very high compared to most surface waters in Minnesota, ranging from 13.7 to 41.4 milligrams per liter (mg/L) in all watersheds. Results from preliminary biotic-ligand modeling suggest that the high DOC content may exert some control on copper concentrations in water, such that complexation with DOC may reduce the bioaccessibility of copper. In the Filson and Keeley watersheds, glacial transport distances of sediments were interpreted to be short, and soil chemistry can be related to nearby bedrock contributions to soil parent materials. For example, mineralized bedrock has relatively high copper concentrations greater than 4,500 milligrams per kilogram (mg/kg) and soil has copper concentrations greater than 1,000 mg/kg over the footprint of the Spruce Road deposit in the Filson watershed. The upper part of the St. Louis watershed has thick glacial cover with minimal bedrock exposure, and soil chemistry is more indicative of glacial transport processes.

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Characterize distribution of major and trace elements in streambed sediment, soil, and bedrock samples from mineralized and non-mineralized watersheds along the basal Duluth Complex.

Description: Solid media (streambed sediments, soils, and bedrock) sampling will be conducted in the first year of the proposed work. A second round of solid media sampling from a reduced number of sites may be done if results from the first round identify areas of special geochemical interest. Collection sites for streambed sediments are in conjunction with water quality sites (Activity 2). Ten streambed sediment samples will be collected from Filson/South Filson Creeks, 4 streambed sediments will be collected from Keeley Creek, and 7

streambed sediments will be collected from the St. Louis River for a total of 21 streambed sediment samples. Within each of the 3 watersheds, 20 upland soil sites will be selected and 2 samples (topsoil/deeper soil) will be collected at each site, for a total of 120 soil samples. Also within each watershed, up to 10 bedrock samples will be collected from outcrop, supplemented by drill core samples for a total of 30 bedrock samples. Bedrock samples and the < 2 mm fraction of streambed and soil samples will be submitted to the USGS geochemistry contract laboratory (SGS) for total analysis for 48 major and trace elements. In addition, soils and streambed sediments will be analyzed by a partial leach method for 10 metals.

Summary Budget Information for Activity 1:

ENRTF Budget: \$ 95,358
Amount Spent: \$ 95,358
Balance: \$ 0

Activity Completion Date: 12/2015

Outcome	Completion Date	Budget
Determine major and trace elements in 30 bedrock samples, 120 soil samples, and 21 streambed sediment samples in 3 watersheds, with the possibility of an additional round of sampling from a reduced number of sites	12/2015	\$ 95,358

Activity Status as of December 31, 2013:

Fine-grained (< 63 micron silt and clay) bed sediment samples were collected at 10 sites in the 3 study watersheds using USGS NAWQA protocols. Samples are dried and ready for analysis for 42 major and trace elements. Bedrock sample of the Virginia Formation collected from the St. Louis River watershed. Funding for the field work (salary and travel expenses = \$5,730) and supplies (\$260) was provided by the U.S. Geological Survey Midwest Region Mining Initiative.

Activity Status as of June 30, 2014:

A GIS with the distribution of bedrock units within each of the watersheds and all known outcrop locations has been completed. Historical geochemical data layers that overlap the study areas, including soils, lake sediments, bedrock, and seepage analyses, have been added to the GIS. Carrie Jennings and Laurel Woodruff have examined the 1-meter hillshade LiDAR data for Lake and parts of St. Louis counties to develop a soil sampling strategy that will be based on the distribution of glacial materials. Mark Severson and Laurel Woodruff met to discuss bedrock sampling. The funding for all future geochemical analyses of solid media has been committed to the USGS geochemical contract. Currently available bedrock samples from the Filson and St. Louis watersheds and <63 micron sediment samples have been submitted for analysis. Environmental and Natural Resources Trust Funding for travel (\$163) and salary for Woodruff (\$6,128) between January 1 and June 30, 2014 was \$6,291.

Activity Status as of December 31, 2014:

Several of the < 63 micron stream sediment samples were had insufficient quantity for analyses, so a second round of collection is planned. A new sieve was purchased to ensure greater success with sample collection. A first round of soil and bedrock sampling is complete. Soil samples were dried and sieved to < 2mm. All soil and bedrock samples have been submitted for analysis to the USGS geochemistry contract lab SGS for the following constituents: total C, carbonate C, Al, Ca, Fe, K, Mg, Na, S, Ti, Ag, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Ga, Hg, In, La, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, Sb, Sc, Se, Sn, Sr, Te, Th, Tl, U, V, W, Y, and Zn. Geochemical data should be back by late winter, 2015. Thus, from June 30 to December 31, 2014 Environmental and Natural Resources Trust Funding for Activity 1, including these analyses (\$8650.28), field work expenses for Woodruff (\$806.69), sample shipping (\$26.61), a new 63 micron sieve (\$121.83), salary for Woodruff (\$28,944.83), field expenses for Jennings [DNR contract] (\$416.83) and salary for Jennings [DNR contract] (\$2,329.14) were a total of \$41,296.01.

Activity Status as of June 30, 2015:

Project personnel from the NRRI, USGS, and MDNR met on April 16 to review geochemical results.

Activity Status as of December 31, 2015:

In September 2015, Laurel Woodruff and Carrie Jennings, Minnesota Department of Natural Resources, completed field-checking of the digital glacial map that Dr. Jennings is constructing for the St. Louis watershed area. In October Woodruff and Jennings met with Quaternary geologist from the Minnesota Geological Survey who are responsible for the St. Louis county atlas surficial map to Dr. Jennings preliminary interpretations of the regional glacial history.

During additional field work in September, soil samples were collected from the St. Louis River watershed (3 sites), the Keeley watershed (1 site) and the Filson watershed (4 sites). At each site, 2 soil samples were collected – a surface mineral soil (A horizon) and a deeper soil (C horizon). At the Keeley and Filson sites, nearby bedrock samples were also collected. The additional sites in the Filson watershed were concentrated along the mineralized horizon of the Spruce Road deposit, proximal to the area of the tracer test. Three new clastic streambed sediment samples were also collected in the Filson watershed, two upstream from the tracer input site and one from a tributary draining the Spruce Road deposit footprint into Filson Creek. Soil, bedrock, and streambed samples were dried and sieved. These samples and thirteen <63 micron streambed sediment samples (collected in 2014) were submitted for analysis to the USGS geochemistry contract lab SGS for carbon, trace metal and major constituent concentrations, listed above in the December 2014 report. Two samples of manganese oxide coatings scrapped from boulders in the St. Louis River at the Moose Line Road were collected but have not been submitted for analyses as these sample require special handling not currently available through the USGS contract.

1. Bedrock – 6 samples (5 new + 1 duplicate) for Hg, Se, As, 42-element ICP-AES/MS = \$261.12
2. A horizon – 9 samples (8 new + 1 duplicate) for Total C, carbonate C, Hg, Se, As, 42-element AES/MS = \$628.20
3. C horizon – 9 samples (8 new + 1 duplicate) for Total C, carbonate C, Hg, Se, As, 42-element AES/MS = \$628.20
4. <2 mm clastic streambed sediment – 4 samples (3 new + 1 duplicate) for Hg, Se, As, 42-element ICP-AES/MS and total S = \$178.08 (note that the weak-leach DIBK method is no longer available through the USGS contract).
5. <63 micron streambed sediment – 14 samples. These samples were collected last year, but not submitted for chemistry until now. The sample quantity may be an issue as most samples are about 2-3 grams, very close to the need quantity for analysis. However, they won't have to be further processed before acid digestion. Because of the limited sample size, they will only be analyzed by the 42-element ICP-AES/MS method = \$325.08

Thus, from June 30 to December 31, 2015 Environmental and Natural Resources Trust Funding for Activity 1, including these analyses (\$2020.68), field work expenses for Woodruff (\$1,547.76), sample shipping (\$25), and salary for Woodruff (\$15,947.96), (field expenses for Jennings (\$643.18) and salary for Jennings (\$10,965.99). Remaining funding for this Activity will be used for Mn-oxide coating analyses and for interpretation of results and completion of a final report.

Activity Status as of June 30, 2016:

Major constituent and trace-element analyses of bedrock, soil, and streambed-sediment sample analyses and interpretations were completed. Methods and interpretations of the analyses were summarized in a draft copy of the final report. Baseline major constituent and trace element concentrations were determined for a total of 38 bedrock samples, 102 soil samples, and 45 streambed sediment samples that were collected from the study watersheds. Geochemical data for bedrock, soils, and streambed samples were entered and stored in the USGS National Geochemical Database (http://minerals.cr.usgs.gov/projects/geochem_database/index.html).

Final Report Summary for Activity 1:

The information within this report has been finalized but remains subject to revision. It is being provided to meet the need for timely best science. The information is provided on the condition that neither the U.S. Geological Survey nor the U.S. Government shall be held liable for any damages resulting from the authorized or unauthorized use of this information.

Methods

Solid Media Sampling

Baseline major and trace element concentrations were determined for soil, bedrock, and streambed sediments in the three study watersheds. A total of 38 bedrock samples, 102 soil samples, and 45 streambed sediment samples were collected from the study watersheds. Sample locations are shown in Figures 1 and 2. Major constituent and trace metal concentrations for bedrock, soil, and streambed sediment samples are given in the Appendix Tables 1, 2, and 3. All samples were analyzed by the same analytical techniques to enable comparison among the different types of solid media. Details of all analytical methods used for this study are described in Taggart (2002).

Bedrock Sampling

Some bedrock sample sites were selected to be proximal to soil and water-quality sample sites (if bedrock was locally present); other sites were selected from opportunistic bedrock outcrops. With limited glacial sediment cover, bedrock outcrop in both the Filson Creek and Keeley Creek watersheds was abundant, and an effort was made to collect samples representative of the variety of exposed bedrock within each. In the St. Louis watershed, bedrock sampling was limited by the sparse bedrock outcrops. Analyses of all bedrock samples including duplicates are in Appendix Table 1.

Soil Sampling

Soil was collected only on dry upland sites, in proximity to bedrock outcrops when possible. In the Filson Creek watershed soil sampling was mainly along two broad transects that cut across the general trend of the

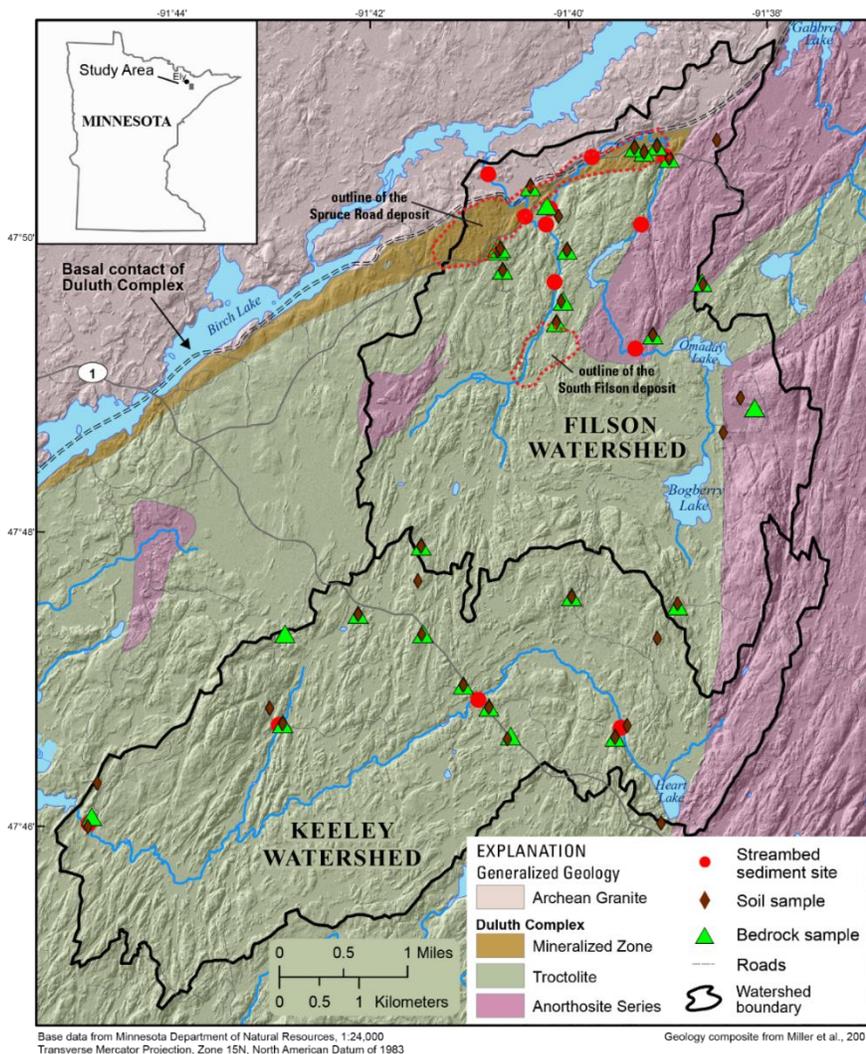


Fig 1. Solid media sample locations and bedrock geology along Filson Creek and Keeley Creek near Ely, MN.

major bedrock types. In the Keeley Creek watershed,

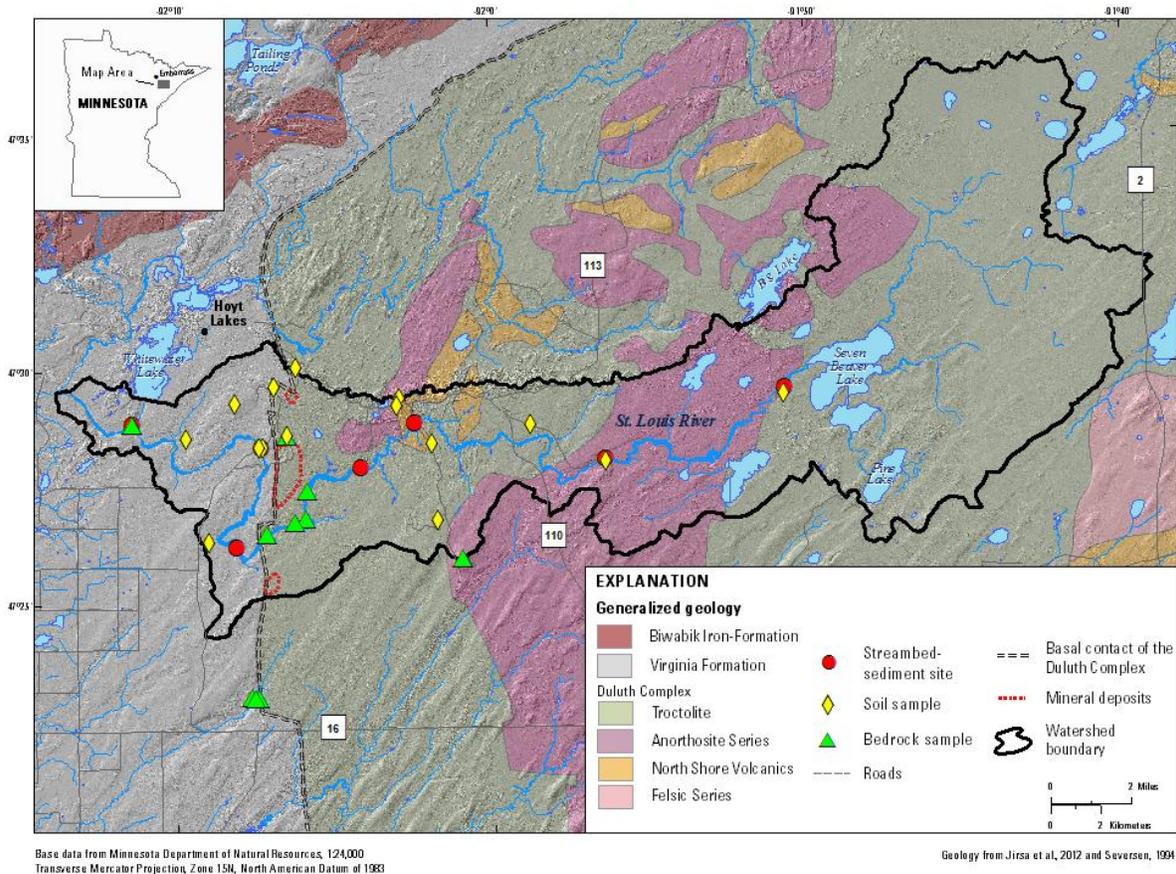


Fig 2. Solid-media sites and bedrock geology in the St. Louis River watershed, near Hoyt Lakes, Minnesota.

sites were selected proximal to 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 and soil sites were selected based on the diverse glacial features.

