

# Copper Toxicity and Organic Matter: Resiliency of Watersheds in the Duluth Complex, Minnesota, USA

Nadine Piatak, Robert Seal, Perry Jones and Laurel Woodruff  
*U.S. Geological Survey, USA*

## ABSTRACT

We estimated copper (Cu) toxicity in surface water with high dissolved organic matter (DOM) for unmined mineralized watersheds of the Duluth Complex using the Biotic Ligand Model (BLM), which evaluates the effect of DOM, cation competition for biologic binding sites, and metal speciation. A sediment-based BLM was used to estimate stream-sediment toxicity; this approach factors in the cumulative effects of multiple metals, incorporation of metals into less bioavailable sulfides, and complexation of metals with organic carbon.

For surface water, the formation of Cu-DOM complexes significantly reduces the amount of Cu available to aquatic organisms. The protective effects of cations, such as calcium (Ca) and magnesium (Mg), competing with Cu to complex with the biotic ligand is likely not as important as DOM in water with high DOM and low hardness. Standard hardness-based water quality criteria (WQC) are probably inadequate for describing Cu toxicity in such waters and a BLM approach may yield more accurate results. Nevertheless, assumptions about relative proportions of humic acid (HA) and fulvic acid (FA) in DOM significantly influence BLM results; the higher the HA fraction, the higher calculated resiliency of the water to Cu toxicity. Another important factor is seasonal variation in water chemistry, with greater resiliency to Cu toxicity during low flow compared to high flow.

Based on generally low total organic carbon and sulfur content, and equivalent metal ratios from total and weak partial extractions, much of the total metal concentration in clastic streambed-sediments may be in bioavailable forms, sorbed on clays or hydroxide phases. However, organic-rich fine-grained sediment in the numerous wetlands may sequester significant amount of metals, limiting their bioavailability. A high proportion of organic matter in waters and some sediments will play a key role in the resiliency of these watersheds to potential additional metal loads associated with future mining operations.

**Keywords:** baseline characterization, mineral deposits, water quality criteria, Biotic Ligand Model

INTRODUCTION

The characterization of baseline conditions in unmined mineralized watersheds of the Mesoproterozoic Duluth Complex, northeastern Minnesota (Figure 1), is essential to responsibly extract minerals from a region with some of the greatest mineral development potential in the United States. Mining has the potential to release metals into watersheds that already contain ecologically-significant naturally-occurring concentrations of some elements such as Cu and nickel (Ni). The potential for metals to be toxic to aquatic organisms is influenced by the amount of organic carbon in the aquatic environment, the cumulative effects of multiple metals, cation competition for biologic binding sites, and speciation of metals. As a result, we estimated toxicity in mineralized watersheds using approaches that incorporate these water and sediment quality parameters.

