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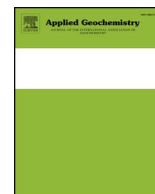
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Water quality impacts and river system recovery following the 2014 Mount Polley mine tailings dam spill, British Columbia, Canada

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ABSTRACT

The Mount Polley mine tailings embankment breach on August 4th, 2014, in British Columbia, Canada, is the second largest mine waste spill on record. The mine operator responded swiftly by removing significant quantities of tailings from the primary receiving watercourse, stabilizing the river corridor and beginning construction of a new river channel. This presented a unique opportunity to study spatial patterns of element cycling in a partially-restored and alkaline river system. Overall, water quality impacts are considered low with Cu, and to a lesser extent V, being the only elements of concern. However, the spatial pattern of stream Cu loading suggested chemical (dominant at low flow) and physical (dominant at high flow) mobilization processes operating in different parts of the watershed. Chemical mobilization was hypothesized to be due to Cu sulfide (chalcopyrite) oxidation in riparian tailings and reductive dissolution of Cu-bearing Fe oxides in tailings and streambed sediments whereas physical mobilization was due to erosion and suspension of Cu-rich stream sediments further downstream. Although elevated aqueous Cu was evident in Hazeltine Creek, this is considered a relatively minor perturbation to a watershed with naturally elevated stream Cu concentrations. The alkaline nature of the tailings and the receiving watercourse ensures most aqueous Cu is rapidly complexed with dissolved organic matter or precipitates as secondary mineral phases. Our data highlights how swift removal of spilled tailings and river corridor stabilization can limit chemical impacts in affected watersheds but also how chemical mobilization (of Cu) can still occur when the spilled tailings and the receiving environment are alkaline. We present a conceptual model of Cu cycling in the Hazeltine Creek watershed.

1. Introduction

On August 4th, 2014, a partial embankment breach of the Mount Polley tailings storage facility (TSF) in British Columbia, Canada, led to the release of approximately 25 Mm³ of mine tailings and supernatant water into the Quesnel River Watershed (WISE, 2016; Petticrew et al., 2015). The embankment breached due to a geotechnical failure of a layer of glacio-lacustrine clay in the foundation materials below the dam (Independent Expert Engineering Investigation and Review Panel, 2015). The Mount Polley event was significant for four reasons. First, at the time of the accident it was the largest ever documented spill of mine

tailings into the environment (WISE, 2016). Second, among tailings spills, the Mount Polley accident was unusual in that the tailings are not acid-generating and contain generally low levels of trace metals and metalloids when compared to typical tailings (Golder Associates Ltd, 2015; Kossoff et al., 2014). Third, the environmental clean-up operations were swift; within one year of the event a significant volume of the spilled tailings had been removed from the major receiving watercourse and an extensive river restoration scheme was under construction (Independent Expert Engineering Investigation and Review Panel, 2015). Fourth, the Mount Polley spill highlighted the increasing global environmental risk of such events, due to the growing number of

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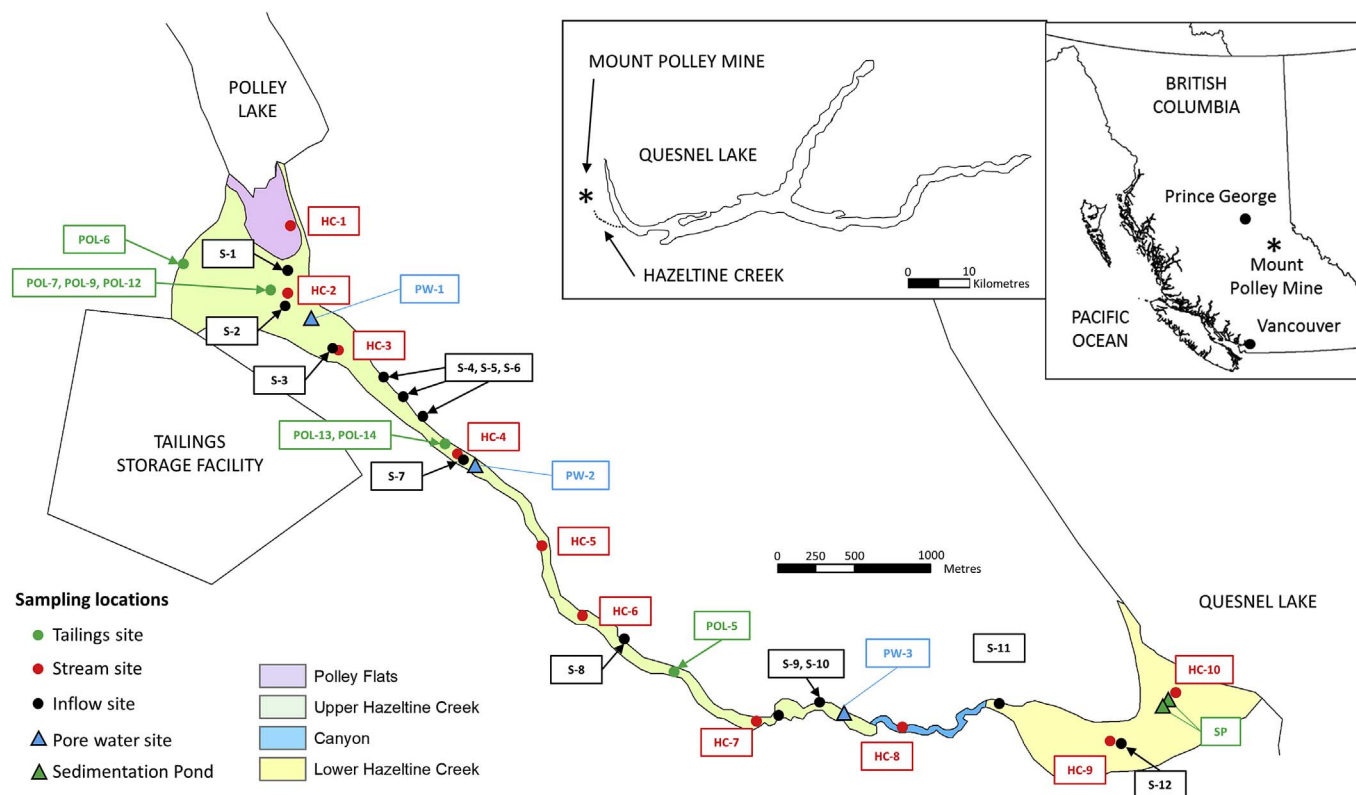


Fig. 1. Location of study area showing tailings, stream (streamflow and water quality) and inflow (water quality only) sample sites.

mining operations and higher waste to ore ratios, and due to the growing vulnerability of these types of environments to extreme hydro-meteorological events (Hudson-Edwards, 2016).

Following the embankment breach, tailings material initially discharged north into Polley Lake before forming a ‘plug’ (area known as Polley Flats in Fig. 1) that blocked water flowing from Polley Lake. The tailings material subsequently flowed south-east into Hazeltine Creek and then discharged into the West Basin of Quesnel Lake. The tailings material initially eroded the existing valley, both vertically and laterally (SNC-Lavalin Inc, 2015). Subsequently, thick deposits of tailings (up to 3.5 m thick) occurred primarily near Polley Lake and in Lower Hazeltine Creek with thinner layers occurring in other parts of the creek. Tailings were deposited within the riparian zone up to 100 m from Hazeltine Creek.

The ore body at Mount Polley is a typical alkalic porphyry Cu-Au deposit with supergene enrichment (McMillan, 1996). The dominant ore mineral is chalcopyrite (CuFeS_2), but Cu also occurs as other sulfide (bornite – Cu_5FeS_4 , covellite – CuS , digenite – Cu_9S_5), silicate (chrysocolla – $(\text{Cu},\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$) and carbonate hydroxide minerals (malachite – $\text{Cu}_2\text{CO}_3(\text{OH})_2$) (Henry, 2009). Importantly, the ore has a low sulfide (0.1–0.3 wt. %) and high calcite (5–10 wt. %) content giving it a high neutralization potential. Tailings generated from the processing of Mount Polley ore also have generally low metal concentrations (mg kg^{-1} : As, 8–13; Cd, 0.1–0.3; Cr, 8–55; Cu, 65–1475; Pb, 4–12; Hg, < 0.1–0.3; Ni, 6–36.4; Se, 0.3–1.9; V, 86–295; Zn, 40–82) (SRK Consulting (Canada) Inc, 2015c) when compared to other spilled tailings (Bird et al., 2008; Hudson-Edwards et al., 2003).