The target soil 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 the uppermost mineral soil; and (3) a deeper soil sample representing the B or C horizon, assumed to best approximate the soil parent material. Analyses of all soil samples including duplicates are given in Appendix Table 2.

Streambed Sediment Sampling

Two different streambed sediment size fractions (<2 millimeters (mm) and <63 microns (µm)) were collected at the water-quality sites. Three additional streambed sediment samples were collected from Filson Creek and a small tributary within the mapped footprint of the Spruce Road deposit. Analyses of all streambed sediment samples including duplicates are given in Appendix Table 3.

St. Louis River Watershed Glacial Geology

A surficial geology map for the St. Louis River watershed was constructed using a glacial landform-sediment association model to interpret landforms visible in a high-resolution 1-meter digital elevation model (DEM)

derived from light detection and ranging (LiDAR) technology. Mapping was done by on-screen digitizing directly into a geographical information system (GIS). Interpretations were checked in the field at various locations, and compared to prior mapping in the area done by Hobbs and Goebel (1982), Lehr and Hobbs (1992), Lehr (2000), and Jennings and Reynolds, (2005).

Results and Discussion of Solid Media Geochemical Data

Bedrock

Duluth Complex bedrock has comparatively high concentrations of aluminum (Al), calcium (Ca), iron (Fe), and magnesium (Mg), as expected from rocks dominated by the silicate minerals plagioclase, olivine, and pyroxene; dark-colored melatroctolite (with olivine and pyroxene contents greater than plagioclase) has comparatively higher Fe and Mg concentrations. In contrast, Virginia Formation argillite, a fine-grained (locally metasedimentary) rock originally made up of consolidated clay and silt, is enriched in potassium (K) with relatively low Ca concentrations compared to rocks from the Duluth Complex. Granitic bedrock of the Archean Giants Ridge Batholith, consisting mainly of quartz, plagioclase and K-feldspar, has relatively high K and sodium (Na), distinct from both the Duluth Complex and Virginia Formation bedrock.

Trace-element concentrations follow tendencies observed in major elements (Ca, Mg, K, Na). Major and trace elements can create distinctive geochemical signatures for the differing rock types. For example, melatroctolite has enriched cobalt (Co), chromium (Cr), manganese (Mn), and nickel (Ni) elements that preferentially partition into olivine and pyroxene. Archean granite has the highest barium (Ba) and strontium (Sr) values measured, likely because of the presence of K-feldspar in the granite.

Sulfide mineralized rock of the Spruce Road deposit (fig. 1) can have exceptionally high Ni (up to 1,967 mg/kg) and copper (Cu) (up to 7,722 mg/kg) concentrations, although not all bedrock samples collected within the mapped area of the Spruce Road deposit are mineralized, reflecting the heterogeneous nature of mineralization. Bedrock from the Keeley watershed has a range of 109 to 705 mg/kg Ni and 6 to 81 mg/kg Cu. Nickel and Cu in bedrock from the St. Louis watershed range from 28 to 546 mg/kg and 10 to 257 mg/kg, respectively. Sulfur (S) in mineralized bedrock in the Filson watershed ranges from 0.03 to 1.69 weight percent (wt. %). There is no apparent contribution from the Fe-titanium (Ti)-oxides mineralization in the St. Louis watershed. The influence of mineralization on soil and streambed sediments is discussed in more detail below.

Soil

Soil O horizon

The relatively high organic C concentrations of the soil O horizon (28 to 52 weight percent; Appendix Table 2) provide a large binding capacity for cations (Ca, Mg, Na, K) and trace elements. A number of elements have positive Spearman correlations (>0.5) with organic carbon (C), including Ca, cadmium (Cd), Cu, Mn, molybdenum (Mo), phosphorus (P), S, antimony (Sb), tungsten (W), and zinc (Zn). Some element concentrations are higher than might be expected if derived only from local geologic sources, including (1) 0.86 weight % S for two samples from the Filson Creek watershed; (2) Mn greater than 6,000 mg/kg for a site in Filson and in site Keeley; (3) 153 mg/kg lead (Pb) for a site in Keeley; and (4) 481 mg/kg Zn for a different site in Keeley. It is possible that these somewhat enriched levels are the result of atmospheric deposition from anthropogenic sources, with subsequent sequestration by the organic material. For the overall small data set, there are no significant differences among the 3 watersheds.

Soil A horizon

Soil A horizon samples are transitional between the soil O and C horizons both in space and in chemistry. In many cases where aggressive invasive earthworm activity has destroyed the soil O horizon, that organic material (and its element load) has been incorporated into a worm-worked thick mineral soil A horizon. Median

concentrations of all elements in the soil A horizon are highly dependent on the organic C concentrations; higher organic C results in a lower proportion of mineral soil. Thus, those elements that typically correlate with organic C have higher concentrations in more organic C-rich soils, whereas elements more characteristic of the mineral component of the soil have lower concentrations.

Soil C horizon

In the Filson Creek and Keeley Creek watersheds, some major and trace elements closely reflect regional bedrock. For example, soil is typically enriched in the major elements Al, Ca, Fe, and Mg, which are the principal constituents of plagioclase, olivine, and pyroxene. Soil samples in the St. Louis watershed have higher K, Ba, beryllium (Be), bismuth (Bi), cerium (Ce), lanthanum (La), rubidium (Rb), scandium (Sc), thorium (Th), and uranium (U) compared to soil samples from the Filson Creek and Keeley Creek watersheds.

The spatial distribution of different elements and scatter plot clearly reveals the influence of local bedrock to soil parent materials. A plot of Rb vs. Ba for all bedrock and soil C horizon samples is shown in fig. 3. These two trace elements have distinct bedrock signatures; Virginia Formation argillite is high in both Rb and Ba; Archean granite is high in Ba, but not Rb; all lithologies from the Duluth Complex have low concentrations of both elements. Soil in the western end of the St. Louis watershed (where glacial materials incorporated rocks of the Virginia Formation) are in a group trending towards the Virginia Formation argillite Rb-enriched field. In the Filson Creek watershed, there is a slight tendency for soil in the northern part of the watershed to trend towards the high granitic Ba point (fig. 3). This trend may be a result of limited down-ice movement of granitic materials onto Duluth Complex bedrock following glaciation.

Enriched Ni and Cu concentrations in soil collected within the mineralized map area of the Spruce Road deposit reflect weathered Cu-Ni sulfide-bearing bedrock in soil parent materials (fig. 4). Soil collected within the mineralized area of the Spruce Road deposit have relatively enriched Ni and Cu. The source of somewhat enriched Ni in some soil C horizon samples in the Keeley watershed likely reflects the influence of the silicate mineral olivine, which can contain high Ni but low Cu.

Streambed Sediments

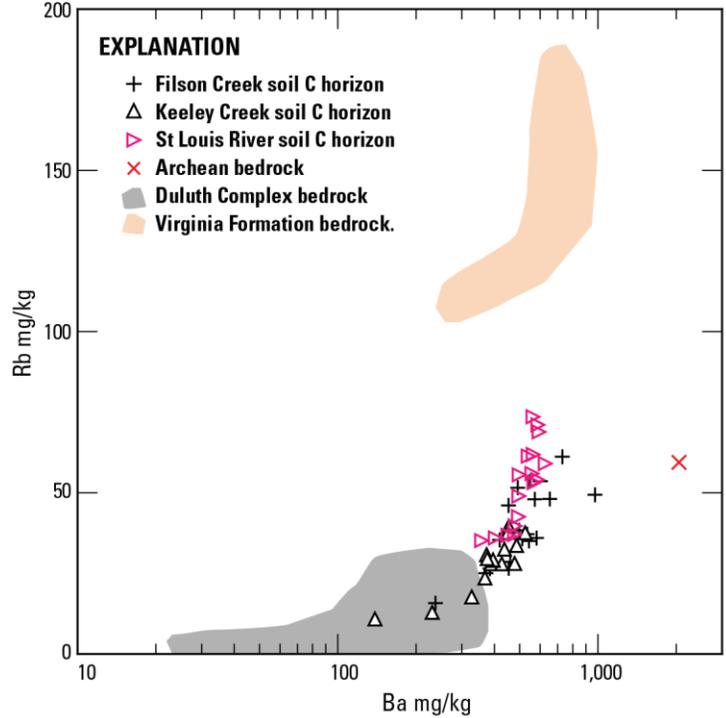


Fig. 3. Concentrations of Ba versus Rb (plotted on a log scale) for bedrock and soil C horizon samples from the three study watersheds. The gray field represents Duluth complex bedrock, the orange field represents bedrock of the Virginia Formation, and the red cross is the single sample of Archean granite. Soil from northern part of the Filson watershed trend towards the granite point; soil from the western St. Louis watershed trend towards the Virginia Formation field.

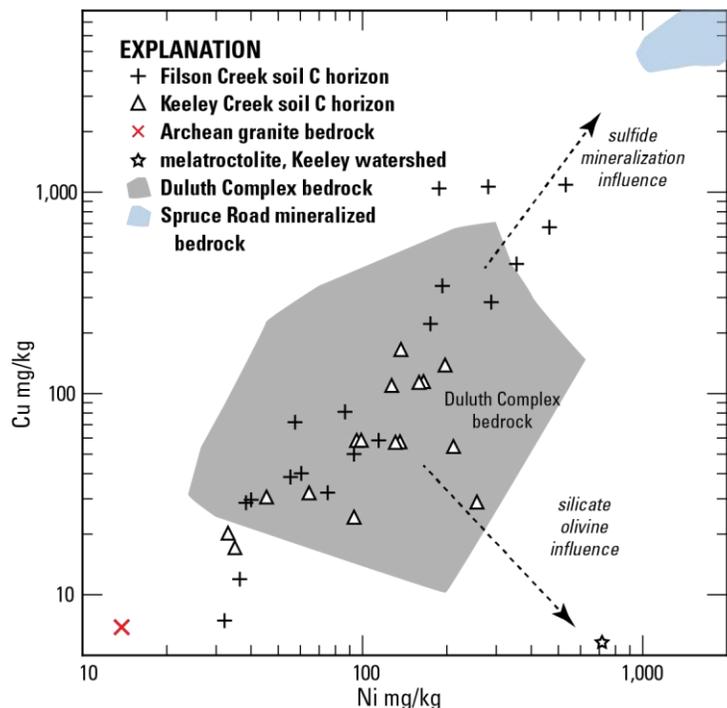


Fig 4. Concentrations of Ni versus Cu (plotted on a log scale) for bedrock and soil from Filson and Keeley watersheds. Soil collected within the mineralized zone have Ni and Cu values that trend towards mineralized bedrock (blue field); some soil in the Keeley watershed have Ni values that trend towards olivine-bearing, Ni-rich/Cu-poor melatroctolite (star).

Less than (<) 2 mm fraction

Four of the clastic streambed sediment samples collected where Filson Creek crosses the outline of the Spruce Road deposit have Cu values that range from 108 to 404 mg/kg, with corresponding Ni values ranging from 165 to 586 mg/kg. Where Filson Creek is proximal to Archean granite, streambed sediments have high K (1.69 and 1.81 wt. %, respectively), Na (4.25 and 4.39 wt. %, respectively) and Ba (1,400 and 1,070 mg/kg, respectively), reflecting the local bedrock influence. Few samples have S values above the lower limit of detection (0.1 wt. %).

Seven of ten metals analyzed by a partial weak leach method that extracts only the soluble metal portion can be compared to the equivalent metal analyzed by a near-total digestion method. Spearman correlation coefficients comparing concentrations from the weak-leach method vs. concentrations from the 4-acid near-total extraction are 0.936 for arsenic, 0.945 for Cd, 0.979 for Cu, 0.918 for Mo, 0.975 for Pb, 0.200 for Sb, and 0.988 for Zn (for example, fig. 5). The excellent correlation for all metals other than Sb indicates that these metals are loosely bound by Fe- and/or Mn-oxy-hydroxides in the streambed sediments, and are not in sulfide or silicate mineral structures. Thus, these metal could be mobilized by redox reactions that would change the state of the Fe-Mn-oxy-hydroxides.

Less than (<) 63 μm fraction

The concentration of trace elements in streambed sediment is strongly affected by particle-size distribution. Typically, the concentrations increases as particle size decreases. In this dataset, when the <63 μm fraction in the streambed sediment is compared to the <2 mm fraction from the same sampling reach, the finer fraction has lower Al, Ca, K, Mg, Na, and Ti than the coarser fraction. Trace elements with the same pattern include Ba, Sc, Sr, and vanadium (V). These element differences are likely because of the presence of feldspar, olivine, pyroxene, and Fe-Ti-oxides in the <2 mm fraction samples. In contrast, mean Fe and Mn concentrations are higher in the finer fraction, suggesting a greater concentration of Fe-Mn-oxy-hydroxides. A good example of this is the Mn concentrations in the <63 micron samples from the St. Louis watershed, which are strikingly high, ranging from 12,450 mg/kg Mn to 22,280 mg/kg. In Filson Creek, a <63 μm sample collected within the mineralized zone of the Spruce Road deposit, has 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. Other metals that show the same tendency (higher concentrations in the <63 μm fraction compared to the <2 mm fraction) include Bi, Co, Mo, Pb, and Zn. Sulfur values in the fine fraction range from 0.08 to 0.19 wt. %.

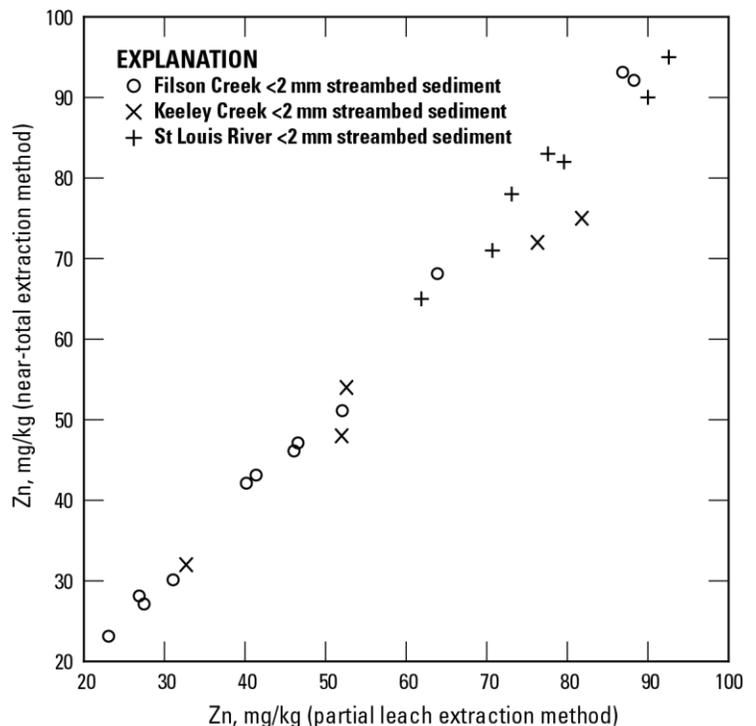


Fig 5. Concentrations of Zn in <2 mm streambed sediments from a partial leach extraction method that mobilizes only the soluble portion of the metal and from a near-total extraction that extracts all Zn in the sediment. Good correlation indicates that all Zn is soluble, likely sorbed onto Fe-Mn-oxy-hydroxides.

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ACTIVITY 2: Determine natural metal and major constituent loads in streams.

Description: Streamflow will be continuously monitored at three USGS gage sites. One gage will monitor flow rates in Filson Creek, one gage on Keeley Creek, and a third gage, which has been operating since 2011, will monitor flow in the St. Louis River. Two USGS stream gages (Filson and Keeley Creeks) will be installed in the fall of 2013 and maintained for two years. Once the gages are in operation, stream discharge measurements will be taken between October 2013 and September 2015 under varying flow rates to develop a water-level/flow rating curve at each gage. This water-level/flow rating curve will be used with continuous water-level data collected at the gages to determine continuous flow data over the two years. Water quality samples will be collected from Filson/South Filson Creeks, Keeley Creek, and the St. Louis River between August 2013 and September 2015 and analyzed for 18 metals, 12 major constituents, and dissolved oxygen to determine temporal and spatial variations in metals, major constituents, and dissolved oxygen concentrations. A total of 96 samples (12 quarterly samples over 8 quarters) will be collected over the two years from the three streams under differing flow rates. Streamflow and water-quality data will be used to compute metal and major constituent loads in each of the stream systems and assess variations in loads under various flow rates.

