

1 Water quality impacts and river system recovery 2 following the 2014 Mount Polley mine tailings dam 3 spill, British Columbia, Canada

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23 ABSTRACT

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

41 but also how chemical mobilization (of Cu) can still occur when the spilled tailings and the
42 receiving environment are alkaline. We present a conceptual model of Cu cycling in the Hazeltine
43 Creek watershed.

44 1. Introduction

45 On August 4th 2014, a partial embankment breach of the Mount Polley tailings storage
46 facility (TSF) in British Columbia, Canada, led to the release of approximately 25 Mm³ of mine
47 tailings and supernatant water into the Quesnel River Watershed (WISE, 2016; Petticrew et al.,
48 2015). The embankment breached due to a geotechnical failure of a layer of glacio-lacustrine clay
49 in the foundation materials below the dam (Independent Expert Engineering Investigation and
50 Review Panel, 2015). The Mount Polley event was significant for four reasons. First, at the time
51 of the accident it was the largest ever documented spill of mine tailings into the environment
52 (WISE, 2016). Second, among tailings spills, the Mount Polley accident was unusual in that the
53 tailings are not acid-generating and contain generally low levels of trace metals and metalloids
54 when compared to typical tailings (Golder Associates Ltd, 2015; Kossoff et al., 2014). Third, the
55 environmental clean-up operations were swift; within one year of the event a significant volume
56 of the spilled tailings had been removed from the major receiving watercourse and an extensive
57 river restoration scheme was under construction (Independent Expert Engineering Investigation
58 and Review Panel, 2015). Fourth, the Mount Polley spill highlighted the increasing global
59 environmental risk of such events, due to the growing number of mining operations and higher
60 waste to ore ratios, and due to the growing vulnerability of these types of environments to extreme
61 hydro-meteorological events (Hudson-Edwards, 2016).

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

70 The ore body at Mount Polley is a typical alkalic porphyry Cu-Au deposit with supergene
71 enrichment (McMillan, 1996). The dominant ore mineral is chalcopyrite (CuFeS₂), but Cu also
72 occurs as other sulfide (bornite – Cu₅FeS₄, covellite – CuS, digenite – Cu₉S₅), silicate (chrysocolla
73 – (Cu,Al)₂H₂Si₂O₅(OH)₄.nH₂O) and carbonate hydroxide minerals (malachite – Cu₂CO₃(OH)₂)
74 (Henry, 2009). Importantly, the ore has a low sulfide (0.1 – 0.3 wt. %) and high calcite (5 – 10 wt.
75 %) content giving it a high neutralization potential. Tailings generated from the processing of
76 Mount Polley ore also have generally low metal concentrations (mg kg⁻¹: As, 8 – 13; Cd, 0.1 – 0.3;
77 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,
78 40 – 82) (SRK Consulting (Canada) Inc, 2015c) when compared to other spilled tailings (Bird et
79 al., 2008; Hudson-Edwards et al., 2003).

80 Evidence from water sampling surveys carried out in Hazeltine Creek shortly after the
81 breach revealed elevated (above British Columbia Water Quality Guidelines – BCWQG (British
82 Columbia Ministry of Environment (BCMoe), 2017)) filtered concentrations of several metals
83 (including Cu (maximum: 86 µg L⁻¹) and Se (maximum 33 µg L⁻¹) that have decreased
84 substantially since the event (Golder Associates Ltd, 2015). Following the breach, Mount Polley

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

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

110

111 2. Methods

112 2.1. Study site

113 Mount Polley Cu and Au mine is located approximately 275 km south-east of Prince
114 George, British Columbia, Canada (Fig. 1). Hazeltine Creek is the main outlet of Polley Lake,
115 draining an area of 112 km^2 , and flowing approximately 9.5 km into Quesnel Lake. Bedrock
116 geology in the catchment is dominated by Mesozoic (252 – 66 Ma) basaltic and andesitic volcanic
117 assemblages. The upper watershed sits partially within Late Triassic (235 – 201 Ma) alkalic
118 intrusions that host the porphyry mineralization (McMillan, 1996).