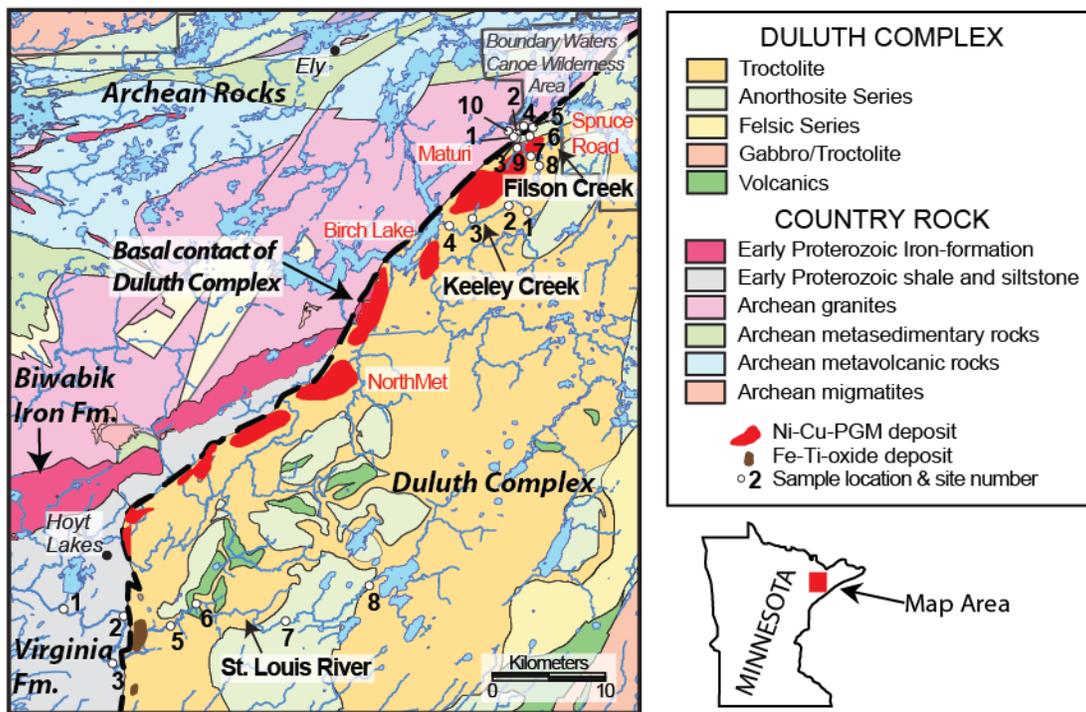


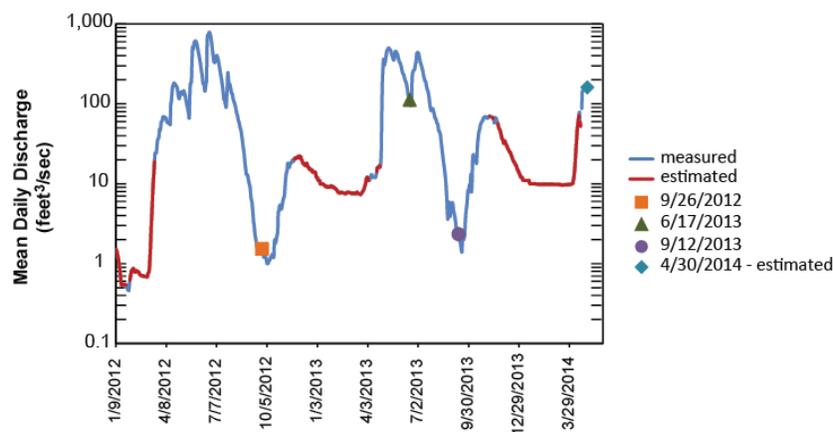
Figure 1 Bedrock geology, mineral deposits, and sample locations in northeastern Minnesota.

Surface-water and streambed-sediment samples shown in Figure 1 were collected from sites along three geologically distinct watersheds: 1. Filson Creek, where Cu-Ni-PGM (Platinum Group Metal) mineralization occurs at the bedrock surface along the basal Duluth Complex; 2. Keeley Creek, where Cu-Ni-PGM mineralization occurs only at great depth; and 3. the headwaters of the St. Louis River in the vicinity of iron (Fe) and titanium (Ti) oxide ultramafic intrusions, which occur in the subcrop beneath glacial cover. The headwaters of the St. Louis River are upstream of drainage from the taconite mining. Samples were collected in watersheds characterized by abundant wetlands, and some lakes and streams. Filson and Keeley creeks have smaller flows compared to the St. Louis River, which is a significantly larger river system. The watersheds are characterized by times of relatively low baseflow during the hot and dry late summer and early fall and again during winter

when creeks and rivers are ice-covered. Medium to high flow rates occur following storms, generally wet periods, and snowmelt, commonly in the spring and early summer.

## METHODOLOGY

Surface-water and streambed-sediment samples were collected during September 2012 under baseflow conditions and surface waters were resampled during June 2013 (at medium-high flow), September 2013 (near baseflow), and April 2014 (near peak flow). In Figure 2, the daily mean discharge and instantaneous flow for the separate sampling events are shown for site 6 in the St. Louis River. Sampling locations included 10 sites in Filson Creek, 4 sites in Keeley Creek, and 7 sites in the St. Louis River (Figure 1); however, not every site was sampled during each sampling event.



**Figure 2** Daily mean discharge for St. Louis River, site 6, from <http://waterdata.usgs.gov/nwis>. Instantaneous discharge measured during sample collection shown as discrete symbols.