Summary Budget Information for Activity 2:

ENRTF Budget: \$ 277,760
Amount Spent: \$ 277,760
Balance: \$ 0

Activity Completion Date: June 30, 2015

Outcome	Completion Date	Budget
1. Determine temporal flow rates in streams/installation and maintenance of two stream gages	6/2015	\$ 127,240
2. Determine background metal and major constituent loads in streams	6/2015	\$ 150,520

Activity Status as of December 31, 2013:

Streamflow was measured and water-quality samples were collected between September 11-13 in the three study watersheds in northeastern Minnesota. The sample sites were located along, upgradient, or downgradient of the basal Duluth Complex. Water-quality samples were collected at 5 sites on Filson Creek, 4 sites on Keeley Creek, and 4 sites on the headwaters of the St. Louis River. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). Funding for this field work, including salary (\$20,520), travel expenses(\$3,350), shipping (\$462), vehicle expenses(\$400), water-quality analytical costs (\$12,100), and water-quality supplies (\$660), was provided by the U.S. Geological Survey Midwest Region Mining Initiative.

Permits were submitted to the U.S. Forest Service, Superior National Forest to install continuous streamflow gages on Filson and Keeley Creek. These permits have yet to be approved, with final approval delayed in part by the federal government shutdown and retirements in the U.S. Forest Service. Continuous streamflow data were collected at the St. Louis River near Skibo, MN gage between July 1, 2013 and December 31, 2013. Streamflow measurements were measured at the gage on July 30, September 10, September 12, and October 22. Operation and maintenance costs for the St. Louis River near Skibo, MN gage between July 1, 2013 and December 31, 2013 was \$9,244 (\$5,546 charged to **ENRTF**, \$3,698 charged to U.S. Geological Survey Water Cooperative Program).

Activity Status as of June 30, 2014:

Streamflow was measured and a second and third round of water quality sampling were completed in April 28-May 1, 2014 and June 16-20, 2014, in the three study watersheds. Sample sites are located along, upgradient, or downgradient of the basal contact of the Duluth Complex. During the second round of water quality sampling, samples were collected at 5 sites on Filson Creek, 3 sites on Keeley Creek, and 4 sites on the headwaters of the St. Louis River. During the third round of sampling, water-quality samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 4 sites on the headwaters of the St. Louis River. During both sampling trips, poor road access and high water levels prevented access to some sites on Keeley Creek and on the headwaters of the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during both trips at one site on Filson Creek and one site on Keeley Creek. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). Environmental and Natural Resources Funding for water-quality sampling between January 1 – June 30, 2014 was \$39,905, including expenses for salary (\$24,012), travel expenses (\$2,198), shipping expenses (\$545), vehicle expenses (\$500), water-quality analytical costs (\$9,449), and water-quality supplies expenses (\$3,201).

Permits were approved by the U.S. Forest Service, Superior National Forest to install continuous streamflow gages on Filson and Keeley Creek in February 12, 2014. The streamflow gages were installed on the south fork of Filson Creek (USGS station number 05124982) on March 13, and on Keeley Creek above its confluence with Birch Lake (USGS station number 05125039) on February 19. Streamflows were measured at the south fork of Filson Creek gage on March 18, April 28, May 13, June 19, and June 23. Streamflows were measured at the Keeley Creek gage on March 18, April 28, April 29, and June 18. Gage height is measured at each gage at 15-minute intervals, and the real-time data are available on the USGS National Water Information System web site (<http://waterdata.usgs.gov/mn/nwis/rt>). Continuous streamflow values will be available once a stream discharge/gage height rating curve is established with additional stream discharge measurements. Continuous streamflow data were collected at the St. Louis River near Skibo, MN gage between January 1, 2014 and June 30, 2014. Streamflows were measured at the gage on January 28, March 10, April 15, April 23, and June 16. Environmental and Natural Resources Trust Funding for stream gage installation and streamflow monitoring work between January 1 – June 30, 2014 was \$24,766.

Activity Status as of December 31, 2014:

Streamflow was measured and a fourth and fifth rounds of water-quality sampling were completed in August 4-8, 2014 and September 29 – October 3, 2014, respectively, in the three study watersheds. During the fourth and fifth rounds of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 7 sites on the headwaters of the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during both trips at one site on Filson Creek and one site on Keeley Creek. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS)

(<http://waterdata.usgs.gov/nwis>). Environmental and Natural Resources Funding for water-quality sampling between July 1 and December 31, 2014 was \$69,072, including expenses for salary (\$28,743), travel expenses (\$4,707), shipping expenses (\$1,976), vehicle expenses (\$2,000), water-quality analytical costs (\$27,720), and water-quality supplies expenses (\$3,926).

Continuous gage height data were collected and streamflows were determined between July 1, 2014 and December 31, 2014 at the south fork of Filson Creek (USGS station number 05124982) and Keeley Creek above its confluence with Birch Lake (USGS station number 05125039), and between September 10 and December 31, 2014 at the St. Louis River near Skibo, MN gage (USGS station number 04015438). Continuous data at the St. Louis River near Skibo, MN gage was lost between April 22 and September 10 due to an inability to download the data from the data logger and pressure transducer at the site. The logger was sent back to the manufacturer to see if the gage height data could be recovered by specialists, but no data were recoverable. The data logger and pressure transducer were replaced with a new data logger and pressure transducer on September 10. Continuous streamflows will be estimated for this data gap from streamflows measured at nearby stream gages.

On-site streamflow measurements were done at the Keeley Creek gage on six days (June 24, July 21, August 6, September 16, September 29, and October 27), at the Filson Creek gage on six days (June 23, July 21, August 6, September 16, September 30, and October 27), and at the St. Louis River near Skibo, MN gage on six days (July 23, August 7, August 26, October 2, October 7, and November 24) between July 1, 2014 and December 31, 2014. These measurements were used to determine continuous stream discharge from continuous gage heights. Gage height is measured at each gage at 15-minute intervals, and the real-time streamflow and gage height data are available on the USGS National Water Information System web site (<http://waterdata.usgs.gov/mn/nwis/rt>). Environmental and Natural Resources Trust Funding for stream gage and streamflow monitoring work between July 1 and December 31, 2014 was \$14,881.

Water-quality data were examined to determine trends within and across the three watersheds. Dissolved ion concentrations generally were low in all of the water-quality samples collected in the three watersheds, with specific conductance values for all of the samples less than 110 $\mu\text{s}/\text{cm}$. Waters generally were neutral to slightly acidic, with pH values ranging from 5.0 to 8.3. The lower pH values were likely related to stream water interactions with acidic waters in attached or nearby wetlands and bogs or more mineralized parts of local bedrock. Sulfate concentrations in all of the water samples were relatively low, less than 3.0 mg/L. The range of sulfate concentrations varied little with flow conditions and among the three watersheds. Concentrations for the major cations (calcium, magnesium, sodium, iron, manganese, and dissolved organic carbon) were higher during periods of lower flows. Dissolved copper and nickel concentrations in all water samples were less than 10 and 6 $\mu\text{g}/\text{L}$, respectively, with the highest mean concentrations of both copper and nickel present in waters sampled from Filson Creek. Dissolved organic carbon concentrations were high in all three watersheds, with concentrations ranging from 17 to 46 mg/L. The streams and river likely obtain much of their dissolved organic carbon from interaction with waters from attached or nearby wetlands, which are abundant in all three watersheds.

Activity Status as of June 30, 2015:

Streamflow was measured and a sixth and seventh rounds of water-quality sampling were completed in April 20-24 and June 8-12, 2015, respectively, in the three study watersheds. During the sixth round of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 7 sites on the headwaters of the St. Louis River. During the seventh round of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 5 sites on the headwaters of the St. Louis River. High water levels and limited access to the sites during the week of June 8-12 prevented the collection of samples at 2 sites on the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during both trips at one site on Filson Creek and one site on Keeley Creek. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon,

alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). Environmental and Natural Resources Funding for water-quality sampling between January 1 and June 30, 2015 was \$22,201.25, including expenses for salary (\$8,500), travel expenses (\$3,641.50), shipping expenses (\$411.75), vehicle expenses (\$600), water-quality analytical costs (\$3,110), and water-quality supplies expenses (\$5,938).

Continuous gage height data were collected and streamflows were determined between Jan 1, 2015 and June 30, 2015 at the south fork of Filson Creek (USGS station number 05124982), Keeley Creek above its confluence with Birch Lake (USGS station number 05125039), and at the St. Louis River near Skibo, MN gage (USGS station number 04015438). On-site streamflow measurements were done at the Keeley Creek gage on four days (March 5, April 15, April 20, and May 19), at the Filson Creek gage on four days (March 5, April 16, April 21, and May 27), and at the St. Louis River near Skibo, MN gage on seven days (January 6, March 2, April 1, April 17, April 23, May 12, and June 22) between January 1 and June 30, 2015. These measurements were used to determine continuous stream discharge from continuous gage heights. Gage height is measured at each gage at 15-minute intervals, and the real-time streamflow and gage height data are available on the USGS National Water Information System web site (<http://waterdata.usgs.gov/mn/nwis/rt>). Environmental and Natural Resources Trust Funding for stream gage and streamflow monitoring work between Jan 1 and June 30, 2015 was \$25,200.

Activity Status as of December 31, 2015:

Streamflow was measured and the eighth, and final, round of water-quality sampling was completed in July 27-30, 2015 in the three study watersheds. During the eighth round of water-quality sampling, samples were collected at 9 sites on Filson Creek, 4 sites on Keeley Creek, and 7 sites on the headwaters of the St. Louis River. Water-quality sampling was done in cooperation with the U.S. Forest Service during the trip at one site on Filson Creek and one site on Keeley Creek. Water-quality samples were submitted to the USGS National Water Quality Laboratory and EMERSC Stable Isotope Laboratory for analyses for total and dissolved concentrations of major constituents (ions) and trace metals, dissolved organic carbon, alkalinity, sulfate-sulfur, oxygen, and hydrogen isotopes. All streamflow measurements and water-quality data were entered in USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). Environmental and Natural Resources Funding for water-quality sampling between July 1 and December 31, 2015 was \$10,569.94, including expenses for salary (\$8,441.00), travel expenses (\$997.19), shipping expenses (\$394.15), and water-quality supplies expenses (\$737.60).

Continuous gage height data were collected and streamflows were determined between July 1 and December 31, 2015 at the south fork of Filson Creek (USGS station number 05124982) and Keeley Creek above its confluence with Birch Lake (USGS station number 05125039), and at the St. Louis River near Skibo, MN gage (USGS station number 04015438). On-site streamflow measurements were done at the Keeley Creek gage on five days (July 7, August 3, October 6, November 23, and December 21), at the Filson Creek gage on five days (July 7, August 4, October 6, November 23, and December 21), and at the St. Louis River near Skibo, MN gage on five days (August 7, September 9, October 8, November 24, and December 29) between July 1 and December 31, 2015. Environmental and Natural Resources Trust Funding for stream gage and streamflow monitoring work between Jan 1 and June 30, 2015 was \$25,200.

Activity Status as of June 30, 2016:

Water-quality analyses were completed and data was interpreted. Metal and major constituent concentrations for water samples collected in the project were entered and stored in the USGS NWIS (<http://waterdata.usgs.gov/nwis>). Water qualities in the streams were found to be reflective of the bedrock and glacial geology. The water chemistry in Filson and Keeley Creeks generally is similar, which can be attributed to the similar geology within the watersheds. Bedrock is at or near the surface throughout the watersheds, 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 watershed. Opposed to Filson and Keeley, the St. Louis

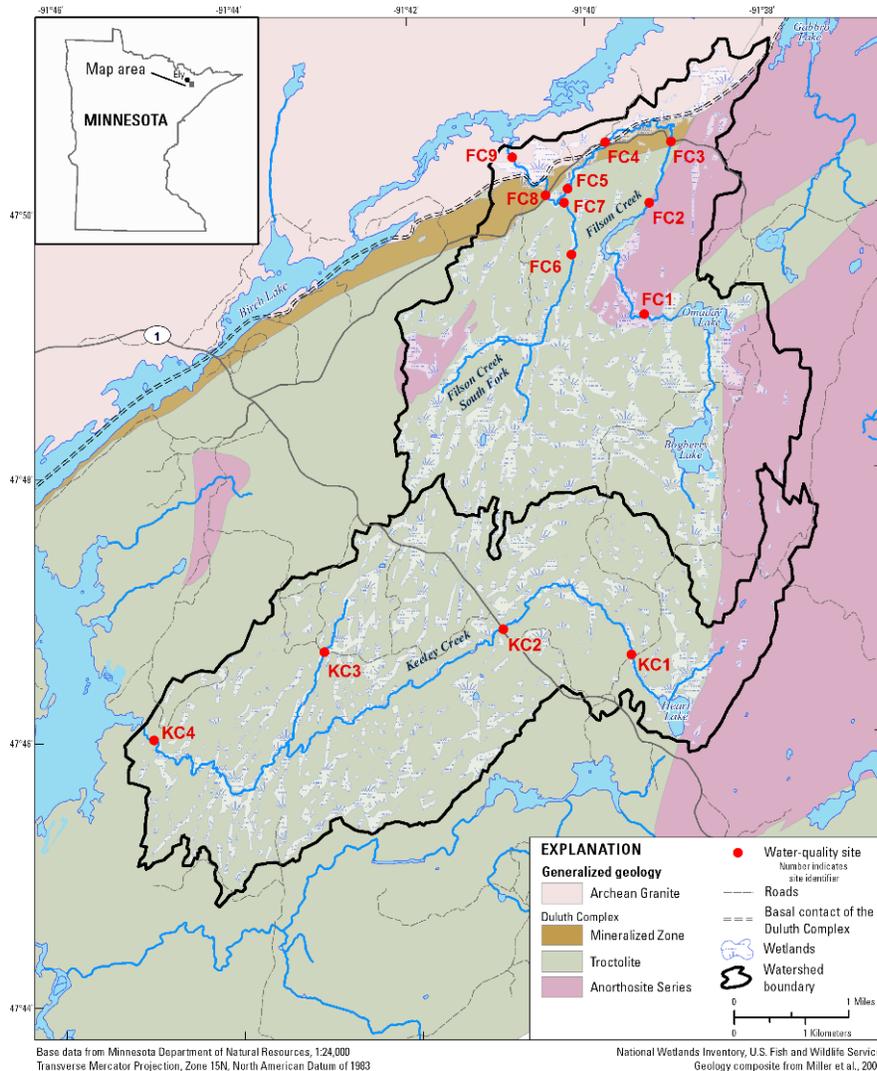


Fig. 6. Water-quality stream sites with bedrock geology, wetlands, and watershed boundaries, Filson Creek and Keeley Creek watersheds near Ely, Minnesota.

watershed was influenced by depositional, not erosive, glaciers resulting in a surface geology dominated by thick glacial sediment (generally greater than 100 feet). The St. Louis River is underlain by Duluth Complex intrusions, but the thick glacial sediment cover precludes any influence from underlying bedrock. This key difference in geology contributes to noticeable differences in St. Louis River water quality compared to Filson and Keeley Creek (e.g., higher ion concentrations). The higher concentrations in the St. Louis River likely reflects the larger percentage of groundwater contribution from the glacial sediments to the river.

Environmental and Natural Resources Funding for water-quality analyses between January 1 and June 30, 2016 was \$2,148.45.

Continuous stream stage data were collected and streamflows were

determined between January 1 and June 30, 2016 at the south fork of Filson Creek (USGS station number 05124982) and Keeley Creek above its confluence with Birch Lake (USGS station number 05125039), and at the St. Louis River near Skibo, MN gage (USGS station number 04015438). On-site streamflow measurements were done at the three streamflow gages on five days between January 1 and June 30, 2016. All continuous stream stage and flow data, and streamflow measurements were entered and are available in USGS National Water Information System (NWIS) at <http://waterdata.usgs.gov/nwis>.

Final Report Summary for Activity 2:

The information within this report has been finalized but remains subject to revision. It is being provided to meet the need for timely best science. The information is provided on the condition that neither the U.S. Geological Survey nor the U.S. Government shall be held liable for any damages resulting from the authorized or unauthorized use of this information.