Evidence from water sampling surveys carried out in Hazeltine Creek shortly after the breach revealed elevated above British Columbia Water Quality Guidelines – BCWQG (British Columbia Ministry of Environment (BCMoE), 2017) filtered concentrations of several metals including Cu (maximum: $86 \mu\text{g L}^{-1}$) and Se (maximum $33 \mu\text{g L}^{-1}$) that have decreased substantially since the event (Golder Associates Ltd, 2015). Following the breach, Mount Polley Mining Corporation

implemented an on-going rehabilitation and remediation strategy that has involved removing tailings from Lower and Upper Hazeltine Creek and construction of a new rock-lined channel and fish habitat (MPMC, 2015). Early evidence from geochemical investigations (humidity cell and column tests) suggests Cu has limited environmental mobility (predicted maximum Cu concentration of $20 \mu\text{g L}^{-1}$) due to the low acid generating potential of the tailings (SRK Consulting (Canada) Inc, 2015c). Overall, this result suggests the tailings may be relatively non-reactive, thereby limiting the potential long-term chemical impacts of the spill. However, column tests, while very useful, cannot entirely replicate environmental conditions in complex field sites, especially at the interface between deposited tailings and the river corridor, where temperature, daylight, microbial activity, redox potential, pH and hydrology are constantly changing. Watershed-scale investigations of trace metal dynamics are therefore required to supplement existing laboratory-based microcosm data and to determine the environmental risk of residual tailings in the stream corridor.

The Mount Polley tailings spill presents a unique opportunity to study water quality impacts and water-sediment interactions in a receiving watercourse whose valley morphology was re-set by the spill event and whose channel has subsequently been modified and realigned. Since the event, there have been several environmental impact studies conducted by consultants on behalf of Mount Polley Mining Corporation (Golder Associates Ltd, 2015; Minnow Environmental Inc, 2015; SNC-Lavalin Inc, 2015; SRK Consulting (Canada) Inc, 2015a, b). The initial impacts of the spill on Quesnel Lake have also been documented (Petticrew et al., 2015). However, this work represents the first peer-reviewed study of the chemical impacts of the tailings spill on the primary receiving watercourse. Our specific objectives were to: (1) establish the spatial pattern and sources of element loading (specifically Cu) in Hazeltine Creek and (2) assess the potential for residual alkaline tailings in a partially-restored river corridor to influence short-to long-term aqueous chemistry.

2. Methods

2.1. Study site

Mount Polley Cu and Au mine is located approximately 275 km south-east of Prince George, British Columbia, Canada (Fig. 1). Hazeltine Creek is the main outlet of Polley Lake, draining an area of 112 km², and flowing approximately 9.5 km into Quesnel Lake. Bedrock geology in the catchment is dominated by Mesozoic (252–66 Ma) basaltic and andesitic volcanic assemblages. The upper watershed sits partially within Late Triassic (235–201 Ma) alkalic intrusions that host the porphyry mineralization (McMillan, 1996).

Prior to the spill, the Hazeltine Creek corridor was well forested with an average bank full width of 5 m and consisted of riffle-pool sequences and a bedload of predominantly cobbles and gravel (SNC-Lavalin Inc, 2015). Following the spill, a thick deposit of tailings (typically 1 m deep, but in some locations > 3.5 m) was deposited near the dam and in parts of upper Hazeltine Creek. Most of Upper Hazeltine Creek experienced rapid and steep erosion and eventually a thin layer of tailings deposition (10–20 cm deep). At approximately 4800–4900 m and 5600–6600 m downstream of the TSF, the spilled tailings were funneled through narrow canyons resulting in incision to bedrock and the removal of fine-grained sediments from within the channel zone. Within Lower Hazeltine Creek, the floodplain was eroded, and tailings and native material were deposited to depths from 0.15 to 1.5 m. Average bank full channel width after the breach was 18 m.

2.2. Water analyses and modelling

A synoptic sampling mass balance approach was utilized to identify the spatial pattern of constituent concentrations and loads in the Hazeltine Creek watershed and to study the main hydrological and geochemical processes driving the observed patterns. The synoptic mass balance methodology for management of mine pollution was developed by the U.S. Geological Survey (USGS) as part of the Abandoned Mine Lands Initiative and is based on synchronous water quality and flow measurements made at multiple locations across a catchment that provide detailed spatial assessments of pollutant sources (Kimball et al., 2002). Water sampling and discharge measurements were acquired under low flow conditions in 2015 and high flow conditions in 2016. Low flow sampling was performed using the velocity-area method at 10 stream sites on August 2nd, 2015 (denoted as ‘stream site’ in Fig. 1; flow range was 140–250 L s⁻¹ and typical of long-term values for August (based on 91 measurements taken over spring, summer and autumn from 1995 to 2014) (Knight Piesold Ltd, 2014)). At the time of sampling, much of the tailings had been removed in Lower Hazeltine Creek and two sedimentation ponds were operating to settle out suspended particles prior to entry to Quesnel Lake (Fig. 1). Samples were also collected at 12 locations where water was flowing from riparian tailings into the creek from seeps or drainage ditches (denoted as ‘inflow site’ in Fig. 1). In-situ pore water samples were collected (from 10 cm to 20 cm depth) at three locations in Hazeltine Creek using a stainless steel piezometer and peristaltic pump. Four additional water chemistry and flow measurements (using the tracer dilution technique) were collected in Hazeltine Creek under high flow conditions (flow range was 600–680 L s⁻¹ and typical of long-term spring freshet values (Knight Piesold Ltd, 2014)) in July 2016 in order to investigate potential water quality impacts during fall storm events or spring snowmelt. Measurements from four creeks in the Quesnel River Watershed that were unaffected by the tailings spill were also collected in July 2016 in order to establish the magnitude of impact in Hazeltine Creek compared to the regional baseline.

Total and filtered (0.45 µm) cation (Al, Ca, K, Mg, Na, Si) and trace element concentrations (As, Cd, Cu, Cr, Fe, Mo, Mn, Ni, Pb, Se, V, Zn) were determined by inductively coupled plasma – optical emission spectroscopy (Thermo Scientific iCAP 6500 Duo) and – mass

spectroscopy (Thermo X-series 1), respectively. Filtered anion concentrations (Cl, F, SO₄) were determined by ion chromatography (Dionex ICS-2500). Speciation-solubility calculations, using the measured aqueous concentrations of the Hazeltine Creek water and inflow samples, were carried out using the PHREEQC code and the wateq4f.dat. thermodynamic database distributed with the code (Ball and Nordstrom, 1991; Parkhurst and Appelo, 1999). Additional information on the quality control and sampling and analytical protocols can be found in the [electronic Supplementary Information](#). As a result of the physical impacts of the tailings spill in Hazeltine Creek, the stream was not considered to be fish habitat at the time of this study. However, even though the stream is currently not significantly utilized by aquatic organisms, aquatic habitat is an intended future use in the longer term. Therefore, water quality was assessed based on comparisons to British Columbia Water Quality Guidelines (BCWQG) (British Columbia Ministry of Environment (BCMoE), 2017). The 0.45 µm fraction is defined as ‘filtered’ in this study and is not intended to be representative of the truly dissolved fraction.

2.3. Sediment analyses

The concentration of Cu in within-channel sediments, deposited at the channel margin along Hazeltine Creek, were measured in the field by portable X-ray fluorescence (pXRF) (Niton XLp 300) with an analysis time of 60 s. Polished blocks of selected samples of tailings deposited soon after the 2014 spill, and of sediments and ochres remaining in the floodplain in 2016 (denoted as ‘tailings site’ in Fig. 1), were examined under low vacuum with the BSE detector on the Mineral Liberation Analysis (MLA) 650 FEG ESEM at Queen's University, Canada. SEM-MLA has previously been used in environmental mineralogical studies to characterize and quantify mine waste metal- and metalloid-bearing phases (Bromstad et al., 2017; DeSisto et al., 2016). A Cu-bearing Fe oxide phase was added to the library of minerals included in the SEM-MLA software, for which Fe oxides with c. > 0.1 wt% Cu could be detected and mapped.