Surface-water samples were collected using United States Geological Survey (USGS) protocols (Wilde & Radtke, 1998; Wilde et al., 1999). Water quality parameters (e.g., pH, water temperature) were determined by discrete measurements at the time of water sample collection. Water samples included a less than 0.45  $\mu\text{m}$  filtered (dissolved) sample and an unfiltered (total) sample. Major ions and trace elements in filtered and unfiltered surface waters acidified with ultrapure nitric acid were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Taggart, 2002). Major anions were analyzed on non-acidified filtered splits using ion chromatography (Taggart, 2002). Samples were analyzed for alkalinity on non-acidified filtered splits by titration; dissolved organic carbon (DOC) was measured by infrared spectrometry on filtered samples preserved with trace element grade hydrochloric acid (Taggart, 2002).

Composite streambed-sediment samples were collected according to USGS protocols (Shelton & Capel, 1994). Sediments were composites of approximately 30 surface subsamples collected in a grid pattern. The composite was homogenized and then sieved to a diameter of less than 2 mm. Samples were analyzed for total concentrations of major and trace elements using a combination of ICP-MS and ICP-AES following acid digestion using a mixture of HCl-HNO<sub>3</sub>-HClO<sub>4</sub>-HF. Total organic carbon is calculated as the difference between total carbon and carbonate carbon, which were determined using an elemental analyzer and coulometric titration, respectively. In order to

determine elements not tightly bound to silicates, partial extractions were conducted using HCl-H<sub>2</sub>O<sub>2</sub> and a Diisobutyl Ketone (DIBK) solution; extracted metal concentrations were determined by ICP-AES. (For details regarding previously mentioned analytical methods for sediments see: [http://minerals.cr.usgs.gov/projects/analytical\\_chem/references.html](http://minerals.cr.usgs.gov/projects/analytical_chem/references.html)). Samples were also analyzed for acid volatile sulfide - simultaneously extracted metals (AVS-SEM) using a procedure modified after United States Environmental Protection Agency (USEPA, 1991). The AVS is operationally defined here as the sulfide fraction released by extraction with 1.2 N HCl at approximately 80° C; the metal fraction released during the AVS extraction is the SEM.