Streamflow gages

One streamflow gage was maintained in each of the three watersheds during the study to continuously monitor stream stage at 15-minute intervals. The station names for the three gages were 1)the Filson Creek in SWSE Sec. 24, near Winton, MN gage (USGS site number 05124982, site FC5, fig. 6); 2)the Keeley Creek above mouth near Babbitt, MN gage (USGS site number 05125039, site KC4, fig. 6); and 3) the St. Louis River near Skibo, MN (USGS site number 04015438, site SLR3, fig. 7). Stream stage data collected at the three gages were compared to stage-streamflow relations established from streamflow measurements to determine streamflows at 15-minute intervals. The streamflow data was used to 1) assess changes in streamflow during the study; 2) estimate constituent loads during the water-quality sampling; and 3) estimate annual groundwater recharge and evapotranspiration in the three watersheds (**described under Activity 3 – Final Report Summary**).

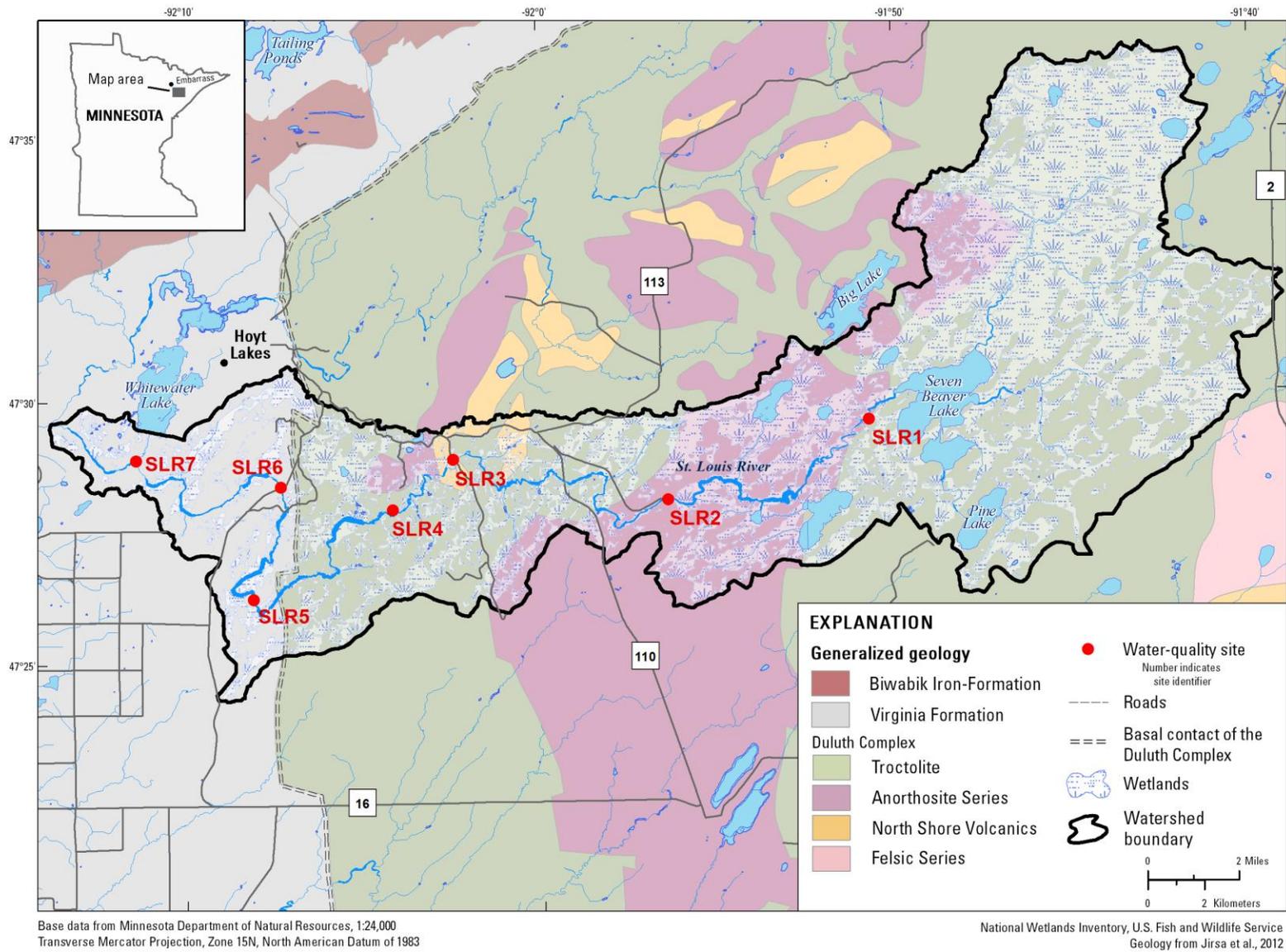
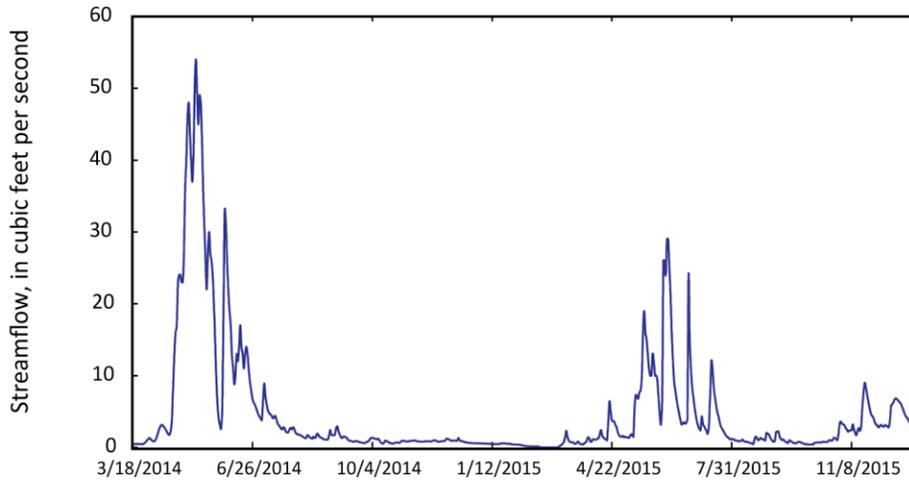
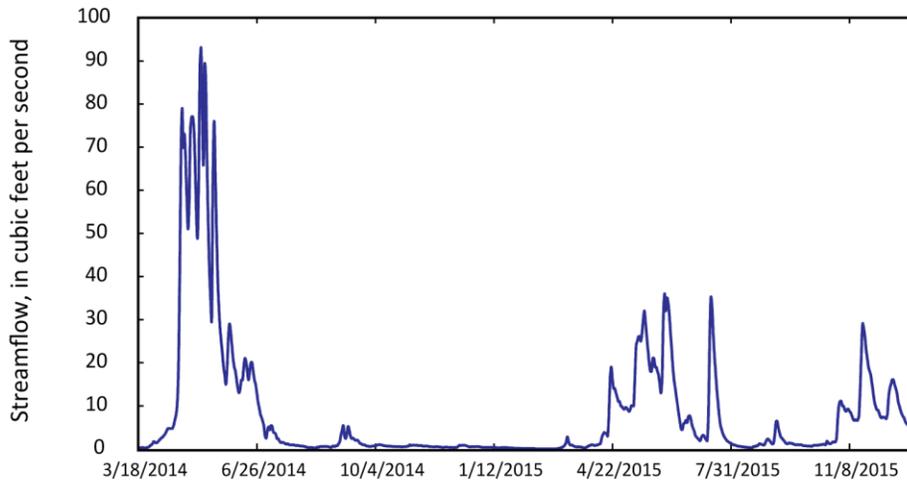


Fig 7. Water-quality stream sites with bedrock geology, wetlands, and watershed boundaries, St. Louis River watershed, near Hoyt Lakes, Minnesota.

A, Filson Creek in SWSE Sec. 24, Near Winton, MN (USGS Site Number 05124982) (FC5)



B, Keeley Creek above mouth near Babbitt, MN (USGS Site Number 05125039) (KC4)



C, St. Louis River near Skibo, MN (USGS Site Number 04015438) (SLR3)

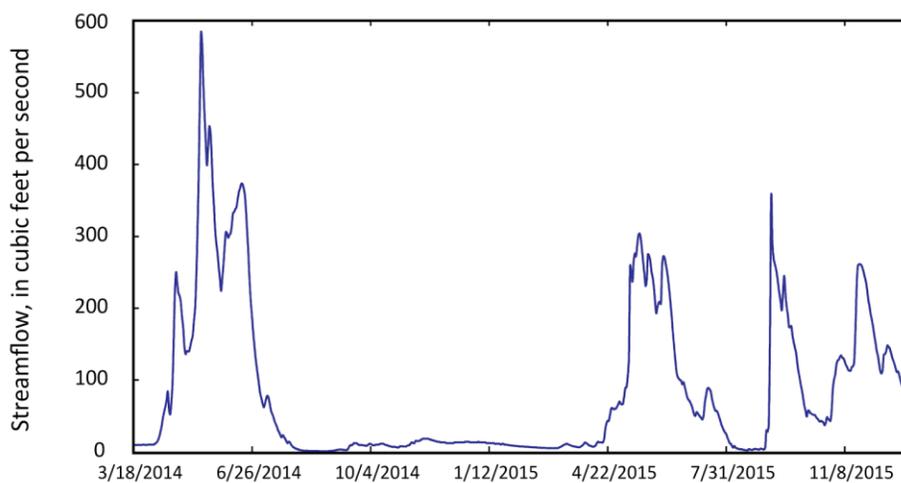


Fig. 8. Daily streamflow at continuous streamflow gage sites A, Filson Creek in SWSE Sec. 24, near Winton, MN (USGS Site Number 05124982) (FC5); B, Keeley Creek above mouth near Babbitt, MN (USGS Site Number 05125039) (KC4); C, St. Louis River near Skibo, MN (USGS Site Number 04015438) (SLR3), March 18, 2014 through December 31, 2015, northeastern Minnesota.

A wide range in streamflow occurred during the 2014-15 water-quality sampling period, allowing for a comparison of water quality during high, medium, and low streamflow. Peak streamflows in the three watersheds were higher in the spring of 2014 than in 2015 because snowmelt and spring precipitation were higher in 2014 (fig. 8). A period of relatively low flows (less than 10 ft³/sec in Filson and Keeley Creeks, less than 20 ft³/sec in the St. Louis River) occurred in the watersheds between the middle of July and November 2014. Flows in the St. Louis River, in general, are much higher than in Filson and Keeley Creeks (fig. 8) because the watershed for the St. Louis River is much larger than the watersheds for the creeks.

In addition to the continuous stage data collected at the three streamflow gages, a total of 201 instantaneous streamflow measurements were taken at surface-water-quality sample sites, coincident with water-quality sample collection or during periodic maintenance trips for the streamflow gage. All continuous streamflow data and streamflow measurements were entered and are available in USGS National Water Information System (NWIS) at <http://waterdata.usgs.gov/nwis>.

Surface-Water Quality

A total of 141 stream (river) samples and eight precipitation samples were collected from a total of 21 sites in the three watersheds from September 2013 to July 2015 (figs. 6, 7). Median concentrations of all measured elements in stream waters are provided in table 4.

Stream (river) waters are fairly dilute with specific conductance ranging from 24 to 110 μ S/cm in all watersheds. Specific conductance values above 100 μ S/cm were observed at KC3 (fig. 6), a tributary site of Keeley Creek that is most likely under the influence of brackish groundwater. All three watersheds have relatively neutral pH, with values ranging from 4.4 to 8.7, however, median pH in Filson and Keeley Creeks (6.1 and 6.2, respectively; table 4) were slightly lower compared to the median pH in St. Louis River (6.9). Dissolved organic carbon is consistently high (median concentrations around 26 mg/L) and similar across all three watersheds. Waters in all three watersheds have a low buffering capacity, with alkalinity ranging from approximately 3 to 40 mg/L as CaCO₃.

Major ion concentrations followed the general pattern of the lowest concentrations in Filson Creek, the highest concentrations in St. Louis River, and concentrations in Keeley Creek falling between the other watersheds (fig. 9). Sulfate concentrations were consistently low (less than 4 mg/L) across all three watersheds. Trace metal and element concentrations were generally similar in Filson and Keeley watersheds, with concentrations in the St. Louis deviating slightly, depending on the constituent. Slightly higher concentrations of Fe and Mn were observed in the St. Louis compared to Filson and Keeley Creeks. The most distinguishable difference in trace metal concentrations among the watersheds is in dissolved Cu and Ni (explained below) which are elevated in Filson Creek compared to the other watersheds (fig. 9). Trace metals concentrations in surface-water samples were all below human-health guidelines and aquatic life standards established by the state of Minnesota and the U.S. Environmental Protection Agency (table 4) (Minnesota Department of Health, 2017; Minnesota Office of the Revisor of Statutes, 2017).

Table 4. Median concentrations of measured physical parameters, organic carbon, trace metals, and elements in surface-water samples collected in Filson, Keeley, and St. Louis watersheds during September 2013 to October 2015 and northeastern Minnesota during 1976-1977.

µS/cm, microsiemens per centimeter; --, no data; mg/L, milligram per liter; CaCO ₃ , calcium carbonate; µg/L, micrograms per liter										
Parameter	Filson		Keeley		StLouis		Northeastern Minnesota ¹	Minnesota water quality chronic standard for aquatic life in class 2 waters of Lake Superior Basin ³	Minnesota human health-based water guidance - chronic ^{3,4}	U.S. federal drinking water standards ⁴
	Total	Dissolved	Total	Dissolved	Total	Dissolved	Dissolved	Total	Total	Total
Physical Parameters										
Specific conductance (µS/cm)	30	--	47	--	48	--	55	--	--	--
Dissolved oxygen (mg/L)	7.6	--	6.8	--	8.3	--	--	--	--	--
pH	6.1	--	6.2	--	6.9	--	6.9	--	--	--
Alkalinity (mg/L as CaCO ₃)	--	7.1	--	8.1	--	16	19	--	--	--
Organic Carbon (mg/L)	29	26	27	25	28	26	15 ²	--	--	--
Major Ions (mg/L)										
Calcium	--	2.9	--	3.2	--	4.8	6	--	--	--
Magnesium	--	2.1	--	2.3	--	3.6	3	--	--	--
Sodium	--	1.1	--	2.4	--	1.5	1.6	--	--	--
Potassium	--	0.18	--	0.17	--	0.31	0.6	--	--	--
Chloride	--	0.26	--	1.6	--	0.44	1.6	--	--	--
Sulfate	--	0.84	--	1.2	--	1.3	--	--	--	--
Fluoride	--	0.03	--	0.03	--	0.07	0.18	--	--	4,000 ⁵
Silica	--	5.3	--	5.5	--	4	--	--	--	--
Trace Metals (µg/L)										
Aluminum	--	205	--	240	--	100	90	--	--	--
Chromium	0.59	<0.6	0.66	<0.6	0.4	<0.6	--	11 ⁶	100 ⁶	--
Cobalt	--	0.68	--	0.59	--	0.33	0.4	--	--	--
Copper	4.4	3.65	1.4	1.1	0.83	<0.8	1.3	52 ⁷	--	1,300 ⁸
Iron	1200	770	985	760	1300	915	560	--	--	--
Lead	0.29	0.21	0.24	0.19	0.39	0.28	0.5	--	--	15 ⁸
Nickel	3.4	3.2	2.3	2.2	1.1	1.1	1	29 ⁷	100	--
Strontium	--	13	--	14	--	20	--	--	--	4,000 ¹⁰
Titanium	2.1	1.7	2	1.6	2.8	1.8	--	--	--	--
Zinc	2.6	2.4	2.5	2.4	2.8	<2	2	67 ⁷	2,000	2,000 ¹⁰
Trace Elements (µg/L)										
Arsenic	0.53	0.47	0.51	0.41	0.82	0.82	0.8	148	2	10 ⁵
Barium	--	5.05	--	4.5	--	5.1	--	--	2,000	2,000 ⁵
Beryllium	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	--	--	0.08 ⁹	4 ⁵
Boron	--	4	--	4	--	7.9	--	--	1,000	--
Manganese	47	33	30	30	84	50	35	--	100	--
Lithium	--	0.33	--	0.27	--	0.58	--	--	--	--
Selenium	<0.1	0.11	<0.1	0.11	<0.1	0.13	--	--	30	50 ⁵
Vanadium	<0.6	0.43	<0.6	0.43	0.9	0.58	--	--	50	--
1 - Median concentration reported from Thingvold and others (1979).										
2 - Median concentration reported is total organic carbon.										
3 - Minnesota Office of the Revisor of Statutes, 2017 (https://www.revisor.leg.state.mn.us/mles/?id=7052.0100)										
4 - Minnesota Department of Health, 2017 (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										
5 - U.S. Environmental Protection Agency (EPA) Maximum Contaminant Level (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										
6 - Standard for Chromium VI										
7 - standard for total hardness of 50 mg/L as calcium carbonate (standards vary with total hardness (total calcium and magnesium concentration)).										
8 - U.S. Environmental Protection Agency (EPA) Maximum Contaminant Level - action level at tap (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										
9 - standard for cancer										
10 - U.S. Environmental Protection Agency (EPA) Lowest Health Advisory (http://www.health.state.mn.us/divs/eh/risk/guidance/water/guidance.htm#s)										