3. Results and discussion

3.1. Water quality impacts

Stream pH values were generally greater than 8.5 throughout the entire reach but ranged between a high of 9.3 in Upper Hazeltine Creek (HC-5) and a low of 7.5 in Lower Hazeltine Creek just upstream of the sedimentation pond (HC-9) (Supplementary Table S1). Prior to the dam spill, the mean pH of Hazeltine Creek was reported as 8.2 (Minnow Environmental Inc, 2009). Diel variation in stream pH (Supplementary Fig. S1) recorded opposite the TSF over a 4-day period (30th July to 2nd August 2015) showed a range from 7.0 to 8.7 before and on the day of the synoptic sampling (2nd August). Some variation on the day of synoptic sampling may reflect enhanced photosynthesis due to clear skies (Gammons et al., 2015) and lower water levels due to the operation of a streamflow control device (a weir was installed to control flow during stream reconstruction). The pH values of sampled inflows (range: 7.8–8.7) were generally lower than stream samples (range: 7.5–9.3) (Supplementary Table S1), particularly at sites in Upper Hazeltine Creek, suggesting that the inflow waters pHs were buffered by mixing with the stream water. The pH values of inflow and stream waters were more similar in Lower Hazeltine Creek suggesting mixing of subsurface water and stream water in this reach. This result may explain the spatial variation of stream pH with more buffering capacity existing in Upper Hazeltine Creek. The high buffering capacity of stream water (range: 139–178 mg L⁻¹ CaCO₃) in Hazeltine Creek, combined with the high calcite and low sulfur content of the spilled tailings (SRK Consulting (Canada) Inc, 2015b), explains the alkaline pH of the stream water. Concentrations of most major ions (filtered, mg L⁻¹: Ca, 44–357; K, 19–117; Mg, 8–77; Na, 8–120; Si, 3–11) were highest in inflows in

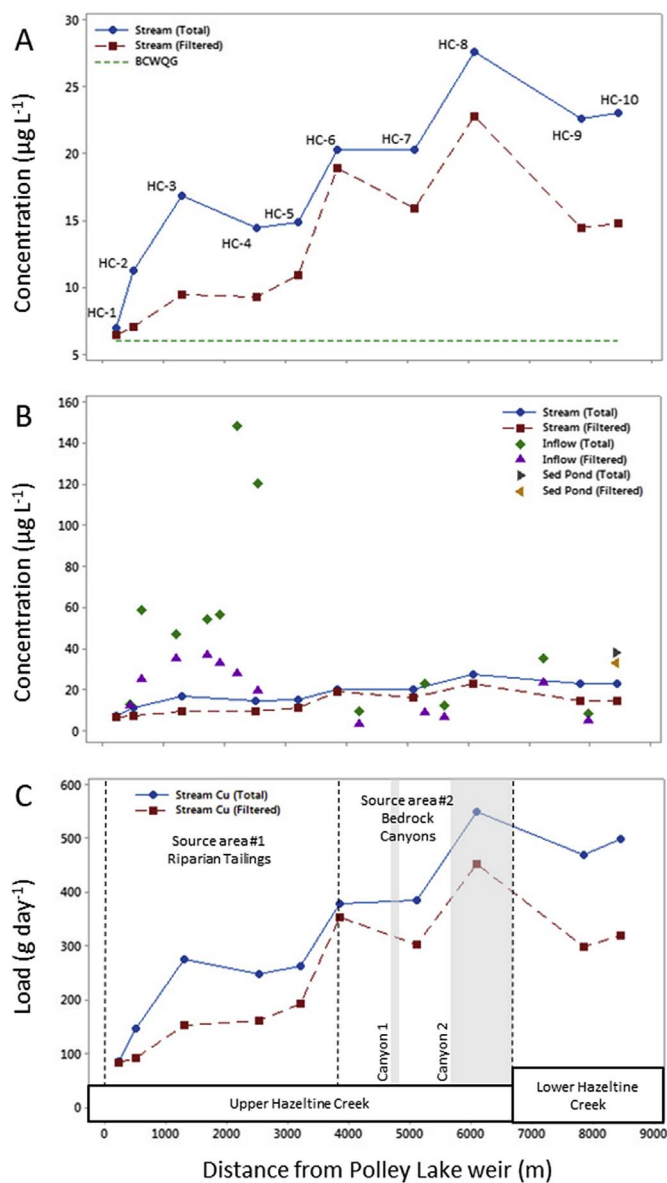


Fig. 2. (A) Spatial profiles of stream total and filtered Cu concentrations with British Columbia Water Quality Guideline (BCWQG). (B) Spatial profile of stream filtered Cu concentration and inflow (total and filtered) Cu concentrations. (C) Spatial profiles of total and filtered Cu loads. Samples were collected in August 2015.

Upper Hazelatine Creek, and gradually decreased in the downstream direction (Supplementary Table S1 and Supplementary Table S2).

Total and filtered (0.45 µm) concentrations of Cd, Mo, Ni, Pb, Se and Zn in Hazelatine Creek stream water were found to be less than British Columbia Water Quality Guidelines (BCWQGs – filtered concentrations, µg L⁻¹: Cd, 1; Mo, 500; Ni, 150; Pb, 170; Se, 2; Zn, 97). Filtered As (range: 7–8 µg L⁻¹) and Cr (range: 2–5 µg L⁻¹) concentrations were slightly above environmental standards (BCWQGs – µg L⁻¹: As, 5; Cr, 1) but Cr concentrations were comparable with pre-event concentrations (range: < 1–4 µg L⁻¹) (Golder Associates Ltd, 2015). Fe and Mn (and Al) concentrations were within aquatic environmental standards and similar to pre-event concentrations (Golder Associates Ltd, 2015). Filtered V concentrations (range: 7–12 µg L⁻¹) were elevated compared to pre-event concentrations (median: 1 µg L⁻¹) (Golder Associates Ltd, 2015) suggesting further investigation into the fate and behavior of this element is warranted. However, the main element with elevated concentrations was found to be Cu; total (range: 7–28 µg L⁻¹) and filtered (range: 7–23 µg L⁻¹) concentrations were above environmental

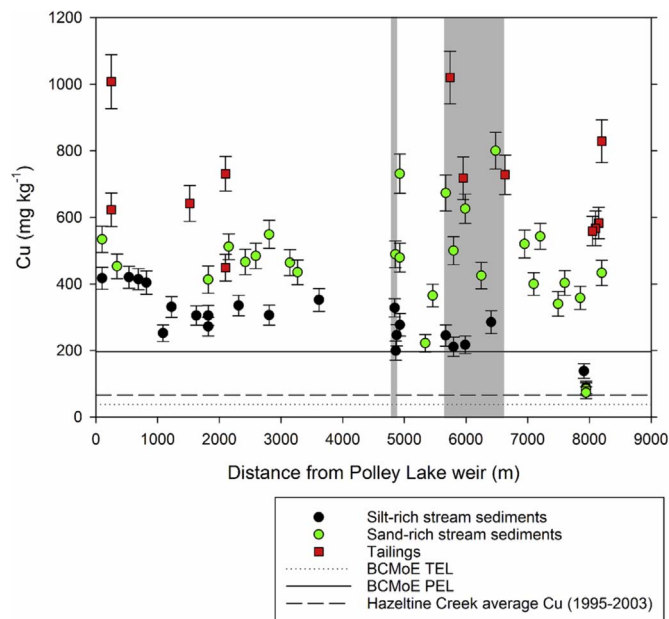


Fig. 3. pXRF-derived Cu concentrations of sediments in Hazelatine Creek sampled on August 1st, 2014. Dotted line and solid line represent British Columbia Ministry of Environment (BCMoE) Threshold Effect Limits (TEL) and Predicted Effect Limits (PEL), respectively (British Columbia Ministry of Environment (BCMoE), 2015). The dashed line represents the Hazelatine Creek average Cu concentration from 1995 to 2003 (Golder Associates Ltd, 2015). Grey vertical bars represent the locations of two bedrock canyons at 4800–4900 m and 5600–6600 m below Polley Lake weir.

guidelines (BCWQGs – µg L⁻¹: Cu, 6) throughout Hazelatine Creek and increased with distance downstream (Supplementary Table S1 and Fig. 2a). In Upper Hazelatine Creek, around the area known as the Polley Flats (0–3000 m below Polley Lake weir), Cu was higher in inflows than in the stream water (Fig. 2b). This result suggests that the inflows were receiving Cu from residual tailings and caused an increase in stream Cu in this part of the watershed. However, inflow Cu concentrations farther downstream (3000–8500 m below Polley Lake weir) were more similar to, or lower than, stream water concentrations in Lower Hazelatine Creek, suggesting surface inflow waters were not the only source of Cu in the watershed.

