

## Implications of high dissolved organic carbon concentrations on potential copper toxicity in surface waters in the vicinity of Cu-Ni-PGM deposits of the Duluth Complex, northeastern Minnesota

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**Abstract** Regional baseline surface-water sampling was conducted in northeastern Minnesota to understand the potential effect of high dissolved organic carbon (DOC) concentrations on copper toxicity to aquatic organisms in the context of proposed new mining in the area. The low-sulfide magmatic Cu-Ni-platinum group metal (PGM) deposits of the Duluth Complex have significant potential for future mining. The four main deposits that currently represent advanced exploration targets are Spruce Road, Maturi, Birch Lake, and NorthMet. They are distributed along a 40 km strike length trending NE–SW. These deposits are dominated by disseminated Cu-Ni-Fe sulfide minerals and occur near the base of troctolitic intrusions that comprise the complex. The surface-water hydrology of the area consists of lakes and wetlands connected by streams and rivers. The average annual precipitation is 71 cm, the average low temperature in January is  $-23^{\circ}\text{C}$  and the average high temperature in July is  $9^{\circ}\text{C}$ .

Nineteen sites along streams that transect the complex were sampled in September 2012 near base-flow conditions to document pre-mining baseline water-quality conditions. The samples were neutral ( $\text{pH } 6.9 \pm 0.4$ ), dilute ( $\text{EC } 59 \pm 20 \mu\text{S/cm}$ ), and oxic (dissolved oxygen  $7.6 \pm 1.8 \text{ mg/L}$ ). The dissolved cations were dominated by Ca ( $5.1 \pm 2.2 \text{ mg/L}$ ) and Mg ( $4.2 \pm 1.6 \text{ mg/L}$ ) with lesser Na ( $1.8 \pm 0.9 \text{ mg/L}$ ) and K ( $0.3 \pm 0.1 \text{ mg/L}$ ). Bicarbonate, as reflected by the alkalinity values ( $19.8 \pm 8.7 \text{ mg/L CaCO}_3$ ), and sulfate ( $2.2 \pm 0.7 \text{ mg/L}$ ) were the dominant anions. Water hardness ranged from 18.1 to 49.6  $\text{mg/L CaCO}_3$  and DOC concentrations were substantial, ranging from 17.7 to 46.7  $\text{mg/L}$ . Substantial dissolved trace elements were Fe ( $472 - 3,950 \mu\text{g/L}$ ), Al ( $54.4 - 228 \mu\text{g/L}$ ), Cu ( $0.8 - 7.7 \mu\text{g/L}$ ), Ni ( $1 - 4.8 \mu\text{g/L}$ ), and Co ( $0.4 - 2.5 \mu\text{g/L}$ ).

The toxicity of Cu and other trace elements to aquatic organisms commonly associated with mining is known to vary with water chemistry. Site-specific water-quality criteria for Cu were calculated for these samples using both the U.S. Environmental Protection Agency hardness-base equation and the Biotic Ligand Model (BLM) to evaluate the potential role of local water chemistry on the toxicity of dissolved Cu. Results using the hardness-based equation suggest acute toxicity can be expected from dissolved Cu concentrations beginning at 3.5 to 9.2  $\mu\text{g/L}$ . Based on this model, six samples exceeded acute criteria. In contrast, results from the BLM, which uses a broader range of water-quality parameters including DOC concentrations, suggest that acute toxicity can be expected from significantly higher concentrations beginning at 4.3 to 130.5  $\mu\text{g/L}$ . All samples were below the BLM-based criteria. Thus, results from the BLM suggest that complexation with DOC should significantly mitigate the toxicity of Cu in the watersheds in the vicinity of the Duluth Complex.

**Keywords** platinum-group metals, copper, surface water, biotic ligand model, Minnesota