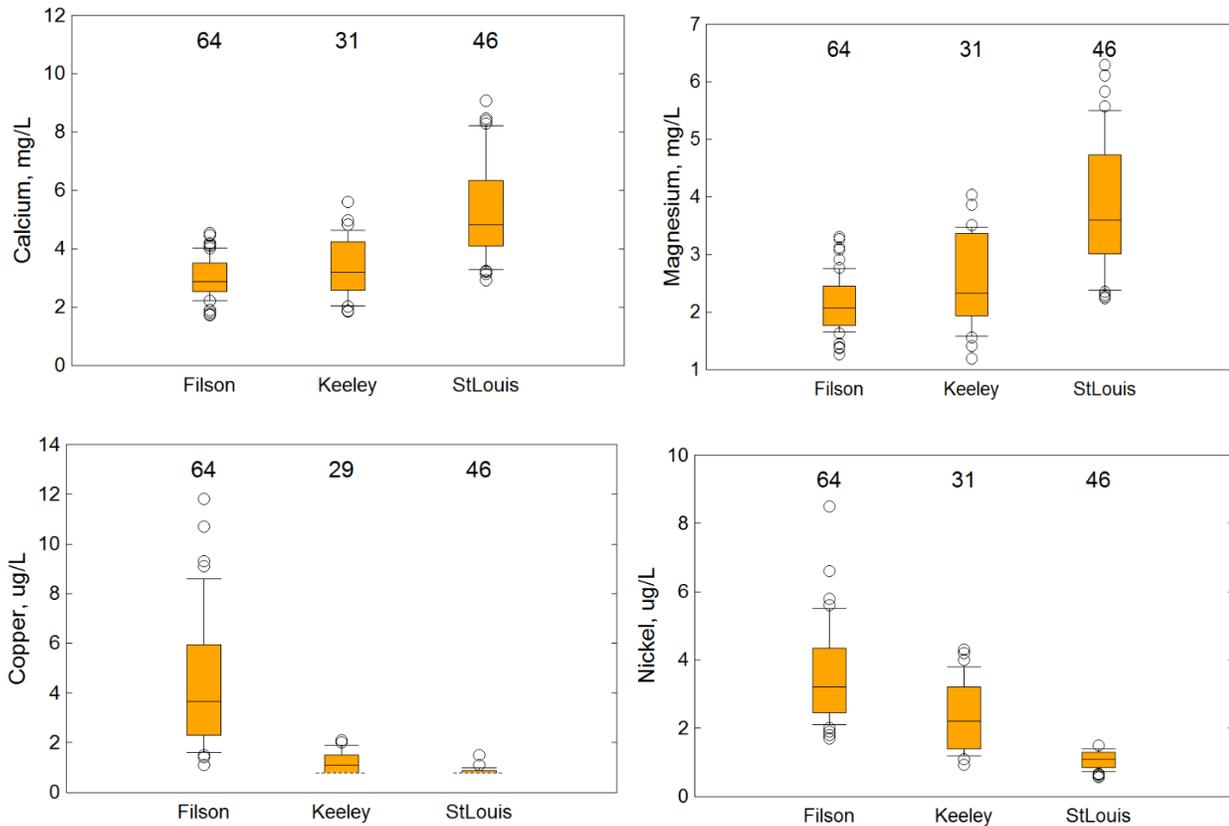


Fig. 9. Boxplot summaries of calcium, magnesium, copper, and nickel concentrations in Filson Creek, Keeley Creek, and St. Louis River, 2013-2015. Numbers above boxes indicate number of samples. Lines in middle of boxes indicate median, with the bottom and top of the boxes representing 25th and 75th percentiles and whiskers extending to 10th and 90th percentiles. Dashed line represents the laboratory reporting limit. mg/L, milligrams per liter; ug/L, micrograms per liter

Influence of Bedrock Geology on Water Quality

The similar water chemistry in Filson and Keeley Creeks generally can be attributed to the similar geology (igneous bedrocks of the Duluth Complex) within the watersheds. Bedrock is at or near the surface throughout the watersheds, 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 watershed. Opposed to Filson and Keeley, the St. Louis watershed was influenced by depositional, not erosive, glaciers resulting in a surface geology dominated by thick glacial sediment (generally greater than 100 feet). This key difference in geology contributes to noticeable differences in St. Louis River water quality compared to Filson and Keeley Creek (e.g., higher ion concentrations). The higher concentrations in the St. Louis River likely reflects the larger percentage of groundwater contribution from the glacial sediments to the river.

Although Filson and Keeley watersheds share similar bedrock geology, the Filson Creek watershed contains Cu-Ni-Platinum-Group-Elements (PGE) sulfide mineralization (Spruce Road deposit) exposed along the basal contact of the Duluth Complex. Similar Cu-Ni sulfide deposits occur only at great depth in the Keeley Creek watershed. The influence of the Spruce Road 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 Keeley Creek concentrations (figs. 10, 11). A slight downstream increase in Ni concentration occurs in Keeley Creek, between KC1 and KC2 (fig. 11), whereas the Cu concentrations remain relatively low (below detection limit of 1.6 $\mu\text{g/L}$). This difference can be attributed to the presence of olivine-rich bedrock that crops out along the trace of Keeley Creek between site KC1 and KC2. Olivine, an igneous silicate mineral, can commonly incorporate Ni into its molecular structure. Olivine is also the first silicate mineral to succumb to the effects of chemical weathering, thereby freeing-up Ni to water. Similar patterns (enriched Ni without commensurate Cu enrichment) are also

noted for soil and streambed sediment Cu and Ni concentrations within the Keeley watershed, attributed to presence of olivine in the bedrock rather than sulfide. Surface water in the St. Louis River has low Cu and Ni concentrations. The St. Louis River is also underlain by Duluth Complex intrusions, but the thick glacial sediment cover precludes any influence from underlying bedrock. In fact, Cu concentrations were below the detection limit in 69% of all samples collected from the St. Louis River.

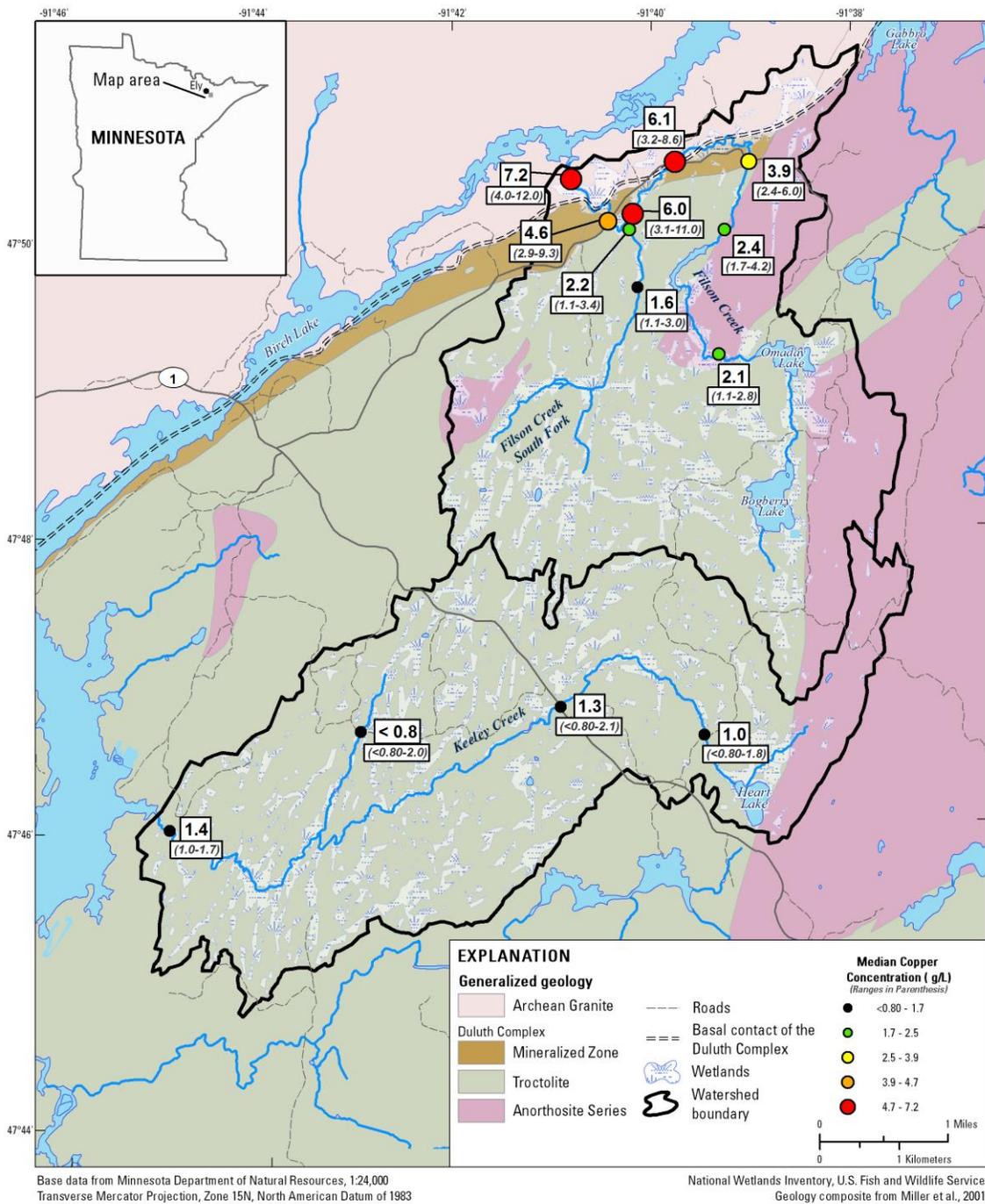
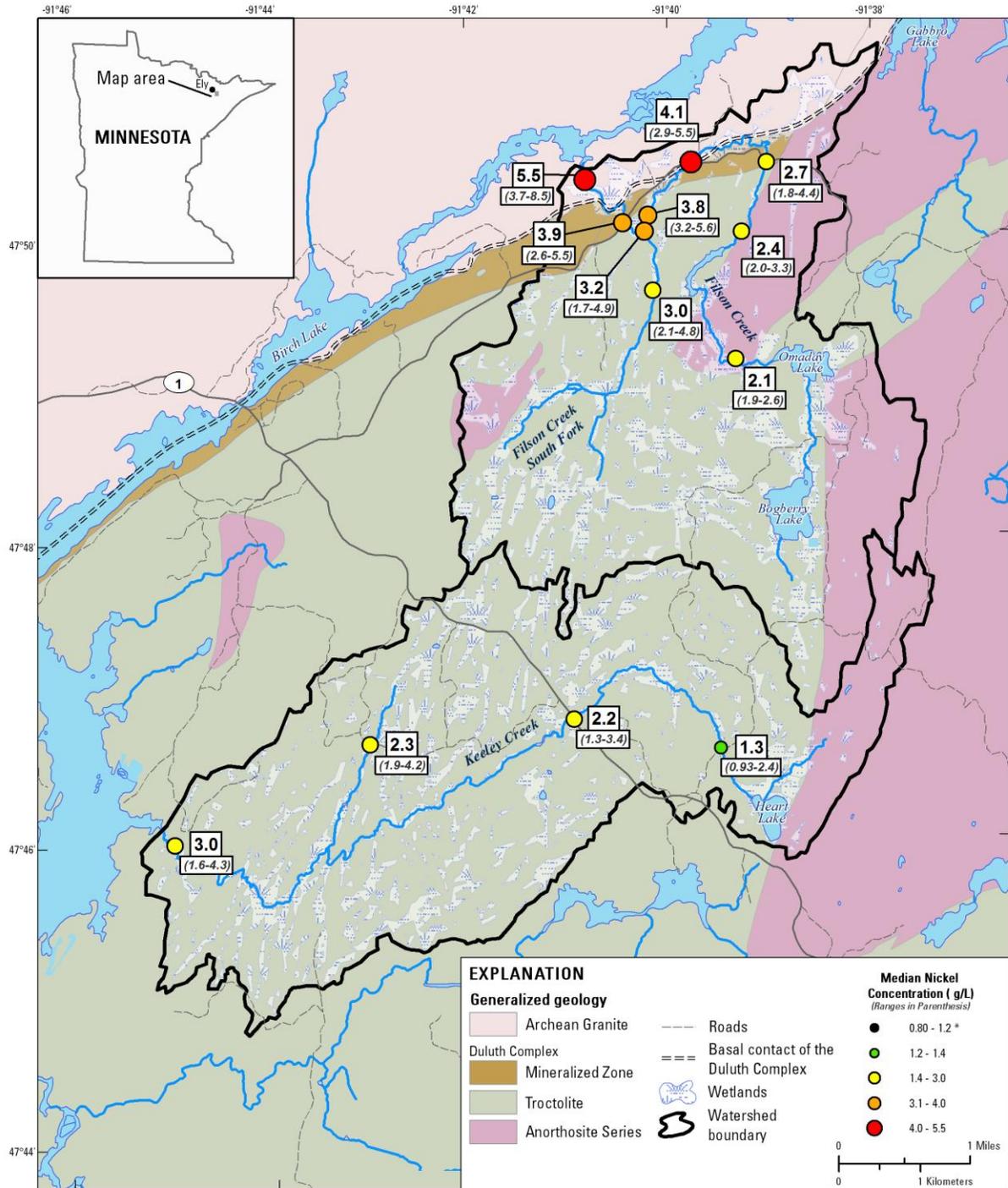


Fig 10. Median copper concentrations in stream water with bedrock geology, wetlands, and watershed boundaries, Filson Creek and Keeley Creek watersheds, Minnesota, September 2013 - July 2015.



Base data from Minnesota Department of Natural Resources, 1:24,000
 Transverse Mercator Projection, Zone 15N, North American Datum of 1983
 * Lower concentrations only observed in St. Louis watershed

National Wetlands Inventory, U.S. Fish and Wildlife Service
 Geology composite from Miller et al., 2001

Fig 11. Median Nickel concentrations in stream water with bedrock geology, wetlands, and watershed boundaries, Filson Creek and Keeley Creek watersheds, Minnesota, September 2013 - July 2015.

Comparison of Recent Water Quality Data with the Cu-Ni Regional Study

A regional study conducted during 1975-1977 measured major elements and trace metals in Northeastern Minnesota surface and ground waters (Thingvold and others, 1979), including one site each on Filson and Keeley Creeks. Median 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 (Thingvold and others, 1979) (table 4). Median concentrations observed in surface water of the St. Louis River generally were more similar to the regional median concentrations, compared to Filson and Keeley Creeks. Specifically, median Cu and Ni concentrations in Keeley Creek and St. Louis River were more similar to the regional median, whereas median concentrations in Filson Creek were higher reflecting the influence of the mineralization in the watershed. Similar to observations obtained during this study, Thingvold and others (1979) observed increasing Cu and Ni concentrations moving downstream in Filson Creek. The average Ni concentrations in 1979 near the mouth of Filson Creek were 3-5 µg/L, similar to concentrations observed during the current study. Comparison of the data obtained from the two different studies indicates that the chemical composition of the surface waters in the three study watersheds (and specifically, Filson) has not changed significantly under natural (i.e. no active mining) conditions.

Loads

Background median, maximum, and minimum instantaneous loads for Cu, Ni, and S in the three watersheds for the water-quality sampling events are provided in table 5. The instantaneous loads were determined for the furthest downgradient water-quality site in each watershed for each water-quality sampling trip by multiplying the concentrations in the water-quality samples by the daily streamflows in the synthetic hydrographs. Median, maximum, and minimum values were determined from these instantaneous loads.