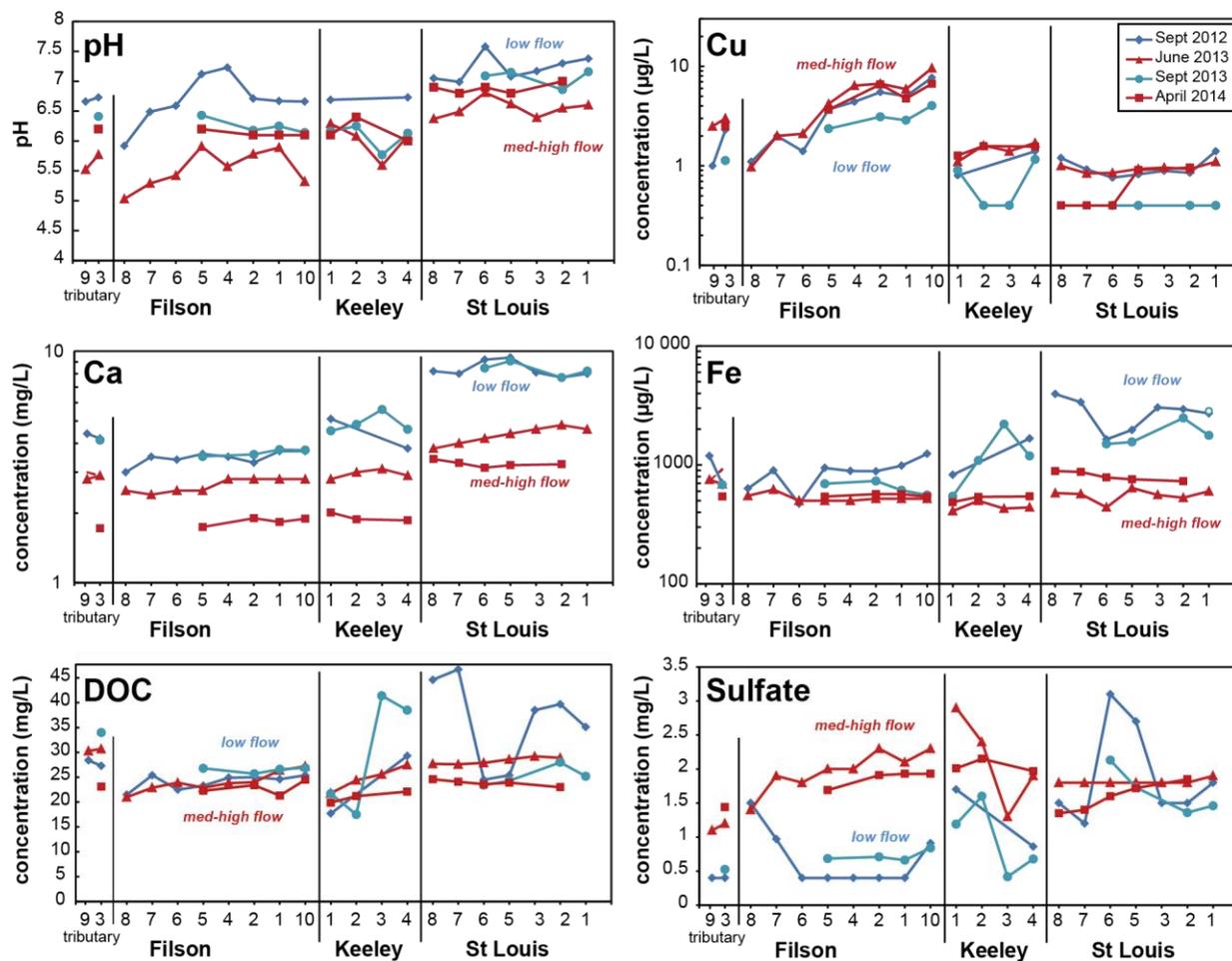
## RESULTS AND DISCUSSION

### Water and sediment chemistry

The geochemistry of the surface waters and stream sediments reflects underlying rock types, glacially transported unconsolidated materials, mineralization style within each watershed, and geochemical processes occurring in the streams. The water chemistry is also influenced by the ambient and flow conditions and therefore changes daily and seasonally. In general, the surface water is oxic, near neutral to slightly acidic (pH 5.0 to 7.6), has low total dissolved solids (38 to 110 mg/L), and is characterized by low hardness (10 to 53 mg/L CaCO<sub>3</sub>), moderate carbonate species concentrations (4 to 44 mg/L CaCO<sub>3</sub> as bicarbonate), low sulfate (< 0.8 to 3.1 mg/L), and high DOC concentrations (18 to 47 mg/L) (Figure 3). The dominant dissolved trace elements are Fe (400 to 4,000 µg/L), Al (59 to 320 µg/L), Cu (< 0.8 to 9.6 µg/L), and Ni (0.6 to 7 µg/L).

For each specific sampling event, the average pH values are slightly lower and Cu and Ni concentrations are higher in water samples collected from the Filson Creek watershed, where the basal contact of the Duluth Complex is exposed. In contrast, the concentrations of major cations such as Ca and Mg, and, thus, hardness, as well as alkalinity are commonly highest in the St. Louis River for each sampling event compared to the other watersheds. Dissolved organic carbon is found in similar ranges of concentrations for all three watersheds during all sampling events, with a few exceptions; sulfate is generally low (Figure 3).

In addition to variation among watersheds, the chemistry of the streams changes with flow. Water samples collected during medium-high and peak flows (June 2013 and April 2014) are slightly more acidic, less alkaline, and generally more dilute with lower concentrations of some major and trace elements including Ca, Fe, Mg, and Na compared to water samples collected during low flow (Figure 3). Lower dissolved concentrations of elements are consistent with dilution after rainstorms or periods of snowmelt. However, despite generally more dilute conditions, the amount of dissolved elements (load) transported by the stream is greater under high flow conditions relative to low flow conditions as illustrated in Figure 4. In fact, the instantaneous loads for nearly all elements are greater during medium-high flow than under low flow and not correlated with element concentrations (Figures 3 and 4). During the drier and/or winter low flow conditions, major and trace elements and sulfate may accumulate in the wetland areas and in groundwater. These constituents may then be flushed from the reservoirs downstream during spring and summer high flow events. Similarly, DOC loads in the streams increase significantly during higher flow conditions, which also may be result of stream recharge through wetland areas that are organic-rich and oxygen-poor, as suggested by Berndt & Bavin (2012) for increased DOC concentrations following a major storm event in the St. Louis River watershed in August 2010.