3.2. Sediment quality impacts

pXRF survey of within channel sediments along the entire length of Hazelatine Creek revealed elevated Cu concentrations throughout the river corridor at the time of our sampling in 2015 (Fig. 3). Copper concentrations in material present on the floodplain surface up to 50 m distance from the channel ranged from 88 to 1020 mg kg⁻¹. These values exceeded both the threshold effect level (TEL: 37.5 mg kg⁻¹) and predicted effect level (PEL: 197 mg kg⁻¹) for Cu (British Columbia Ministry of Environment (BCMoE), 2015), and also the mean Cu concentrations of Hazelatine Creek sediments before the breach (Minnow Environmental Inc, 2015). The Cu concentrations reported were comparable to other rivers affected by tailings spills (Bird et al., 2008; Hudson-Edwards et al., 2003; Kossoff et al., 2014) and historical mining operations (Gilchrist et al., 2009; Macklin et al., 2006). Cu concentrations were elevated in both silt-sized material, believed to reflect tailings-dominated material (range 89–419 mg kg⁻¹) and sand-sized material, believed to reflect magnetite-rich sands (range 72–800 mg kg⁻¹). The highest concentrations occurred in the magnetite sands in the second canyon between 5700 and 6700 m (Fig. 3).

3.3. Stream copper loading and source areas

Synoptic sampling of streamflow and stream Cu concentrations is

used here to identify and quantify sources of Cu to Hazeltine Creek under low flow conditions. Flow measurements are presented in [Supplementary Fig. S2](#). Spatial profiles of filtered and total Cu loading show a general increase downstream of the Polley Lake weir ([Fig. 2c](#)); the maximum filtered (453 g day^{-1}) and total (549 g day^{-1}) loads were recorded at HC-8. The primary source of total (67%) and filtered (68%) Cu loading in Hazeltine Creek was the reach from HC-1 to HC-6 (0–4000 m) which comprised residual tailings in Upper Hazeltine Creek ([Fig. 2c](#); source area #1). In this reach, filtered Cu loads increased consistently and there was no difference between cumulative (the sum of all loadings in the reaches where a positive change in loading was measured) and measured filtered Cu loads ([Supplementary Fig. S3](#)), suggesting there was no chemical attenuation (precipitation or adsorption) of Cu here. Total loads exhibit a similar profile to filtered loads in this reach aside from a slight decrease in load between HC-3 and HC-4. The general increase in Cu loading through this reach is most likely due to inflow waters with elevated filtered and particulate Cu concentrations that are draining the residual tailings ([Fig. 2b](#)). The increase in filtered and total loads between HC-5 and HC-6 was probably due to surface and/or subsurface inflows that were not sampled. The secondary source of total (33%) and filtered (32%) Cu loading was the reach from HC-6 to HC-10 which comprised the two bedrock canyons and Upper Hazeltine Creek ([Fig. 2c](#); source area #2). Copper loading through this reach was more variable than further upstream but a notable increase in total and filtered loads occurred through Canyon 2 (HC-8) followed by similar magnitude decreases downstream of the canyon in Lower Hazeltine Creek (HC-9). A slight increase in loads downstream of the sedimentation pond (HC-10) prior to discharge into Quesnel Lake was probably due to elevated Cu concentrations in the sedimentation pond ([Fig. 2b](#)). Considering stream Cu loading in the entire watershed, the differences between cumulative and measured Cu loads suggests 18% and 39% of the total and filtered Cu, respectively, added to Hazeltine Creek along its course was attenuated prior to discharge into Quesnel Lake ([Supplementary Fig. S3](#)). The alkaline stream water and high calcite and low sulfur content of the Mount Polley tailings undoubtedly limits mobilization and transport of Cu and other trace metals in Hazeltine Creek ([Nordstrom, 2011](#)). Nevertheless, the gradual increase in Cu concentrations and loads in the stream suggests aqueous and total Cu phases were influencing stream chemistry ([Fig. 2](#)). The following sections present results and discussion aimed at elucidating the mechanisms that may be responsible for the observed spatial pattern of Cu loading.

3.4. Copper mobilization and transport

The primary source of stream Cu loading identified in 2015 was the residual tailings (0–4000 m) in Upper Hazeltine Creek. Whilst on-going remediation activities in Hazeltine Creek have removed much of the spilled tailings, substantial volumes remain in the river corridor (most notably in the Polley Flats area opposite the TSF in Upper Hazeltine Creek) intermixed with natural materials. Groundwater seeps and drainage ditches in Upper Hazeltine Creek that were connected to Hazeltine Creek in 2015 contained elevated concentrations of filtered (up to $37 \mu\text{g L}^{-1}$) and total Cu (up to $148 \mu\text{g L}^{-1}$) ([Figs. 2b and 4a](#)). At the water pH values measured in these inflows, Cu is predicted to have been present principally as Cu(II) hydroxide ($\text{Cu}(\text{OH})_2$), with Cu(II) carbonate (CuCO_3) also present in some samples. Speciation modelling of inflow waters indicates cuprite was saturated ($\text{SI} = -2$ to $+2$) ([Supplementary Table S3](#)), and minor amounts of cuprite and chrysocolla were identified in SEM-MLA, suggesting these minerals exerted a solubility control over Cu in these waters. The presence of elevated filtered Fe (up to $194 \mu\text{g L}^{-1}$), Cu (up to $38 \mu\text{g L}^{-1}$) and SO_4 (up to 966 mg L^{-1}) in these inflows ([Fig. 4a, b, d](#)) suggests weathering of chalcopyrite (CuFeS_2) was occurring in the tailings in source area #1 ([Fig. 2c](#)). In addition, SEM-MLA investigations provide evidence of chalcopyrite altering directly to Cu-bearing Fe oxides, possibly

ferrihydrite, in the tailings ([Fig. 5a and b](#); [Supplementary Fig. S4](#)). Such Cu-bearing Fe oxide is a commonly-observed product for alkaline oxidation of chalcopyrite ([Vaughan and Coker, 2017](#); [Yin et al., 2000](#)). Weathering of Mn oxides was also indicated with elevated Mn (up to $7343 \mu\text{g L}^{-1}$) and saturation of rhodocrosite in inflow waters ([Supplementary Table S3](#)). Oxidation of chalcopyrite in near-surface tailings followed by rainfall and infiltration of rainwater into the tailings will dissolve the oxidation products and produce leachate with elevated dissolved Cu, Fe and SO_4 . This leachate could be transported through the tailings to groundwater seeps and drainage ditches through surface run-off and via subsurface flow paths along the tailings/glacial till interface. The hydraulic residence time of mobilized Cu leachate within the tailings will play an important role in Cu transport to groundwater seeps and drainage ditches and, ultimately, to stream water ([Fuller and Harvey, 2000](#); [Gandy et al., 2007](#)). Fine-grained material (such as the clay and silt-sized ‘grey’ tailings) will increase residence time and limit the rate of oxygen diffusion, thereby maintaining Cu in relatively insoluble forms ([Gandy et al., 2007](#)). Evidence from column and humidity cell tests suggests mineral solubility controls (e.g. ferrihydrite) will limit Cu leaching in fine-grained tailings where flow paths are longer than half a meter ([SRK Consulting \(Canada\) Inc, 2015a](#)). Shorter flow paths, such as those that characterize sediments in the riparian zone, are more likely to remain oxic which could explain the elevated Cu measured in riparian groundwater seeps and drainage ditches during this study.