Cu and Ni loads generally are highest in Filson Creek and the St. Louis River, and lowest in Keeley Creek (table 5). This general trend is to be expected because 1) Cu-Ni sulfide mineralization in bedrock of the Filson Creek watershed ; 2) copper concentrations are the highest in Filson Creek (fig. 9, table 4); and 3) streamflows are the highest in the St. Louis River (fig. 8). The mean and maximum sulfate instantaneous loads are greatest in the St. Louis River because the streamflows are the highest (fig. 8). However, median sulfate concentrations generally are similar between the three watersheds (table 4). When normalizing these loads to drainage area, the Filson Creek loads are the highest, with lower values for Keeley Creek and St. Louis River watersheds (table 5).

References

Minnesota Department of Health, 2017, Comparison of state water guidance and federal drinking water standards, accessed March 30, 2017, at <http://www.health.state.mn.us/divs/eh/risk/guidance/waterguidance.html>.

Minnesota Office of the Revisor of Statutes, 2017, 2008 Minnesota administrative rules—Rule 7052.0100 water quality standards, subpart. 1: St. Paul, Minn., Minnesota Office of the Revisor of Statutes Web page, accessed March 30, 2017, at <https://www.revisor.leg.state.mn.us/rules/?id=7052.0100>.

Thingvold, D, Eger, P., Hewett, M., Honetschlager, B., Lapakko, K., and Mustalish, R., 1979, Water Resources, in Minnesota regional copper-nickel study, 1976-1979, Minnesota Environmental Quality Board, v. 3, no. 4, 217 p.

Table 5. Background copper, nickel, and sulfate loads determined for Filson Creek, Keeley Creek, and St. Louis River, Minnesota, 2014-15.

USGS Station Name	USGS Station Number	Mean Streamflow (ft ³ /s)	Constituent Loads								
			Copper (g/day)			Nickel (g/day)			Sulfate (kg/day)		
			Minimum	Median	Maximum	Minimum	Median	Maximum	Minimum	Median	Maximum
Filson Creek above Mouth Near Winton, MN	5124992	17.0	20	200	1300	18	120	700	3.1	44	187
Keeley Creek above mouth near Babbitt, MN	5125039	17.5	1.3	66	200	4.3	74	220	0.37	44	250
St. Louis River, Moose Line Rd., Hoyt Lakes, MN	4015444	130	70	420	1100	7.6	94	1600	7.1	205	1200
Drainage Area (mi ²)			Copper (g/day/mi ²)			Nickel (g/day/mi ²)			Sulfate (kg/day/mi ²)		
			Minimum	Median	Maximum	Minimum	Median	Maximum	Minimum	Median	Maximum
Filson Creek above Mouth Near Winton, MN	5124992	10	2.0	20	130	1.8	12	70	0.3	4.4	19
Keeley Creek above mouth near Babbitt, MN	5125039	24	0.05	2.8	8.3	0.18	3.1	9.2	0.02	1.8	10
St. Louis River, Moose Line Rd., Hoyt Lakes, MN	4015444	135	0.52	3.1	8.1	0.06	0.70	12	0.05	1.5	8.9

ACTIVITY 3: Assess hydrologic conditions prior to potential future mine development. Report all findings.

Description: Existing hydrologic data and streamflow and water-quality data collected during Activity 2 will be used to develop a conceptual hydrologic model for each of the three watersheds between September 2014 and September 2015. The type of conceptual model (i.e., watershed rainfall/runoff model, groundwater-flow model) chosen to represent each watershed will be based on: 1) the main factors controlling stream water chemistry in each of the watersheds determined from the water-quality data and streamflow data collected during this study, and 2) the ability of the model to represent potential water-quality impacts from different mine settings (i.e., surface mine versus underground mine). Once constructed, these conceptual models will be used to assess hydrologic settings present in the watersheds prior to mine development and to assess potential mining-related impacts on water quality. A final interpretive report will be written, summarizing all collected data, interpretations, and hydrologic modeling results, and describing the regional geochemical and hydrological landscape.

Summary Budget Information for Activity 3:

ENRTF Budget: \$ 211,882
Amount Spent: \$ 211,882
Balance: \$ 0

Activity Completion Date:

Outcome	Completion Date	Budget
1. Develop conceptual hydrologic models – 3 watersheds	12/2015	\$ 23,598
2. Develop hydrologic scenarios of various mining activities – 3 watersheds	5/2016	\$ 90,419
3. Preparation of final interpretive report of all data and hydrologic modeling results	12/2016	\$ 97,865

Activity Status as of December 31, 2013:

Geographic Information System (GIS) coverages outlining hydrologic, geologic, and other physical characteristics for the three watersheds (Filson Creek, Keeley Creek, headwaters of the St. Louis River) were constructed in ArcMap 10. LiDAR data for the study sites were also downloaded. The hydrologic models will be developed using these coverages. Funding for the construction of the GIS coverages (salary = \$13,700) was provided by the U.S. Geological Survey Midwest Region Mining Initiative.

Activity Status as of June 30, 2014:

Additional Geographic Information System (GIS) coverages outlining hydrologic, geologic, and other physical characteristics for the three watersheds (Filson Creek, Keeley Creek, headwaters of the St. Louis River) were constructed in ArcMap 10. These coverages include surficial and bedrock geology, hydrology, LiDAR, and historic geochemical data from MGS, DNR, and USGS data bases. The hydrologic models will be developed using these coverages. Funding for the construction of the GIS coverages (salary = \$13,700) was provided by the U.S. Geological Survey Midwest Region Mining Initiative. Environmental and Natural Resources Trust Funding for this work between January 1 – June 30, 2014 was \$7,098.

Activity Status as of December 31, 2014:

Water-quality data were analyzed to assess stream water interactions with wetlands and groundwater. Dissolved organic carbon concentrations were compared to the percentage and topographic location of wetlands in the three watersheds to determine the relations between wetlands and water quality. Geographic Information System (GIS) coverages outlining hydrologic, geologic, and other physical characteristics for the three watersheds (Filson Creek, Keeley Creek, headwaters of the St. Louis River) were updated with lineament assessments in ArcMap 10. The lineament assessment identified potential features in the shallow bedrock in Filson and Keeley Creek watersheds, and will be used with water-quality data to identify where groundwater flow may be prevalent in the two watersheds. Data interpretation and hydrologic models will be developed using these coverages. Base maps have been compiled into a GIS in ArcMap. These coverages include surficial

and bedrock geology, hydrology, LiDAR, and historic geochemical data from MGS, DNR, and USGS data bases. Environmental and Natural Resources Trust Funding for this work between July 1 – December 31, 2014 was \$12,471.

Activity Status as of June 30, 2015:

Hydrologic data were used to estimate annual water balances for Filson Creek, Keeley Creek, and headwaters of the St. Louis River watersheds. Historical and recent streamflow records were analyzed to determine total annual runoff and estimate groundwater recharge to the three project watersheds. Annual and 30-year normal precipitation data were compiled for precipitation stations located in Tower, Embarrass, Isabella, and Babbitt, MN and used with the total annual runoff and groundwater recharge estimates to produce estimates of annual evapotranspiration. These annual evapotranspiration estimates were similar to estimates determined in other USGS and other water-balance studies for these and nearby watersheds.

Water-quality model simulations for parts of the Filson Creek watershed where the Spruce Road copper-nickel deposits is exposed at or near the land surface were constructed and run to assess water-quality conditions and chemical processes that may be controlling trace metal transport occurring in the creek. Equilibrium water-quality models (PHREEQC and Visual MINTEQ) were used to evaluate equilibrium chemistry at water-quality sampling sites in Filson Creek, assessing the effects of dissolved iron and organic carbon concentrations on trace metal concentrations. Chemical transport simulations using a USGS water-quality transport model (OTIS) were constructed and will be used with results from the equilibrium water-quality simulations to assess transport of metals between water-quality sampling sites.

Environmental and Natural Resources Trust Funding for work under Activity 3 between January 1 – June 30, 2015 was \$26,138.56.

Activity Status as of December 31, 2015:

Water-quality data from the first seven water-quality sampling trips were analyzed by Sarah Elliott and Perry Jones, and Daniel Morel reviewed water-quality data in the NWIS database. Water-quality model simulations for parts of the Filson Creek watershed where the Spruce Road copper-nickel deposits is exposed at or near the land surface were updated by Joshua Messenger and Sarah Elliott and run to assess water-quality conditions and chemical processes that may be controlling trace metal transport occurring in the creek. Equilibrium water-quality models (PHREEQC and Visual MINTEQ) were used to evaluate equilibrium chemistry at water-quality sampling sites in Filson Creek, assessing the effects of dissolved iron and organic carbon concentrations on trace metal concentrations. Chemical transport simulations using a USGS water-quality transport model (OTIS) were constructed and were used with results from the equilibrium water-quality simulations to assess transport of metals between water-quality sampling sites.

Synthetic hydrographs were developed by Aliesha Diekoff for each of the water-quality sampling sites in the three study watersheds using streamflow data collected at the three continuous stream gages operated in the three study watersheds. Estimated streamflows from synthetic hydrographs in Filson Creek were used in the Visual MINTEQ simulations for evaluating equilibrium chemistry at water-quality sampling sites.

A potassium-bromide tracer test was conducted between September 11 and 17 in a part of Filson Creek where mineralized bedrock is exposed at the land surface. The objective of the tracer test was to determine stream storage and dissolved metal movement in the creek. Water-quality samples were collected by USGS and NRRI staff, and analyzed for bromide, trace metal, major constituent, iron species and dissolved organic carbon concentrations by USGS water-quality laboratories. Results from the tracer test are being used to calibrate the OTIS model simulations of Filson Creek. Funding from the USGS Toxics Program were used to conduct and analyze the tracer test water-quality and hydrologic data.

Environmental and Natural Resources Trust Funding for work under Activity 3 between July 1 – December 31, 2015 was \$8,433.91.

Activity Status as of June 30, 2016:

The conceptual hydrology of the three watersheds was completed, producing annual evapotranspiration and groundwater recharge estimates for the study period (2014-15) using streamflow and precipitation data. Synthetic hydrographs for each of the ungaged, water-quality sampling sites were developed and used to estimate instantaneous constituent loads at the water-quality sampling sites.

Water-quality analyses of water samples collected during the potassium-bromide (KBr) tracer test conducted in Filson Creek in September 2015 was completed. This water-quality data was interpreted to gain a better understanding of stream channel morphology streamflow dynamics, and water-quality over sulfide-bearing bedrock (the mineralized zone). Water-quality results from the tracer test and synthetic hydrographs are being used in water-quality models to assess factors controlling stream water-quality, under present conditions and higher metal concentrations that might be associated with potential mining in the watershed.

A surficial geology map for the St. Louis River watershed was constructed using a glacial landform-sediment association model to interpret landforms visible in a high-resolution 1-meter digital elevation model (DEM) derived from light detection and ranging (LiDAR) technology. Mapping was done by on-screen digitizing directly into a geographical information system (GIS). Interpretations were checked in the field at various locations, and compared to prior mapping in the area done by Hobbs and Goebel (1982), Lehr and Hobbs (1992), Lehr (2000), and Jennings and Reynolds, (2005). The map will be included in the U.S. Geological Survey Scientific Investigations Report. Environmental and Natural Resources Trust Funding for the surficial geology map work between January 1 and June 30, 2016 was \$7,798.15.

A draft of the U.S. Geological Survey Scientific Investigations Report is almost completed for colleague and USGS review. The report will 1) summarize analytical results; 2) present interpretations of bedrock, soil, streambed sediment, and water-quality data; and 3) describe conceptual hydrology for the three watersheds. Figure and tables for the report are completed. The report will be completed for review by July 31, 2016, with an on-line version of the report completed by December 31, 2016.

Environmental and Natural Resources Trust Funding for work under Activity 3 between January 1 and June 30, 2016 was \$ 61,930. This amount includes the \$7,798.15 used to construct the surficial geology map.

Final Report Summary for Activity 3:

The information within this report has been finalized but remains subject to revision. It is being provided to meet the need for timely best science. The information is provided on the condition that neither the U.S. Geological Survey nor the U.S. Government shall be held liable for any damages resulting from the authorized or unauthorized use of this information.

Conceptual hydrology of the three watersheds

The conceptual hydrology of a watershed is a general representation of the water budgets and hydrologic systems of the watershed being studied. The annual water budgets for each watershed upgradient of the streamflow gages was assumed to consist of precipitation as the input to the watershed, and streamflow and evapotranspiration were the main output from the watershed. All groundwater flow and surface-water runoff were assumed to discharge to the creek or river upgradient of the streamflow gage, and therefore were accounted for in the measured streamflow.

In this study, four approaches were taken to gain an understanding of the hydrology of the three watersheds: (1) measure streamflow in each of the watersheds (described in Activity 2 – Final Report Summary), (2) estimate annual evapotranspiration (ET), (3) estimate annual groundwater recharge, and (4) develop synthetic hydrographs at each of the sampling sites over the two years of monitoring using the continuous streamflow data. Evapotranspiration is the amount of water lost from a watershed through evaporation and plant transpiration, which is an important component of a watershed's water budget. Although not used in the annual water budgets, groundwater-recharge estimates were determined to gain an understanding of how much of the annual precipitation might be lost to groundwater recharge. Synthetic hydrographs of daily mean streamflow were for seventeen ungaged, water-quality sampling sites to estimate constituent loads for the sampling dates (see Activity 2 – Final Report Summary). A potassium-bromide (KBr) tracer test also was conducted in Filson Creek to gain a better understanding of stream channel morphology streamflow dynamics, and water quality over the mineralized zone between FC3 and FC4 (fig. 10, 11).

Evapotranspiration (ET)

Annual ET estimates for the three watersheds generally were similar between the watersheds, but varied from year to year based on changes in annual precipitation. Annual ET estimates for the three watersheds in 2014 and 2015 ranged from 16.2 to 23.9 inches, with a mean estimate of 19.4 inches (table 6). This mean annual estimate is similar to annual ET estimates made by Siegel and Ericson (1980) for the Kawishiwi River watershed (18.1 inches), Ericson and others (1976) for the Rainy Lake watershed (18.3 inches), and Nichols and Verry (2001) for watersheds at the Marcell experimental forest north of Grand Rapids, Minnesota (20.4 inches). The 2015 estimated ET for both Filson Creek and Keeley Creek watersheds were larger than the estimates for 2014 likely because the total 2015 precipitation at the Tower weather station, used to determine the annual ET, was higher than the actual total 2015 precipitation that fell in the Filson Creek and Keeley Creek watersheds. Lower streamflows were measured in 2015 than in 2014 in both watersheds, indicating that precipitation was lower in 2015 in both watersheds. The estimated fraction of annual precipitation lost to ET for the three watersheds for 2014-15 ranged from 0.61 to 0.76, with a mean estimate of 0.66.

Annual ET estimates for 2014 and 2015 were within ranges for annual ET estimates determined for Filson Creek watershed during 1975-84 and St. Louis River watershed during 1943-86 (tables 3, 4). Annual estimates for 1975-84 for Filson Creek watershed ranged from 11.8 to 28.3 inches, with a mean estimate of 18.3 inches (table 6), and annual estimates for 1943-86 for St. Louis River watershed ranged from 11.0 to 31.5 inches, with a mean estimate of 18.8 inches (table 7). The larger ranges in ET estimates typically occurs with longer year of record because larger variety of climatic conditions occurs over the longer records.

Groundwater Recharge

Annual groundwater-recharge estimates for the three watersheds were similar, varying with annual precipitation. Annual groundwater-recharge estimates in the three watersheds from 2014 and 2015 ranged from 6.6 to 12.0 inches, with a mean value of 9.0 inches. The range of estimates for the three watersheds generally is similar to the range of groundwater recharge estimates (7.9 to 11.8 in) estimated by Delin and others (2007) for the area covering the Filson Creek, Keeley Creek, and St. Louis River watersheds. The 2015 estimated ET for both Filson Creek and Keeley Creek watersheds were smaller than the estimates for 2014 because the total streamflows in 2015 were lower than in 2014 (fig. 8). The estimated fraction of annual precipitation lost to groundwater recharge for the three watersheds for 2014-15 ranged from 0.21 to 0.42, with a mean estimate of 0.31.