**Figure 3** The pH and dissolved (< 45 µm) concentrations of Cu, Ca, Fe, DOC, and sulfate for each watershed plotted upstream to downstream (right to left for each watershed). Site numbers are given on the x-axis.

Stream sediments contain significant Al (7 to 11 weight percent, wt. %), Ca (1.5 to 6 wt. %), Fe (1 to 7 wt. %), and Na (2 to 4 wt. %). Sulfur is very low (< 0.05 wt. %). Organic carbon reaches 4.7 wt. % in one sample but is ≤ 1.5 wt. % in all the other samples. Trace metals are dominated by Cr (14 to 346 mg/kg), Cu (10 to 179 mg/kg), Ni (13 to 127 mg/kg), and Zn (23 to 95 mg/kg). On average, Cu and Ni are highest in Filson Creek stream sediments where Cu-Ni-PGM mineralization occurs at the surface (Figure 5). Samples collected from the St. Louis River watershed, where Fe-Ti oxide-bearing ultramafic rocks and a Paleoproterozoic shale/greywacke unit (Virginia Formation) occur, contain the highest average concentrations of many other trace elements including As, Cr, Fe, Pb, and Zn.

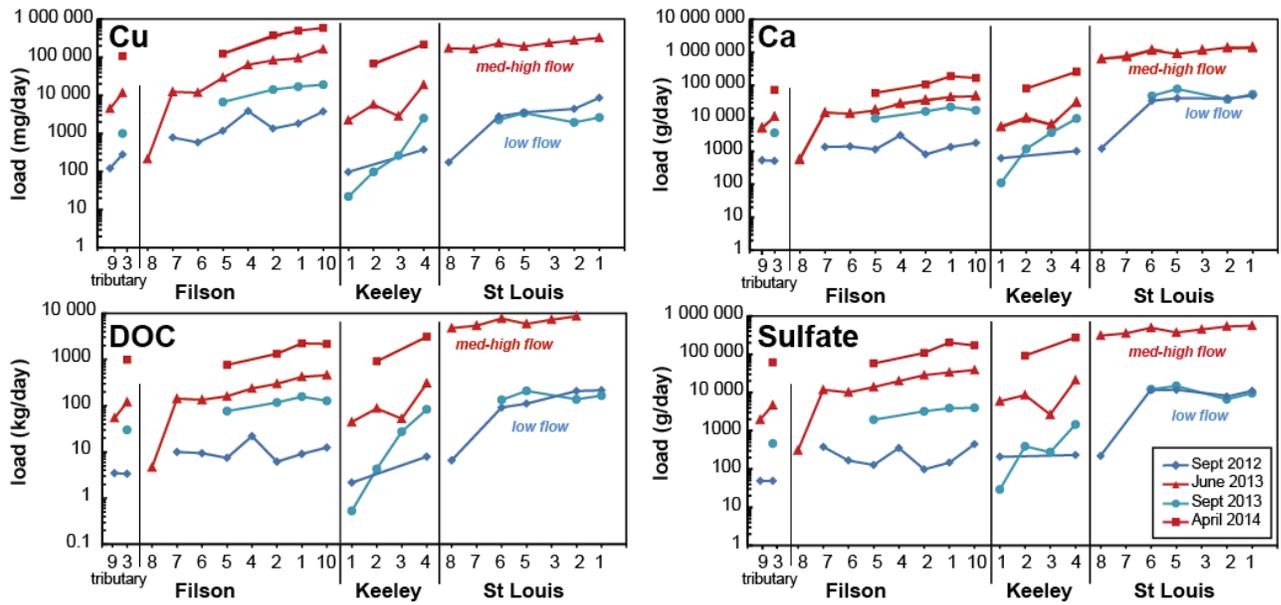


Figure 4 Instantaneous dissolved loads for Cu, Ca, DOC, and sulfate for each watershed plotted upstream to downstream. Flow data are not available for Keeley 1 or sites in the St. Louis River for April 2014.