The impact of Cu weathering in the tailings is clearly evident in the increase in total and filtered Cu concentrations in drainage ditches and inflows, and in the increase in stream Cu loads between HC-1 and HC-6. Filtered Cu increased through this reach and the relative contribution of filtered Cu to the overall Cu load increased from 0.5 (at HC-3) to 0.9 (at HC-6). There are three potential explanations for this. First, the increase could have been due to high filtered concentrations in subsurface inflows that were not sampled in this study. The valley morphology in Upper Hazeltine Creek was modified through erosion of natural materials and deposition of a mixture of tailings and natural materials which buried many smaller tributary inflows to the main river channel. Inflows from some of these inundated tributaries were evident as seeps in Upper Hazeltine Creek in 2015 and 2016. Second, complexation with dissolved organic carbon (DOC) could have increased the solubility of Cu in this reach. Copper is well known to bind strongly with DOC in aquatic environments, in the form of fulvic and humic acids, and Cu speciation is often dominated by Cu-organic complexes ([Stumm and Morgan, 1996](#); [Tipping et al., 2002](#)). Whilst DOC concentrations were not measured in the present study (and therefore, not modelled using PHREEQC in this study), a previous study found that elevated Cu concentrations in drainage ditches and stream water in Upper Hazeltine Creek, believed to be due to drainage from a cedar swamp, coincided with elevated concentrations of DOC ([SRK Consulting \(Canada\) Inc, 2016](#)). In addition, speciation modelling suggested that $> 93\%$ of dissolved Cu was complexed with organic ligands ([SRK Consulting \(Canada\) Inc, 2016](#)). Third, kinetic constraints on mineral solubility could have prevented Cu from precipitating between HC-1 and HC-6. Speciation modelling suggests stream water from HC-1 to HC-6 was less saturated with respect to cuprite than inflow waters ([Supplementary Table S3](#)). In reality, it is probably a combination of these three processes that accounts for the behavior of Cu through this reach. Weathering of chalcopyrite in residual tailings, and erosion/suspension of particulate Cu phases in the stream corridor, caused elevated total and filtered Cu concentrations in drainage ditches and surface and subsurface inflow waters. Kinetic constraints in the stream water from HC-1 to HC-6 could then have prevented Cu from precipitating; in this scenario Cu was most likely complexed with DOC.

Whilst chalcopyrite weathering in riparian tailings may have been the primary source of Cu loading in Hazeltine Creek, evidence from this study suggests another potential source of aqueous Cu throughout the stream corridor at the time of sampling. Filtered concentrations of Cu

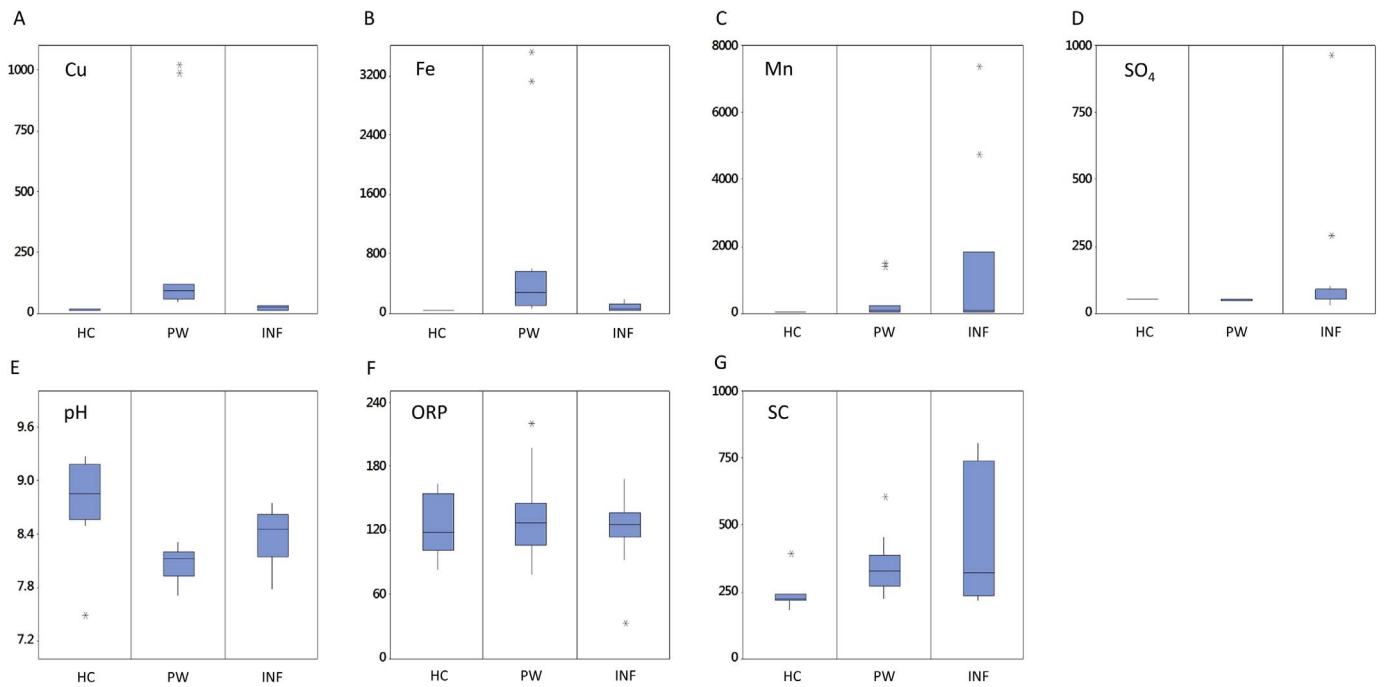


Fig. 4. Summary of (A–C) filtered Cu, Fe, and Mn concentrations ($\mu\text{g L}^{-1}$), (D) sulfate (mg L^{-1}), (E) pH, (F) ORP (mV) and (G) specific conductivity ($\mu\text{S cm}^{-1}$) in Hazeltine Creek stream water (HC), streambed pore waters (PW) and watershed inflows (INF).

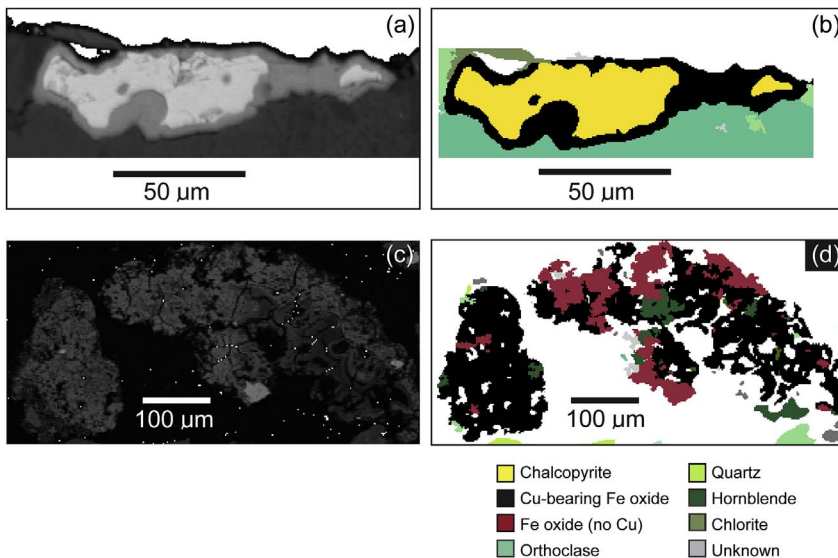


Fig. 5. (a) Backscatter SEM image showing chalcopyrite (white) altered to Cu-bearing Fe oxide (medium grey) in sample POL5; (b) MLA mineral apportionment of (a); (c) backscatter SEM image of Fe ochre sample POL13; (d) MLA mineral apportionment of (c) showing abundance of Cu-bearing Fe oxide.

were found to be elevated (range: $43\text{--}1017 \mu\text{g L}^{-1}$) in sediment pore waters (relative to stream waters) recovered through in-situ sampling (Figs. 4a and 6a), suggesting a mechanism of Cu release was operating in the stream sediments. Release of Cu in the streambed could be related to either oxidation of chalcopyrite or reductive dissolution of Cu-bearing oxides. Whilst Cu sulfides can be oxidized in subaqueous environments if the waters contain sufficient oxygen (Todd et al., 2003), an increase in SO_4 in pore waters would have been expected to accompany the increase in filtered Cu as evidence of Cu sulfide weathering, and this was not evident in Hazeltine Creek pore waters (Figs. 4d and 6d). A more plausible mechanism for Cu release in the streambed is reductive dissolution of Cu-bearing Fe oxides given the elevated filtered concentrations of Fe (range: $63\text{--}3510 \mu\text{g L}^{-1}$) and Mn ($18\text{--}1468 \mu\text{g L}^{-1}$) found in sediment pore waters (relative to stream waters) (Fig. 4b and c and Fig. 6b and c). Filtered Fe and Mn was strongly and significantly correlated with filtered Cu in the streambed pore waters