Annual groundwater-recharge estimates for 2014 and 2015 were similar to annual groundwater-recharge estimates determined for Filson Creek watershed during 1975-84 and St. Louis River watershed during 1943-86 (tables 3,4). Annual groundwater-recharge estimates for 1975-84 for Filson Creek watershed ranged from 6.2 to 12.2 inches, with a mean estimate of 9.2 inches (table 6), and annual estimates for 1943-86 for St. Louis River

Table 6. Annual groundwater recharge and evapotranspiration estimates for Filson Creek, Keeley Creek, and St. Louis watersheds, Minnesota, 1975-2015.

Year	Groundwater Recharge Estimates (in/yr.)	Precipitation (in/yr.)	Groundwater Recharge/Precipitation Ratio	Streamflow (in/yr.)	Evapotranspiration Estimates (in/yr.)	Evapotranspiration/Precipitation Ratio
Filson Creek^{1,2}						
1975	7.7	33.05	0.23	9.2	23.8	0.72
1976	6.6	19.75	0.33	8.0	11.8	0.60
1977	12.2	41.37	0.30	13.1	28.3	0.68
1978	9.5	30.55	0.31	10.8	19.8	0.65
1979	10.4	26.15	0.40	10.8	15.3	0.59
1980	9.5	27.89	0.34	12.5	15.4	0.55
1981	9.8	30.64	0.32	11.0	19.7	0.64
1982	11.2	32.33	0.35	13.4	19.0	0.59
1983	9.0	27.04	0.33	11.4	15.6	0.58
1984	6.2	23.56	0.26	8.0	15.5	0.66
1975-84 Mean	9.2	29.23	0.32	10.8	18.4	0.63
2014	12.0	28.79	0.42	12.6	16.2	0.56
2015	6.6	31.26	0.21	7.4	23.9	0.76
2014-15 Mean	9.3	30.03	0.31	10.0	20.1	0.66
Keeley Creek³						
2014	10.5	28.79	0.36	11.2	17.6	0.61
2015	7.1	31.26	0.23	8.1	23.2	0.74
2014-15 Mean	8.8	30.03	0.30	9.6	20.4	0.68
St. Louis River⁴						
2012	11.7	31.71	0.37	12.8	19.0	0.60
2013	9.1	28.71	0.32	11.7	17.0	0.59
2014	7.6	25.96	0.29	9.2	16.8	0.65
2015	10.3	30.17	0.34	11.4	18.8	0.62
2012-15 Mean	9.7	29.14	0.33	11.2	17.9	0.62

1 - 1975-84 streamflows listed and used for groundwater recharge and evapotranspiration estimates were measured at the Filson Creek in SESW Sec. 24 near Winton, MN gage (USGS site number 05124990)

2 - 2014-2015 streamflows listed and used for groundwater recharge and evapotranspiration estimates were measured at the Filson Creek in SWSE Sec. 24, near Winton, MN gage (USGS site number 05124982)

3 - 2014-2015 streamflows listed and used for groundwater recharge and evapotranspiration estimates were measured at the Keeley Creek above mouth near Babbitt, MN gage (USGS site number 05125039)

4 - 2012-2015 streamflows listed and used for groundwater recharge and evapotranspiration estimates were measured at the St. Louis River near Skibo, MN (USGS site number 04015438).

Table 7. Annual groundwater recharge and evapotranspiration estimates calculated for the watershed of the St. Louis River near Aurora, Minnesota streamflow gage, annual precipitation, and streamflow, 1943-86.

[in./yr, inches per year; -, missing months of data; *, missing some daily values]						
Year	Groundwater Recharge Estimates (in./yr)	Precipitation (in./yr) ¹	Groundwater Recharge/Precipitation Ratio Estimates	Stream flow (in./yr)	Evapotranspiration Estimates (in./yr)	Evapotranspiration/Precipitation Ratio
1943	11.0	30.06	0.37	12.2	17.9	0.59
1944	15.5	36.00	0.43	16.9	19.1	0.53
1945	9.8	28.03*	0.35	11.6	16.5	0.59
1946	11.9	34.73*	0.34	13.6	21.1	0.61
1947	7.2	32.35*	0.22	10.3	22.1	0.68
1948	8.2	23.28	0.35	10.0	13.3	0.57
1949	9.5	31.32*	0.30	10.9	20.4	0.65
1950	14.3	33.49*	0.43	18.2	15.3	0.46
1951	10.6	27.76*	0.38	13.0	14.8	0.53
1952	8.1	23.22	0.35	9.8	13.5	0.58
1953	12.1	31.69*	0.38	12.6	19.1	0.60
1954	12.4	26.10*	0.47	13.4	12.7	0.49
1955	4.8	25.49*	0.19	5.8	19.7	0.77
1956	6.8	19.37*	0.35	8.4	11.0	0.57
1957	8.4	27.08	0.31	9.5	17.6	0.65
1958	6.6	23.23*	0.28	7.4	15.8	0.68
1959	6.5	28.13*	0.23	7.8	20.4	0.72
1960	6.5	23.95*	0.27	7.3	16.6	0.69
1961	5.2	26.63	0.19	5.8	20.9	0.78
1962	6.9	27.16	0.25	8.6	18.6	0.68
1963	5.0	25.87	0.19	5.3	20.6	0.79
1964	8.2	31.67*	0.26	9.3	22.4	0.71
1965	9.5	37.17	0.26	11.4	25.8	0.69
1966	10.3	26.69	0.39	13.0	13.7	0.51
1967	5.7	23.80	0.24	7.3	16.6	0.70
1968	14.4	40.17	0.36	17.3	22.9	0.57
1969	12.0	32.66	0.37	13.9	18.7	0.57
1970	8.5	31.17	0.27	10.1	21.1	0.68
1971	12.8	34.32	0.37	15.3	19.1	0.56
1972	9.2	31.00	0.30	12.3	18.7	0.60
1973	9.9	36.73	0.27	12.2	24.5	0.67
1974	9.3	29.51	0.32	10.2	19.3	0.65
1975	8.8	33.05	0.26	10.1	23.0	0.70
1976	4.9	19.75	0.25	6.8	13.0	0.66
1977	9.7	41.37	0.24	9.9	31.5	0.76
1978	11.3	30.24*	0.37	11.8	18.5	0.61
1979	12.7	25.95*	0.49	13.6	12.4	0.48
1980	4.1	27.49*	0.15	5.8	21.7	0.79
1981	6.8	30.64	0.22	9.8	20.9	0.68
1982	14.4	32.33*	0.44	17.2	15.2	0.47
1983	11.3	—	—	12.6	—	—
1984	8.6	—	—	10.4	—	—
1985	11.8	37.14	0.32	14.2	23.0	0.62
1986	11.1	33.52	0.33	13.2	20.3	0.61
Mean (1943-86)	9.4	30.75	0.31	11.0	18.8	0.63

1 - NOAA precipitation station at Tower, MN (fig. 1)

watershed ranged from 4.1 to 15.5 inches, with a mean estimate of 9.4 inches (table 7). The larger ranges in annual groundwater-recharge estimates typically occur with longer year of record because larger variety of climatic conditions occurs over the longer records.

Synthetic Hydrographs

Estimated daily mean streamflows for each of the ungaged, water-quality sampling sites mimic the measured streamflows at the continuous streamflow gages, with estimated flow generally higher for downgradient ungaged sites and lower in upgradient ungaged sites. Statistical comparisons for the fifteen ungaged water-quality sites indicated that the estimated values are acceptable for all but one, FC6, of the ungaged sites (fig. 6). Therefore, these synthetic hydrographs could be used to determine loads and flows for water-quality modeling, with exception for FC6.

Tracer Test

Results from the KBr tracer test indicated that total and dissolved Cu and Ca concentrations generally increase as the water in the creek flows over the mineralized zone in the watershed, while total and dissolved Ni, Mg, Na, S, and dissolved organic carbon concentrations generally varied little over the mineralized zone. Large changes in total Cu concentrations between water-quality sampling locations did occur along the creek, although often not associated with identified inflow locations where water of different Cu concentrations flowed into the creek. Three locations where water inflow to the creek occurred were identified and sampled along the portion of the creek being tested. Cu concentrations in water from two of the inflow points were lower than water in the creek, while Cu concentrations in water from one inflow point was higher.

Br and K concentrations downgradient from the KBr injection point generally indicated that flow into the creek occurred gradually into the creek as seepage, with only one inflow point affecting Br and K concentrations in the creek. As anticipated, Br and K concentrations abruptly increased at the injection point, gradually decreasing downstream, along the length of the part of the creek being monitored with an abrupt decrease at a point where water inflow from an upgradient wetland occurred. This abrupt decrease mainly was due to dilution from the inflowing water. Water sampled from the inflow at that location had a total Br concentration below the detection limit of 0.03 mg/L and total K concentration 0.21 mg/L, generally an order of magnitude less than K concentrations determined for water sampled in the creek.

Summary of Conceptual Hydrologic Model

Annual ET estimates for 2014-15 determined in this study for the three watersheds indicate that ET accounts for approximately 66% of the total annual precipitation on the watersheds, with 34% leaving the watershed as streamflow at the gages. These ET estimates assume that precipitation is the only source of water entering the watersheds, and all groundwater and surface-water runoff discharges into the creek or river upgradient of the streamflow gages. ET amounts likely are high in the three watersheds due to the abundance of wetlands and forests are abundant. Wetlands provide a large water-surface area and abundant aquatic vegetation for ET. Much of the streamflow occurs in the spring following snowmelt and precipitation and in fall following precipitation events. The highest ET rates occur mostly from late spring to early fall, when air temperatures generally are the highest.

The precipitation data used to determine the annual ET estimates may not be representative of the actual precipitation that fell in the watersheds. The most complete precipitation data used were collected in weather stations outside of the watersheds. However, annual ET estimates using the most complete precipitation data compare well to estimates made in other hydrologic studies in northeastern Minnesota.

Mean annual groundwater recharge in the watersheds for 2014-15 is approximately 9 inches, with approximately 31% of the total annual precipitation recharging into shallow groundwater systems of the watershed. Much of the recharge occurring upgradient of the streamflow gages in the Filson Creek and Keeley Creek watersheds, likely discharges into wetlands and the creeks because low-permeable bedrock is shallow in both watersheds.

References

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Ericson, D.W., Lindholm, G.F., and Helgesen, J.O., 1976, Water resources of the Rainy Lake Watershed, northeastern Minnesota: U.S. Geological Survey Hydrologic Atlas HA-556, 2 sheets, scale 1: 1,000,000.

Nichols, D.S., and Verry, E.S., 2001, Stream flow and groundwater recharge from small forested watersheds in north central Minnesota: *Journal of Hydrology*, v. 245, p. 89–103. [Also available at [http://dx.doi.org/10.1016/S0022-1694\(01\)00337-7](http://dx.doi.org/10.1016/S0022-1694(01)00337-7).]

Siegel, D.I., and Ericson, D.W., 1980, Hydrology and water quality of the copper-nickel study region, northeastern Minnesota: U.S. Geological Survey Water-Resources Investigations Report 80-739, 87 p.

V. DISSEMINATION:

Description: A U.S. Geological Survey Scientific Investigations Report will be prepared that will summarize analytical results, present interpretations of bedrock, soil, streambed sediment, and water-quality data, and describe conceptual hydrologic modeling results. Presentations will be given at mining, geologic, and hydrologic conferences in the State outlining project results. Geochemical data for bedrock, soils, and streambed samples will be entered and stored in the USGS National Geochemical Database (http://minerals.cr.usgs.gov/projects/geochem_database/index.html). Metal and major constituent concentrations for water samples collected in the project will be entered and stored in the USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). A link on the NRRRI website (http://www.nrri.umn.edu/egg/pubs_nonferrous.html) will be established.

Status as of December 31, 2013:

On September 25, Perry Jones gave a presentation at the Lake Superior Cooperative Science and Monitoring Workshop in Duluth, MN outlining water-quality, streamflow, and bed-sediment sampling being conducted in the study. An abstract for a poster presentation was submitted to Minnesota Lake Superior Stream Science Symposium, to be held in Duluth, MN on January 7-8, 2014. The poster will summarize project objectives and activities to be done in the study. Funding for the workshop presentation preparation and attendance (salary and travel expenses = \$10,280) and the symposium abstract/presentation development (salary = \$ 4,940) was provided by the U.S. Geological Survey Midwest Region Mining Initiative.

Status as of June 30, 2014:

Initial drafts of base map figures for the three watersheds were constructed. These figures will be used in the final report.

On April 11, Perry Jones participated in the Rainy River Headwater (RRHW) Core Team Meeting for MN Watershed Restoration and Protection Strategies (WRAPS) process, outlining the team on work done on this project.

A poster titled: *Potential for Copper Toxicity Caused by Surface Water and Stream Sediments in Unmined Mineralized Watersheds of the Duluth Complex*, by Nadine Piatak, Robert Seal, Perry Jones, and Laurel Woodruff (all USGS) was presented at the 60th Annual Meeting of the Institute on Lake Superior Geology, Hibbing, MN, May 15-16, 2014. Funding for the conference presentation preparation and was provided by the U.S. Geological Survey Midwest Region Mining Initiative.

Perry Jones submitted an abstract to U.S. Environmental Protection Agency (EPA), which was accepted, for an oral presentation at the EPA National Conference on Mining-Influenced Waters in Albuquerque, NM from August 12-14, 2014. The presentation will summarize project objectives, activities, and initial findings. Funding for the conference presentation preparation and attendance (salary and travel expenses = \$13,100) will be provided by the U.S. Geological Survey Midwest Region Mining Initiative.

Status as of December 31, 2014:

Perry Jones gave an oral presentation outlining the water-quality data collected in this project in the characterization session of the U.S. Environmental Protection Agency (EPA) National Conference on Mining-Influenced Waters in Albuquerque, NM from August 12-14, 2014. Funding for the workshop presentation, preparation, and attendance (salary and travel expenses = \$13,100) was provided by the U.S. Geological Survey Midwest Region Mining Initiative.

Perry Jones attended the EPA Lake Superior Collaborative meeting in Duluth, Minnesota on November 19 and 20 to discuss water-quality data collection efforts in this study and other studies conducted in the Lake Superior basin. Funds from the Environmental and Natural Resources Trust Funding used for preparing and attending this meeting was \$1,000 (USGS personnel salary – covered under Activity 3 budget).

Status as of June 30, 2015:

Laurel Woodruff, Sarah Elliot, Perry Jones, and John Bumgarner attended the East Range Water Resources Data Collaboration Meeting in Duluth, MN on January 29,. Woodruff and Jones gave presentations outlining results from FY14 water-quality, stream sediment, soil, and bedrock geochemical analyses of samples collected in this project.

On March 18, Laurel Woodruff and Perry Jones gave a presentation on the current status of the project at the Natural Resources Research Institute in Duluth, MN.

Laurel Woodruff and Carrie Jennings presented preliminary soil and bedrock geochemical data from the paired Filson and Keeley watersheds in a poster at the 61st Annual Institute on Lake Superior Geology, held May 20-24 in Dryden, Ontario. Initial interpretations indicate that proximal soil and bedrock geochemistry are similar because glacial cover is thin and transport distances are short. The data also suggest that element ratios (such as Ni versus Cu) can be used to distinguish the concentration of certain metals in sulfide versus ferromagnesian silicate minerals. The abstract for this presentation can be found at <http://www.d.umn.edu/prc/lakesuperiorgeology/Volumes/2015%20Abstracts%20and%20Proceedings%20Volume%20s m.pdf>

Status as of December 31, 2015:

On July 31, Perry Jones gave a presentation at the 2015 Healthy Watershed Conference: Water and Forest, in Cohasset, MN, outlining results from the study.

On September 2, Perry Jones and Laurel Woodruff met with Jay Vanlandingham, Twin Metals Minnesota water-resources specialist, to discuss USGS and Twin Metals Minnesota hydrologic data collection in the Filson Creek and other northeastern Minnesota watersheds.

On November 12, 2015, Perry Jones and Laurel Woodruff (EMERSC) gave a presentation at the Monitoring Trace Metals in the Lake Superior Basin Meeting, Ashland, WI outlining results from the study.

Status as of June 30, 2016:

A draft copy of the U.S. Geological Survey Scientific Investigations Report is near completion. Draft figures and tables for the report are completed. The report will summarize analytical results, present interpretations of bedrock, soil, streambed sediment, and water-quality data, and describe conceptual hydrology for the three watersheds. A draft copy of the report will be completed for review by July 31, 2016, and an on-line version of the report will be completed by December 31, 2016. At that time, a pdf version of the report will be sent to LCCMR staff.