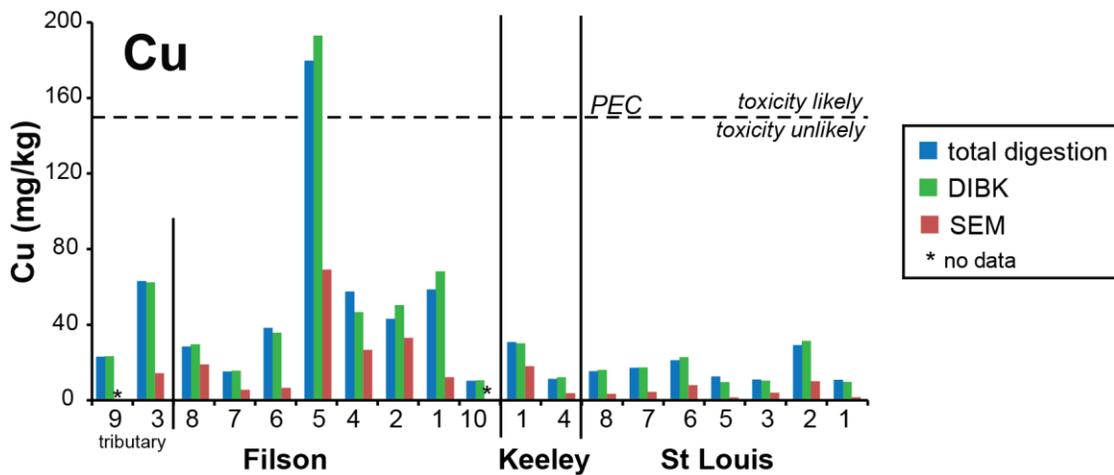


Figure 5 Concentrations of Cu in stream sediments for various digestion procedures for each watershed plotted upstream to downstream. Probable Effect Concentration (PEC) from MacDonald, Ingersoll, & Berger (2000).

### Toxicity

In water, the toxicity of most metals is assessed on the basis of hardness-based criteria that adjust for the protective effects of Ca and Mg ions, which compete with metal ions for binding sites on organisms (USEPA, 2014). For sediment, consensus-based total-metal guidelines (i.e., Probable

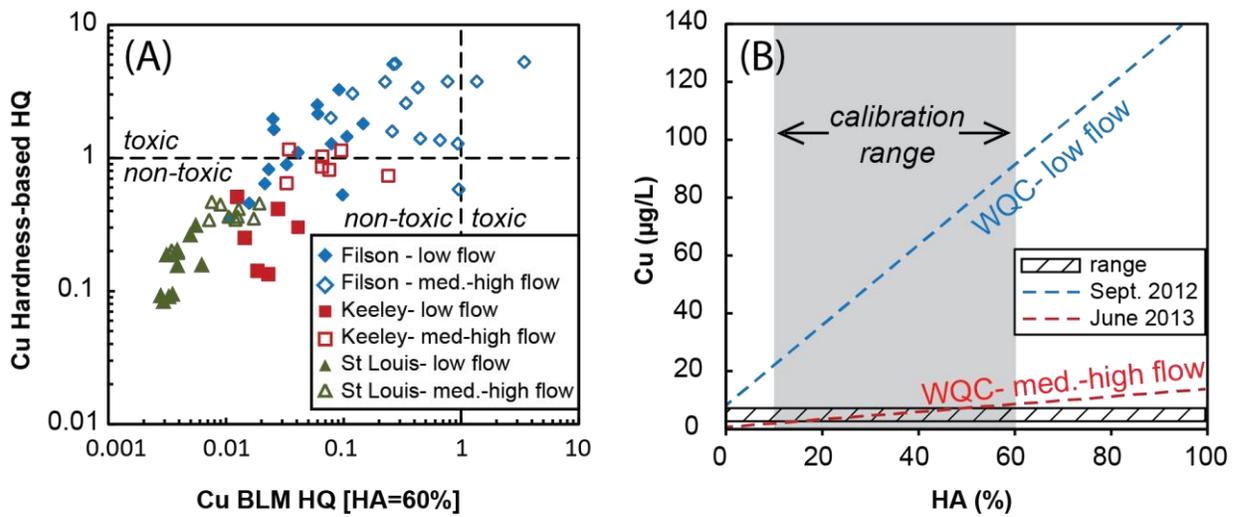
Effect Concentration, PEC) are routinely used and rely on laboratory toxicity tests that document increased toxicity caused by increased metal concentrations (MacDonald, Ingersoll, & Berger, 2000). However, new guidelines that rely on the BLM utilize a more sophisticated approach incorporating a greater array of water and sediment quality parameters including the cumulative effects of multiple metals in sediment, metal speciation in water, and organic carbon complexes in both water and sediment (Di Toro et al., 2005; USEPA, 2007). The surface-water and sediment metal concentrations can be compared to aquatic guidelines using the hazard quotient (HQ), which is the ratio of the concentration of a metal in the sample to the guideline value. Values above 1 imply toxic conditions, whereas those below do not.