(Supplementary Fig. S4). In addition, sequential extraction tests conducted on Hazeltine Creek sediment indicates that the reducible geochemical phase is an important host for Cu (Minnow Environmental Inc, 2015; SRK Consulting (Canada) Inc, 2015c) and several investigations have highlighted reductive dissolution as an important mechanism driving aqueous Cu release in the streambed (Calmano et al., 1993). Although positive ORP values were recorded in pore waters in this study (Fig. 4f), potentially suggesting an oxic system, in the absence of low pH (acidic) streambed pore waters, the only mechanism capable of producing the high filtered Fe and Mn concentrations found in Hazeltine Creek pore waters was reductive dissolution (Kimball et al., 2016). The highest pore water Cu and Fe concentrations were generally recorded at 10 cm depth but then declined at 0 cm depth (surface water) suggesting that diffusion of the released Cu to stream water was mediated by (co)precipitation and/or sorption reactions (Fig. 6). Cuprite was saturated at the sediment-water interface

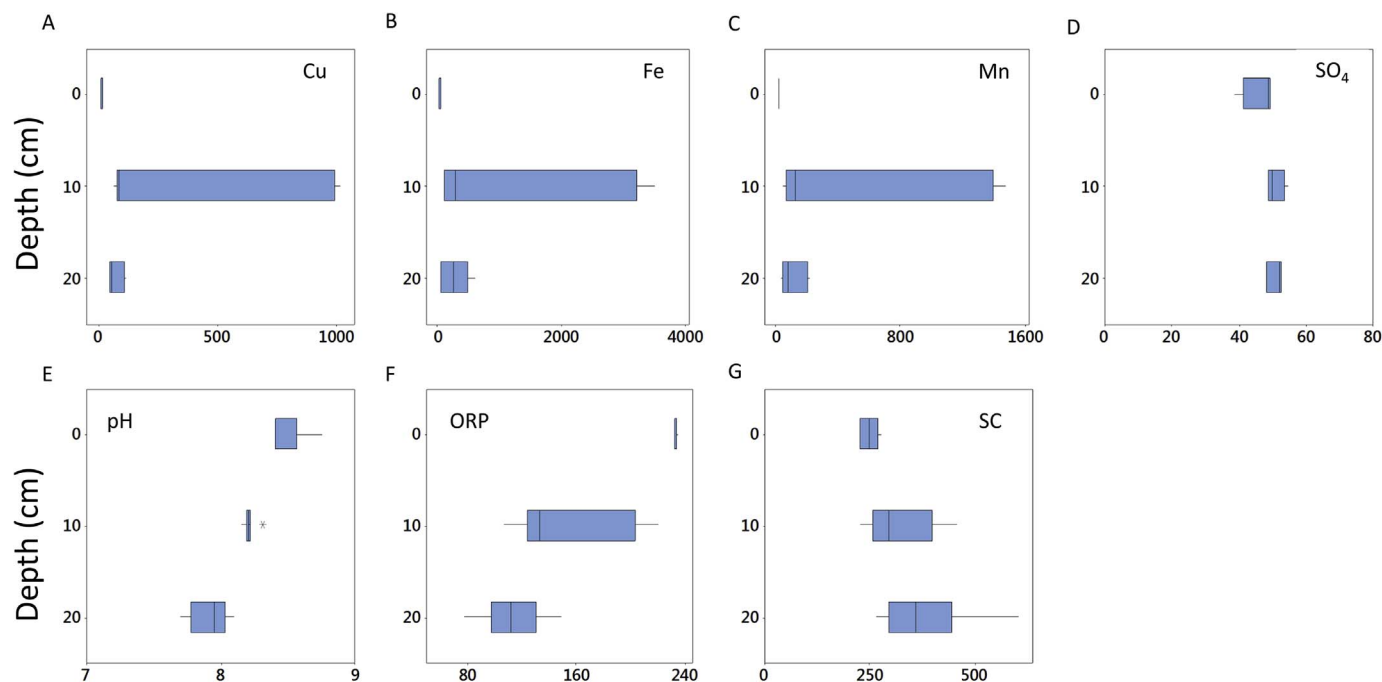


Fig. 6. Summary of (A–C) filtered Cu, Fe, and Mn concentrations ($\mu\text{g L}^{-1}$), (D) sulfate (mg L^{-1}), (E) pH, (F) ORP (mV) and (G) specific conductivity ($\mu\text{S cm}^{-1}$) in Hazeltine Creek streambed pore waters (0 cm = surface water).

(0–10 cm) (Supplementary Table S3), however ferrihydrite was supersaturated and sorption of Cu(II) to Fe oxides is well documented in neutral and alkaline systems (Kimball et al., 2016; Koski et al., 2008). Furthermore, evidence from SEM-MLA analysis indicates the presence of Cu-bearing Fe oxides in the stream sediments (Fig. 5c and d; Supplementary Fig. S4). Oxidation of the tailings chalcopyrite to Cu-bearing Fe oxide could have occurred either before (in the TSF) or after the 2014 tailings spill (in Hazeltine Creek). However, textural evidence strongly suggests that some of the Cu-bearing Fe oxides formed as discrete phases following deposition in Hazeltine Creek; this pattern is particularly evident in the Fe ochre sample collected from a seep midway down Hazeltine Creek (Fig. 5c and d). Also, the chalcopyrite: Cu-bearing Fe oxide ratio decreases from 0.36 to 0.57 in the 2014 deposited tailings, to 0.19–0.24 in the upper part of the Polley Flats, and to 0.00–0.06 in the lower part of the Polley Flats and further down Hazeltine Creek (Supplementary Table S4). This suggests that chalcopyrite oxidation and/or formation of discrete Cu-bearing Fe oxides increased in Hazeltine Creek between 2014 and 2016 and with distance downstream of the TSF.

The secondary source of Cu loading in Hazeltine Creek occurred from HC-6 to HC-10. The highest loading within this reach appeared to be Canyon 2 (5700–6700 m) in Upper Hazeltine Creek, most likely as a consequence of high water velocities and turbulence that eroded and suspended streamside and streambed sediments with high Cu concentrations (Fig. 3). Through this reach, there was a decrease in the relative contribution of filtered Cu to the overall Cu load from 0.9 (at HC-6) to 0.6 (at HC-10), suggesting (co)precipitation and/or sorption of filtered Cu species may have occurred. It appears that although Cu precipitation from HC-1 to HC-6 was limited by kinetic constraints, an approach towards thermodynamic equilibrium occurred from HC-6 to HC-10. Evidence for this can be seen in the shift from under saturation (HC-1 to HC-6) to saturation (HC-6 to HC-10) for cuprite (Supplementary Table S3) and could reflect the reduced number of inflows in the lower reach that could alter stream chemistry. As well as precipitation of secondary Cu minerals, Cu sorption to particulate Fe phases (ferrihydrite) could also have been important for removing filtered Cu (Fig. 5; Supplementary Table S4) (Kimball et al., 2016). Elevated Cu concentrations in the sedimentation pond at the time of

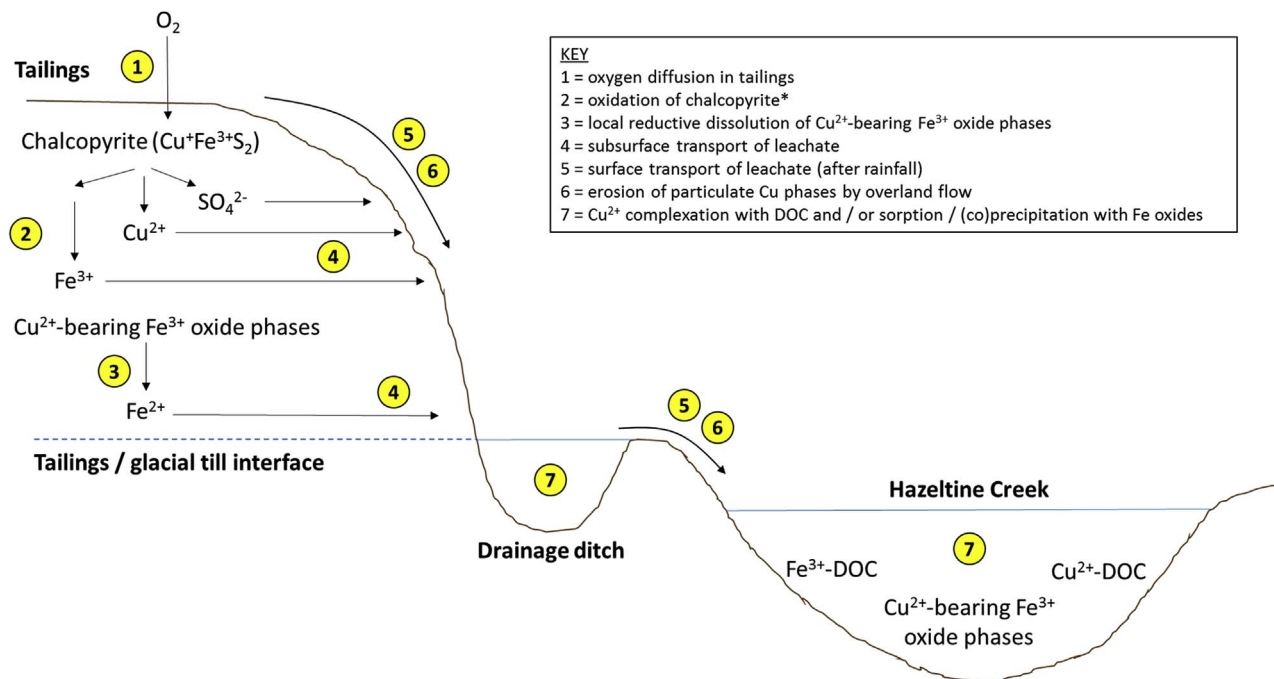
sampling probably caused the slight increase in Cu loads between HC-9 and HC-10.