On March 10, 2016, Sarah Elliott presented at the 2016 International Rainy-Lake of the Woods Watershed Forum describing results from the study. On August 4, Laurel Woodruff will be presenting project results at the White Iron Chain of Lakes Lake Association's Annual Meeting.

Geochemical data for bedrock, soils, and streambed samples were entered and stored in the USGS National Geochemical Database (http://minerals.cr.usgs.gov/projects/geochem_database/index.html). Metal and major constituent concentrations for water samples collected in the project were entered and stored in the USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). All continuous streamflow data and streamflow measurements were entered and are available in USGS National Water Information System (NWIS) at <http://waterdata.usgs.gov/nwis>. A link on the NRRI website (http://www.nrri.umn.edu/egg/pubs_nonferrous.html) will be established by December 31, 2016.

Final Report Summary for Dissemination:

A U.S. Geological Survey Scientific Investigations Report (SIR) is being completed for colleague and USGS review that will summarize analytical results, present interpretations of bedrock, soil, streambed sediment, and water-quality data, and describe conceptual hydrology for the three watersheds (once published, the report will be available through the USGS Publication Warehouse at <https://pubs.er.usgs.gov/>). A draft of the report will be completed for review by June 30, 2017, and an on-line version of the report will be completed by December 31, 2017. At that time, a pdf version of the report will be sent to LCCMR staff.

Numerous oral and poster presentations were given at geologic, water-quality, and hydrologic conferences in the State outlining project results. These presentations also were given at meetings with federal (U.S. Forest Service, U.S. Environmental Protection Agency), state (Minnesota Department of Natural Resources, Minnesota Pollution Control Agency, Minnesota Department of Health), local, and tribal agencies, mining companies, and university researchers. These meetings included the following:

- U.S. Environmental Protection Agency (EPA) Lake Superior Cooperative Science and Monitoring Workshop, Duluth, MN, September 25, 2013.
- Minnesota Lake Superior Stream Science Symposium, Duluth, MN, January 7-8, 2014. (Poster presentation can be found at <http://www.lrcd.org/uploads/1/6/4/0/16405852/mnlsstreamconf172013-2.pdf>).
- U.S. Environmental Protection Agency (EPA) National Conference on Mining-Influenced Waters in Albuquerque, NM, August 12-14, 2014 (participation in the conference was funded by U.S. Geological Survey Midwest Region Mining Initiative) (abstract can be found at <https://clu-in.org/download/issues/mining/mining-influencedwater/Mining-600-R-15-088.pdf>).
- U.S. Environmental Protection Agency (EPA) Lake Superior Cooperative Science and Monitoring Workshop, Duluth, MN, November 19-20, 2014.
- East Range Water Resources Data Collaboration Meeting, Duluth, MN, January 29, 2015.
- University of Minnesota – Duluth, Natural Resources Research Institute, Duluth, MN, March 18, 2015.
- 61st Annual Institute on Lake Superior Geology, Dryden, Ontario, May 20-24, 2015. (participation in the conference was funded by U.S. Geological Survey, Eastern Minerals Research Funds) (abstract can be

found at

<http://www.d.umn.edu/prc/lakesuperiorgeology/Volumes/2015%20Abstracts%20and%20Proceedings%20Volume%20sm.pdf>

- 2015 Healthy Watershed Conference: Water and Forest, Cohasset, MN, July 31, 2015. (presentation can be found at <https://mavenperspectives.com/wp-content/uploads/2015/02/Assessing-the-Influence-of-Copper-Nickel-Bearing-Bedrocks-on-Baseline-Water-Quality-in-Three-Northeastern-Minnesota-Watersheds.pdf>)
- USGS Monitoring Trace Metals in the Lake Superior Basin Meeting, Ashland, WI, November 12, 2015 (gave presentation via web)
- Minnesota Geological Survey, Minneapolis, MN, March 7, 2016
- 2016 International Rainy-Lake of the Woods Watershed Forum, International Falls, MN, March 10, 2016.
- White Iron Chain of Lakes Lake Association’s Annual Meeting, Ely, MN, August 4, 2016

All of the data collected and compiled during this study is too large to be included in the appendix tables of the final LCCMR report, however the data is available in several databases. Geochemical data for bedrock, soils, and streambed samples were entered and stored in the USGS National Geochemical Database

(http://minerals.cr.usgs.gov/projects/geochem_database/index.html). Metal and major constituent concentrations for water samples collected in the project were entered and stored in the USGS National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>). All continuous streamflow data and streamflow measurements were entered and are available in USGS National Water Information System (NWIS) at <http://waterdata.usgs.gov/nwis>.

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget:

Budget Category	\$ Amount	Explanation
Personnel:	\$ 17,500	A total of two positions at NRRRI will be paid: A Geologist to assess bedrock geology.199 FTE ; Project Manager (1) to manage the project (.263 FTE) total over three years.
Professional/Technical/Service Contracts:	\$ 565,500	U.S. Geological Survey, (total: \$538,700) (1) geologist to assess bedrock, glacial overburden, soil, and streambed samples. (.38FTE) Hydrologist (1) to assess water-quality and loads in streams and conduct conceptual hydrologic models for the watersheds (.81 FTE); Hydrologic Technicians (2) to collect and manage water-quality, bed-sediment, and streamflow data (.85 FTE and .1 FTE). All FTEs are expressed as a total over 3 years, not as an average for each year. Geochemical Laboratory - geochemical analysis of soil, bed-sediment, and bedrock samples (\$17,541). U.S. Geological Survey National Water-Quality Laboratory analysis of water-quality samples (major constituents, dissolved oxygen, and trace elements) (\$43,288). U.S. Geological Survey Minnesota Water Science Center, Data Section - installation and maintenance of two stream gages (\$116,507).

		Water-quality sampling equipment and supplies – e.g., peristaltic pumps, filters, sample bottles, preservatives for the samples, tubing for the pumps (\$4,772). Printing: editing and publishing USGS Scientific Investigations Report (\$7,000). Shipping costs to send bedrock, soil, and streambed sediment samples to USGS Geochemical Laboratory, and send water-quality samples to USGS National Water-Quality Laboratory (\$1,395). Vehicle mileage, lodging, and meals costs for (2) bedrock, soil, and streambed sediment sampling trips and (2) water-quality sampling trips (\$44,582). MN DNR (\$26,800) ; One glacial geologist to assist with understanding and interpreting the effects of the glacial material in each watershed (.115 FTE total over 3 years). Mileage, lodging, and meals costs for (2) bedrock, soil, and streambed sediment sampling trips (\$1,000).
Travel Expenses in MN:	\$ 2,000	NRRI Vehicle mileage, lodging, and meals costs for (2) bedrock, soil, and streambed sediment sampling trips.
TOTAL ENRTF BUDGET:	\$ 585,000	All Items listed above

Explanation of Use of Classified Staff: N/A

Explanation of Capital Expenditures Greater Than \$3,500: N/A

Number of Full-time Equivalent (FTE) funded with this ENRTF appropriation: .462 FTE total over 3 years

Number of Full-time Equivalent (FTE) estimated to be funded through contracts with this ENRTF appropriation: 2.25 FTE total over 3 years

B. Other Funds:

Source of Funds	\$ Amount Proposed	\$ Amount Spent	Use of Other Funds
Non-state			
U.S. Geological Survey Water Cooperative Program	\$ 208,748	\$ 208,748	To cover computer, cell phone, office space, and other USGS MN Water Science Center costs for the project (estimated amount; not a specific match commitment)
U.S. Geological Survey Midwest Region Mining Initiative	\$ 216,000	\$ 216,000	To cover computer, cell phone, office space, conference travel, first round of streambed sediment/water-quality/streamflow sampling, and other USGS MN Water Science Center and Eastern Minerals Resources Science Center costs for the project (estimated amount, not a specific match

			commitment)
TOTAL OTHER FUNDS:	\$ 424,748	\$ 424,748	To cover computer, cell phone, office space, and other USGS MN Water Science Center and Eastern Minerals Resources Science Center costs for the project

Please see Attachment A – Final Budget Details

VII. PROJECT STRATEGY:

A. Project Partners:

Partners receiving funding from the Environment and Natural Resources Trust Fund

Duluth Minerals Section of the Natural Resources Research Institute [NRRI]: Steve Hauck (Director) and Stephen Monson Geerts (geologist) will co-manage the project; Mark Severson (geologist) will provide the bedrock samples and mineral deposit expertise. (\$48,000)

U.S. Geological Survey: Laurel Woodruff (geologist) will co-manage the project, overseeing streambed sediment, soil, and bedrock sampling and geochemical analyses; Perry Jones (hydrologist) will oversee stream gaging, water-quality sampling and analyses, and hydrologic model development. (\$505,200)

Minnesota Department of Natural Resources: Carrie Jennings (geologist,) will provide expertise on glacial and sediment geochemistry. (\$26,800)

Collaborative partners not receiving funding from the Environment and Natural Resources Trust Fund

U.S. Forest Service – Superior National Forest
Duluth Metals
Twin Metals Mining
Great Lakes Indian Fish and Wildlife Commission

B. Project Impact and Long-term Strategy:

Minnesota faces a daunting challenge. A world-class domestic resource for copper (Cu), nickel (Ni), cobalt (Co), platinum-group-elements (PGE) and titanium (Ti) hosted by rocks of the Duluth Complex in northeastern Minnesota could provide tremendous economic and employment benefits to that part of the State. However, northeastern Minnesota also contains the Boundary Waters Canoe Area Wilderness, one of the most pristine and environmentally sensitive regions of the country. The large tonnage of metals in the basal part of the Duluth Complex and increasing metal prices strongly suggest that metal mining in the area is inevitable. If regional details about current, existing surface water quality, and the concentration and distribution of elements in rocks, soils, and stream bed sediments are not available before mining begins, then it will not be possible for any regulatory agency to formulate accurate predictions of mining impacts on the environment. This lack of data could make it more problematic for mining companies to demonstrate remediation of mine sites to pre-mining ‘baseline’ water quality levels. Water-quality and modeling results will be compared to data available in the 1979 *Minnesota Environmental Quality Board Regional Copper-Nickel Study* to assess long-term trends in water quality. The new data and hydrologic analysis will be used by Federal, State, local, and tribal entities to better assess water-quality impacts of existing mineralization and potential mining.

C. Spending History:

Funding Source	M.L. 2007 or	M.L. 2008 or	M.L. 2009 or	M.L. 2010 or	M.L. 2011 or
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	FY08	FY09	FY10	FY11	FY12-13
U.S. Geological Survey Midwest Region Mining Initiative					\$72,500

VIII. ACQUISITION/RESTORATION LIST: N/A

IX. MAP(S): N/A

X. RESEARCH ADDENDUM:

Research Addendum will be added following USGS internal review.

XI. REPORTING REQUIREMENTS:

Periodic work program progress reports will be submitted not later than December 31, 2013, June 30, 2014, December 31, 2014, June 30 2015, and December 31, 2015. A final work program report and associated products will be submitted between June 30 and-December 31, 2016 as requested by the LCCMR.

Final Attachment A: Budget Detail for M.L. 2013 Environment and Natural Resources Trust Fund Projects											
Project Title: How Do Natural Copper-Nickel Bedrocks Influence Water Quality?											
Legal Citation: M.L. 2013, Chp. 52, Sec. 2, Subd. 05b											
Project Manager: Stephen Monson Geerts											
M.L. 2013 ENRTF Appropriation: \$ 585,000											
Project Length and Completion Date: 4 years, 06/30/2017											
Date of Update: December 31, 2016											
	Activity 1 Budget Revised 2/2/2016	Amount Spent	Balance	Activity 2 Budget Revised 2/2/2016	Amount Spent	Balance	Activity 3 Budget Revised 2/2/2016	Amount Spent	Balance	Proposed New Total Budget 2/2/2016	TOTAL BALANCE
ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET											
BUDGET ITEM	Characterize streambed sediment, soil, and bedrock chemistry			Determine natural metal and major constituent loads in streams			Assess hydrologic conditions prior to potential future mine development				
Personnel (Wages and Benefits)	\$11,000.00	\$11,000.00	\$0.00	\$0.00	\$0.00	\$0.00	\$6,500.00	\$6,500.00	\$0.00	\$17,500.00	\$0.00
Steve Hauck, Project Manager, Natural Resources Research Institute Director, \$38,400 (.263 FTE over 3 years, 36% fringe)											
Mark Severson, Natural Resources Research Institute Geologist, \$23,400 (.199 FTE over 3 years, 36% fringe)											
Stephen Monson Geerts, Natural Resources Research Institute Geologist, \$23,400 (.199 FTE over 3 years, 36% fringe)											
Professional/Technical/Service Contracts											
USGS Contract Total	\$65,058.00	\$65,058.00	\$0.00	\$277,760.45	\$277,760.45	\$0.00	\$195,881.55	\$195,881.55	\$0.00	\$538,700.00	\$0.00
USGS Personnel	\$51,174.39	\$51,174.39	\$0.00	\$97,562.75	\$97,562.75	\$0.00	\$188,881.55	\$188,881.55	\$0.00	\$337,618.69	\$0.00
Laurel Woodruff, U.S. Geological Survey, Geologist, \$55,497 (.38 FTE over 3 years, 30% fringe)											
Perry Jones, U.S. Geological Survey, Hydrologist, \$140,560 (.81 FTE over 3 years, 26% fringe)											
U.S. Geological Survey, Hydrologic Technician, \$63,203 (.85 FTE over 3 years, 22% fringe)											
U.S. Geological Survey, Hydrologic Technician, \$10,733 (.1 FTE over 3 years, 30% fringe)											
U.S. Geological Survey, Geochemical Laboratory - geochemical analysis of soil, bed-sediment, and bedrock samples	\$11,463.64	\$11,463.64	\$0.00							\$11,463.64	\$0.00
U.S. Geological Survey National Water-Quality Laboratory - analysis of water-quality samples (major constituents, dissolved oxygen, and trace elements)				\$79,605.64	\$79,605.64	\$0.00				\$79,605.64	\$0.00
U.S. Geological Survey Minnesota Water Science Center, Data Section - installation and maintenance of two stream gages				\$70,393.26	\$70,393.26	\$0.00				\$70,393.26	\$0.00
USGS Travel: Eastern Minerals Science Center Lodging/Meals/Vehicle Costs - for soil, bed-sediment, and bedrock sampling	\$2,347.44	\$2,347.44	\$0.00							\$2,347.44	\$0.00
USGS Travel: Minnesota Water Science Center Lodging/Meals/Vehicle Costs - for water-quality sampling and streamflow measurements				\$13,646.76	\$13,646.76	\$0.00				\$13,646.76	\$0.00
USGS Water-Quality Sampling Supplies - bottles, sampling tubing, filters, pumps				\$13,064.59	\$13,064.59	\$0.00				\$13,064.59	\$0.00
USGS Shipping Costs: Soil, Bed-Sediment, and Bedrock Samples	\$72.53	\$72.53	\$0.00							\$72.53	\$0.00
USGS Shipping Costs: Water-Quality Samples				\$3,487.45	\$3,487.45	\$0.00				\$3,487.45	\$0.00
USGS EPN Printing Costs							\$7,000.00	\$7,000.00	\$0.00	\$7,000.00	\$0.00
MN DNR Contract Total	\$17,300.00	\$17,300.00	\$0.00	\$0.00	\$0.00	\$0.00	\$9,500.00	\$9,500.00	\$0.00	\$26,800.00	\$0.00
Carrie Jennings, Minnesota Department of Natural Resources Glacial Geologist, \$12,000 (.115 FTE over 3 years, 30% fringe)	\$16,300.00	\$16,300.00	\$0.00				\$9,000.00	\$9,000.00	\$0.00	\$25,300.00	\$0.00
MN DNR Travel: Minnesota Department of Natural Resources Lodging/Meals/Vehicle Costs - for soil, bed-sediment, and bedrock sampling	\$1,000.00	\$1,000.00	\$0.00				\$500.00	\$500.00	\$0.00	\$1,500.00	\$0.00
Travel											
Natural Resources Research Institute Lodging/Meals/Vehicle Cost - for soil, bed-sediment, and bedrock sampling, management meetings	\$2,000.00	\$2,000.00	\$0.00				\$0.00	\$0.00	\$0.00	\$2,000.00	\$0.00
COLUMN TOTAL	95,358.00	95,358.00	0.00	277,760.45	277,760.45	0.00	211,881.55	211,881.55	0.00	585,000.00	0.00