Copper is the main element of concern in these baseline-condition waters with regard to aquatic toxicity. Using hardness-based criteria, chronic toxicity HQs for Cu in water are greater than 1 for many sites during both medium to high and low flow conditions in the Filson Creek watershed and a few sites in Keeley Creek during medium-high flow (Figure 6A). However, as shown in Figure 6A, nearly all chronic toxicity HQs for Cu in water calculated based on the BLM model are less than 1 (assuming a high HA fraction, i.e., 60 %), suggesting a lack of toxicity in most samples. The radically different results from the hardness-based and BLM-based approaches suggest that the former approach routinely used by regulators may be inadequate to describe metal toxicity in these DOM-rich watersheds because it is based on a more limited set of parameters (i.e., only hardness).

In addition, the complexation of Cu with DOM likely significantly affects the bioaccessibility of dissolved Cu in these watersheds, helping to mitigate its toxicity. However, the relative proportions of HA and FA in DOM greatly influence Cu complexation. The results from the BLM using various ratios of HA and FA at low and medium-high flow conditions for a site in Filson Creek are shown in Figure 6B; also, the range of HA (i.e., 10-60 %) that the BLM model is calibrated for is also shown. The concentration of Cu in the stream exceeds the chronic WQC for a medium-high flow sampling (June 2013) when WQC are calculated assuming a 10 % HA fraction. This is a conservative assumption for the percentage of HA that is recommended by HydroQual (2007) when HA and FA fractions are not known. If this reactive HA component makes up a higher proportion of the DOM, as is suspected for these waters (research currently ongoing), the WQC may increase above the Cu concentrations in the stream (Figure 6B). As illustrated by this example, it may therefore be important to quantify these acid fractions in order to accurately assess toxicity when using BLM, particularly for sites with HQ values close to 1. It is also apparent from Figure 6B that the Cu concentrations in the stream do not vary significantly with flow; however, other chemical changes in the stream result in significantly different WQC under different flow conditions.

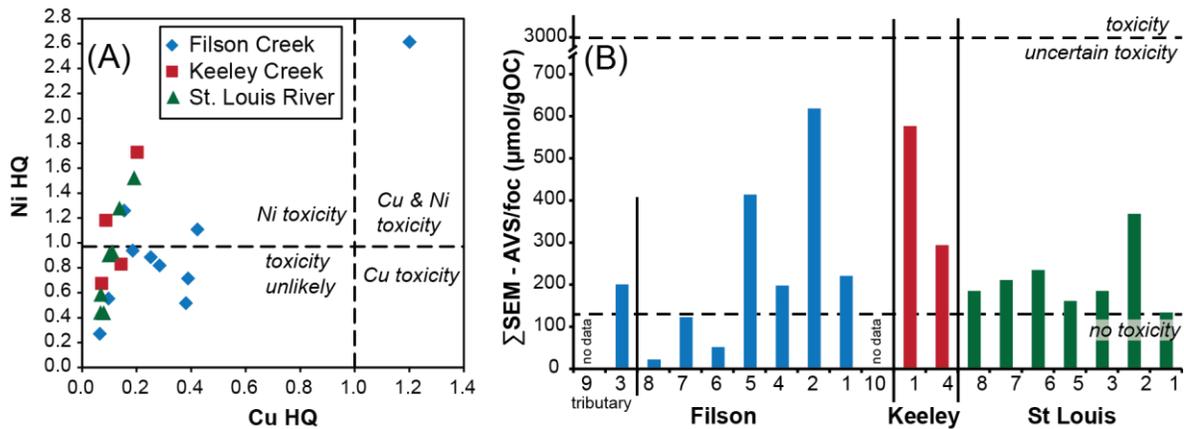
The main elements of concern regarding benthic organism toxicity from streambed sediments include Cu as well as Ni and Cr. Partial digestions using a DIBK extraction suggest metals such as Cd, Cu, Pb, and Zn are likely partitioned into the more soluble and bioaccessible phases and not tightly bound to less reactive silicates (Figure 5). Although not analyzed in the DIKB extractions, only a small fraction of Ni and Cr was extracted during the AVS-SEM procedure suggesting that these elements, in addition to Cu, are not bound to less bioaccessible sulfides (Figure 5). Overall, both extractions suggest potentially toxic metals in sediments may be hosted in more bioaccessible forms such as sorbed onto clays and hydroxide phases that are available for benthic organism uptake.