Consideration of the evidence presented in this study allows us to derive a conceptual model of Cu cycling in the Hazeltine Creek watershed (Fig. 7). Oxygen diffusion in streamside tailings in Upper Hazeltine Creek could drive oxidation of chalcopyrite in near-surface tailings with reductive dissolution of Cu-bearing Fe oxides potentially occurring in deeper, anoxic tailings (Fig. 7a). Rainfall and infiltration in the tailings could dissolve the oxidation by-products which could be transported to drainage ditches and Hazeltine Creek water through surface runoff and/or subsurface flow. Any free ionic Cu present would probably form aqueous organic complexes and/or sorb to particulate Fe oxides. Copper mobilization in stream sediments could occur by reductive dissolution of Cu-bearing Fe oxides (Fig. 7b). The released Cu could form insoluble Cu sulfides in the stream sediment or diffuse through the sediment-water interface where it would be complexed with organic matter and/or sorb to particulate Fe oxides. Finally, physical mobilization of particulate Cu through Canyon 2 could occur through erosion/suspension of Cu-rich sediments and streamside tailings in this high-gradient, turbulent and constrained reach.

3.5. Long-term implications

Following the accident, Mount Polley Mining Corporation acted swiftly and removed most of the spilled tailings in Lower Hazeltine Creek within a few months of the accident. This strategy has undoubtedly reduced the short-to long-term chemical impacts in the watershed. Since this study, further tailings have been removed in Upper Hazeltine Creek, though some tailings still remain intermixed with natural soil and sediment along parts of the stream corridor. Removal of spilled tailings is the most common remedial measure taken for tailings dam spills (Kossoff et al., 2014) and has been shown to considerably reduce long-term impacts on ecosystems (Hudson-Edwards et al., 2003). However, despite the relatively low chemical impacts of the Mount Polley spill, mobilization of particulate and aqueous Cu phases was evident in Hazeltine Creek at the time of this study and could influence stream chemistry into the future. The processes driving Cu mobilization are hypothesized to be (in order of decreasing

A



B

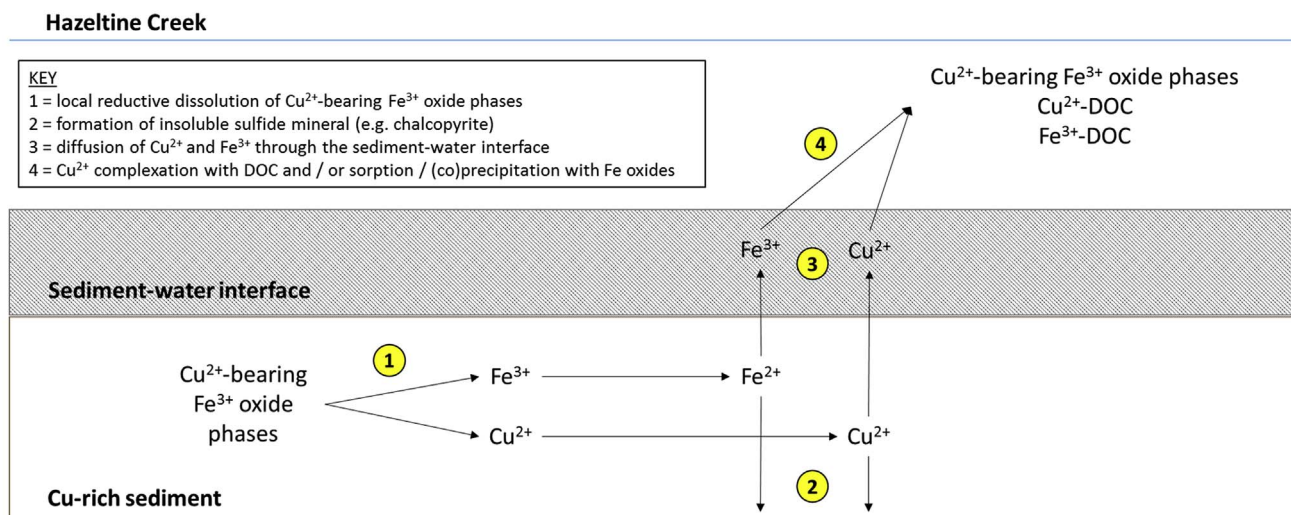


Fig. 7. Conceptual model of Cu transport and cycling in the Hazeltine Creek watershed following the mine tailings spill. A = Polley Flats; B = streambed sediments. *Recent evidence suggests oxidation of chalcopyrite may directly yield Fe³⁺ (Pearce et al., 2006).

importance): (i) chemical mobilization in streamside tailings through primary sulfide oxidation, (ii) physical erosion/suspension of particulate and colloidal phases in residual streamside and streambed tailings, and (iii) chemical mobilization in streambed sediments through reductive dissolution of Cu-bearing Fe oxides. The following sections discuss how these processes may evolve in the future and how the chemical perturbation in Hazeltine Creek compares to pre-event conditions and other mine waste-impacted watersheds around the world.

Restoration of the Hazeltine Creek river corridor was aimed at limiting further erosion of tailings and turbidity in the stream. As a result, significant reductions in element concentrations and turbidity were achieved in the weeks and months after the spill (Golder Associates Ltd, 2015; MPMC, 2015). However, increases in particulate loading observed in this study suggests physical erosion and suspension is a mechanism for Cu mobilization even at low flows. This was most

evident in the reach comprising the two canyons, possibly due to higher stream turbulence in this constricted reach and greater connectivity between the stream and deposited tailings. In the future, as river flow and water levels rise in response to rainfall or snowmelt, it will come into contact with, and possibly erode, streamside tailings (intermixed with native materials) that remain dry during lower flow conditions. This process has been shown to result in order of magnitude increases in both filtered and total metal loads in mining-affected watersheds (Byrne et al., 2013; Canovas et al., 2008; Gozzard et al., 2011; Nordstrom, 2011; Runkel et al., 2016) and is evident in the water samples taken in July 2016 under high flow conditions (Fig. 8 and Supplementary Fig. S2). While transport of Cu was predominantly as filtered load at low flow (64% at HC-9), particulate-bound load was clearly dominant at high flow (85% at HC-9), probably due to the erosion of streamside tailings. Construction of fish habitat was underway during the high flow