Similar to the inconsistent predictions for water toxicity based on the BLM and hardness-based approaches, the sediment BLM approach suggests a different level of toxicity from sediments than would be predicted from consensus-based guidelines.



**Figure 6** (A) Hardness-based and BLM-based HQs of chronic Cu toxicity. (B) Range in Cu concentrations and BLM- based chronic WQC for various proportions of HA for low and medium-high flows for Filson Creek site 2.

Several HQs for Ni and one HQ for Cu are greater than 1 when calculated using the consensus-based guidelines (i.e., PEC), which suggests toxic conditions (Figure 7A). In comparison, no toxicity (< 130 micromoles per gram of organic carbon, µmol/gOC) to uncertain toxicity (130 to 3,000 µmol/gOC) is predicted based on Equilibrium Partitioning Sediment Benchmarks (ESB) (USEPA, 2005) (Figure 7B). This approach includes: 1. determining extractable (a proxy for bioaccessible) metal concentrations (i.e., combined simultaneously extracted metals,  $\Sigma SEM = SEM_{Cd} + SEM_{Cu} + SEM_{Ni} + SEM_{Pb} + SEM_{Zn}$ ); 2. adjusting them for potential incorporation into less bioaccessible sulfides (i.e., acid volatile sulfide, AVS); and 3. Adjusting for complexation with organic carbon (i.e., fraction of organic carbon,  $f_{oc}$ ). The high organic carbon in some of the sediments could sequester significant amounts of trace elements; however, the low AVS suggest trace elements bound to sulfides are not significant components in these sediments.



**Figure 7** (A) Consensus-based HQ for Ni and Cu in sediment. (B) ESB for sediment samples by watershed and plotted upstream of downstream.

## CONCLUSION

The chemistry of surface water and stream sediment in three watersheds from the Duluth Complex is variable due to different mineralization styles. The water chemistry also changes seasonally for most major and trace elements. However, the concentration of Cu, the main element of concern in these watersheds with regard to aquatic toxicity, and DOC only vary within a narrow range for each watershed among the various seasons and flow conditions sampled. The complexation of Cu with DOM significantly limits the bioaccessibility of dissolved Cu, and the generally consistent concentrations of DOM ensure the continued resiliency of water in Duluth watersheds to toxicity year round. As for the sediments, Cu and trace elements may occur in the more bioaccessible forms; however, organic carbon in some of the sediments may help to sequester significant amounts of trace elements. The high organic matter in waters and some sediments certainly plays a key role in protecting aquatic organisms from naturally-occurring concentrations of Cu and other elements in these mineralized watersheds. Nonetheless, the productivity and subsequent organic content of the stream waters and sediments could change if their chemistry is impacted by drainage from future mining (i.e., increase in metals and acidity). Changes in the amount of organic matter and its composition (i.e., changes in the fraction of humic and fulvic acids) could also influence the capacity of organic matter to bind metals and thus limit toxicity to aquatic organisms.

## ACKNOWLEDGEMENTS

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