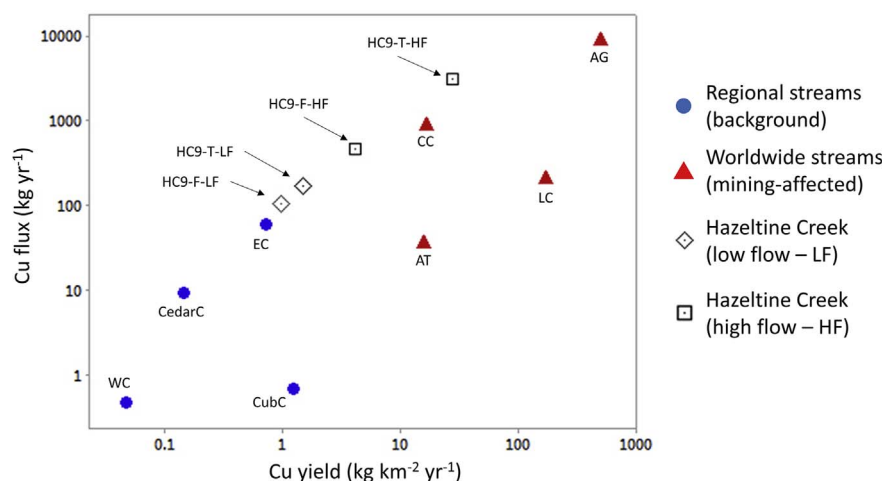


Fig. 8. Cu flux and yield for Hazeltine Creek, regional streams (background) and worldwide streams (mining-affected). Note the logarithmic axes. Hazeltine Creek: HF = high flow; LF = low flow; T = total load; F = filtered load. Regional streams: WC = Winkley Creek; CedarC = Cedar Creek; CubC = Cub Creek; EC = Edney Creek. Worldwide streams: AT = Afon Twymyn (Wales) (Byrne et al., 2013); LC = Lion Creek (USA) (Byrne et al., 2017); CC = Cement Creek (USA) (Runkel et al., 2016); AG = Afon Goch (Wales) (Mayes et al., 2010).

sampling in 2016 which may also partially explain the observed increases in particulate concentrations and loads. However, it is not unrealistic to hypothesize that construction activities in the stream could have a similar effect on particulate transport as high flow events in the future. Streams in the Quesnel River Basin follow a nival hydrological regime driven by spring snowmelt. The high flow data for Hazeltine Creek, although based on a limited number of samples, and collected during construction of fish habitat, suggest that elevated Cu loads due to physical mobilization of residual tailings could be problematic during the spring months due to snowmelt.

Chemical mobilization of Cu in streamside tailings should be expected to decrease in the future due to the gradual exhaustion of reactive materials. This decrease may be superimposed on by short periods of increased mobilization driven by seasonal oxidation of chalcopyrite under snow/ice cover and during prolonged dry periods. Subsequent flushing of accumulated weathering products by snow melt (in spring) and precipitation events (in fall) may drive temporary increases in Cu concentrations in Hazeltine Creek during these times (Canovas et al., 2008; SRK Consulting (Canada) Inc, 2016). The important role of reductive dissolution in metal mobilization in streambed environments has been known for some time (Fuller and Bargar, 2014; Fuller and Harvey, 2000; Gandy et al., 2007), although it has never been studied in a river system whose channel morphology was re-set by a tailings spill and subsequent river restoration. Tailings material is now intermixed with natural sediment in the restored river channel and elevated Cu concentrations are present in the sediment and pore waters. It is unknown how the actively evolving hydrogeomorphic environment may affect hyporheic exchange and biogeochemical processing in the streambed. The future evolution of the geomorphic environment, in response to high magnitude flow events, will control the functioning of hyporheic processes, including those that affect Cu cycling (Krause et al., 2011). For example, changes in stream gradient, morphology and suspended sediment transport, could modify patterns of hyporheic exchange leading to oxic environments favorable for the oxidation of Cu sulfides (chalcopyrite) (Heppell et al., 2013), which are the primary host for Cu in Hazeltine Creek sediments (SRK Consulting (Canada) Inc, 2016). Based on the findings of this study, it is recommended that pore water chemistry in Hazeltine Creek is monitored to chart changes in response to the changing hydrogeomorphic environment. More widely, hyporheic processes should be included in conceptual models of element cycling in watersheds affected by mine tailings spills.

There have been a number of recent high-profile mine tailings and mine waste spills (Minas Gerais, Brazil, 2015; Gold Creek Mine, 2015, USA; Ajka, Hungary, 2010) that highlight the increasing global environmental risk of such events (Hudson-Edwards, 2016; Mayes et al., 2011). Many, but not all, examples of mine tailings spills are characterized by acid-generating and metalliferous materials that can

produce severe and long-lasting chemical impacts in receiving watercourses (Kossoff et al., 2014; Kraus and Wiegand, 2006). This is because acid generating tailings increase the solubility of metals leading to high stream metal concentrations and loads and, frequently, negative biological impacts (Taggart et al., 2006). The data reported here suggest the Mount Polley tailings spill has left a chemical footprint in Hazeltine Creek. However, water and sediment quality impacts are primarily limited to Cu due to the relatively low metal and metalloid content of the spilled tailings. It is important to stress that though chemical mobilization of Cu was apparent in Hazeltine Creek at the time of this study, natural attenuation mechanisms of sorption, precipitation and complexation in the alkaline stream water limit stream Cu concentrations to levels only marginally above BCWQGs. Equilibrium modelling of Cu concentration in Hazeltine Creek suggest an upper limit of $20 \mu\text{g L}^{-1}$ (SRK Consulting (Canada) Inc, 2015a) and this figure is consistent with stream water concentrations (filtered) found in this study (range: $7\text{--}23 \mu\text{g L}^{-1}$). It is also possible that further removal of tailings since this study may have reduced stream Cu loading and concentrations below what was recorded in this study. A useful exercise to contextualize the effects of the tailings spill on water quality and Cu transport is to compare computed flux (kg yr^{-1}) and yield ($\text{kg km}^2 \text{yr}^{-1}$) values for Hazeltine Creek (low and high flow data) with values from unaffected regional watersheds and other mining-affected watercourses around the world (low flow data only) (Fig. 8). Data for Hazeltine Creek are from sample point HC-9 to consider watershed flux without the influence of the sedimentation pond that will not operate in the long-term. Considering the low flow data, watershed Cu flux is elevated when compared with the regional background values. However, the Cu yield (volume of Cu weighted by watershed area) in Hazeltine Creek is only slightly higher than values from Edney Creek (unaffected tributary of Hazeltine Creek) and similar to Cub Creek (unaffected smaller regional watershed) which suggests a relatively minor departure from background Cu yield. Comparison of low flow data with some mining-affected watersheds around the world reveals Cu loads and yields are generally several orders of magnitude greater than in Hazeltine Creek.

4. Conclusions

The Mount Polley mine tailings spill in August 2014 was one of the largest on record (estimated 25Mm^3 of tailings and supernatant water). Valley morphology was significantly altered in the main receiving watercourse, Hazeltine Creek, through erosion of natural materials and then deposition of tailings intermixed with natural materials. Although physical disturbance of Hazeltine Creek was significant, this study has found the chemical impact of the spill to be relatively low and restricted primarily to particulate and aqueous Cu, which was found to be

marginally above BCWQGs. Although the high calcite and low sulfur content of the mine tailings, and the alkaline stream water of Hazeltine Creek, limit the potentially mobility of Cu in this watershed, evidence from this study suggests chemical and physical Cu mobilization were occurring throughout the watershed at the time of our sampling in 2015 and 2016. Copper sulfide weathering in streamside tailings was hypothesized to cause elevated stream Cu loads in Upper Hazeltine Creek. In addition, reductive dissolution of Cu-bearing Fe oxides is thought to have caused elevated filtered Cu in streambed pore waters, though diffusion of this Cu to surface water was probably mediated by sorption to Fe oxides at the sediment-water interface. Physical mobilization was apparently associated with high water velocities and turbulences encountered in a high gradient, bedrock canyon with elevated stream sediment Cu concentrations. River restoration focused on the removal of most deposited tailings, re-introduction of riparian vegetation and the construction of a new stream corridor should, in time, reduce the physical and chemical mobilization of Cu from residual tailings in Hazeltine Creek. However, this long-term decrease in Cu transport will be superimposed on by variability driven by: (i) seasonal oxidation of tailings and flushing of Cu and (ii) high flow events associated with snowmelt and precipitation in spring and fall, respectively. In the meantime, transport of Cu from Hazeltine Creek to Quesnel Lake may be slightly higher than before the tailings dam spill. However, given the size of Quesnel Lake, and the relatively low Cu flux from Hazeltine Creek, this additional Cu load should have a negligible impact on lake water quality and ecosystem processes. Our data highlights how swift removal of spilled tailings and river corridor stabilization can limit chemical impacts in affected watersheds but also how chemical mobilization (of Cu) can still occur when the spilled tailings and the receiving environment are alkaline. This data can be utilized to help design and implement future post-spill restoration schemes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2018.01.012>.

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