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

130

131 **2.2 Water analyses and modelling**

132 A synoptic sampling mass balance approach was utilized to identify the spatial pattern of
133 constituent concentrations and loads in the Hazeltine Creek watershed and to study the main
134 hydrological and geochemical processes driving the observed patterns. The synoptic mass balance
135 methodology for management of mine pollution was developed by the U.S. Geological Survey
136 (USGS) as part of the Abandoned Mine Lands Initiative and is based on synchronous water quality
137 and flow measurements made at multiple locations across a catchment that provide detailed spatial
138 assessments of pollutant sources (Kimball et al., 2002). Water sampling and discharge
139 measurements were acquired under low flow conditions in 2015 and high flow conditions in 2016.
140 Low flow sampling was performed using the velocity-area method at 10 stream sites on August
141 2nd 2015 (denoted as ‘stream site’ in Fig. 1; flow range was 140 – 250 L s⁻¹ and typical of long-
142 term values for August (based on 91 measurements taken over spring, summer and autumn from
143 1995 to 2014) (Knight Piesold Ltd, 2014)). At the time of sampling, much of the tailings had been
144 removed in Lower Hazeltine Creek and two sedimentation ponds were operating to settle out
145 suspended particles prior to entry to Quesnel Lake (Fig. 1). Samples were also collected at 12
146 locations where water was flowing from riparian tailings into the creek from seeps or drainage
147 ditches (denoted as ‘inflow site’ in Fig. 1). In-situ pore water samples were collected (from 10 cm
148 and 20 cm depth) at three locations in Hazeltine Creek using a stainless steel piezometer and
149 peristaltic pump. Four additional water chemistry and flow measurements (using the tracer dilution
150 technique) were collected in Hazeltine Creek under high flow conditions (flow range was 600 -
151 680 L s⁻¹ and typical of long-term spring freshet values (Knight Piesold Ltd, 2014)) in July 2016
152 in order to investigate potential water quality impacts during fall storm events or spring snowmelt.
153 Measurements from four creeks in the Quesnel River Watershed that were unaffected by the
154 tailings spill were also collected in July 2016 in order to establish the magnitude of impact in
155 Hazeltine Creek compared to the regional baseline.

156 Total and filtered (0.45 µm) cation (Al, Ca, K, Mg, Na, Si) and trace element concentrations
157 (As, Cd, Cu, Cr, Fe, Mo, Mn, Ni, Pb, Se, V, Zn) were determined by inductively coupled plasma
158 – optical emission spectroscopy (Thermo Scientific iCAP 6500 Duo) and – mass spectroscopy
159 (Thermo X-series 1), respectively. Filtered anion concentrations (Cl, F, SO₄) were determined by
160 ion chromatography (Dionex ICS-2500). Speciation-solubility calculations, using the measured
161 aqueous concentrations of the Hazeltine Creek water and inflow samples, were carried out using
162 the PHREEQC code and the wateq4f.dat. thermodynamic database distributed with the code (Ball
163 and Nordstrom, 1991; Parkhurst and Appelo, 1999). Additional information on the quality control
164 and sampling and analytical protocols can be found in the electronic Supplementary Information.
165 As a result of the physical impacts of the tailings spill in Hazeltine Creek, the stream was not
166 considered to be fish habitat at the time of this study. However, even though the stream is currently
167 not significantly utilized by aquatic organisms, aquatic habitat is an intended future use in the
168 longer term. Therefore, water quality was assessed based on comparisons to British Columbia
169 Water Quality Guidelines (BCWQG) (British Columbia Ministry of Environment (BCMoe),
170 2017). The 0.45 µm fraction is defined as ‘filtered’ in this study and is not intended to be
171 representative of the truly dissolved fraction.

172

173 **2.3 Sediment analyses**

174 The concentration of Cu in within-channel sediments, deposited at the channel margin
175 along Hazeltine Creek, were measured in the field by portable X-ray fluorescence (pXRF) (Niton

176 XLp 300) with an analysis time of 60 seconds. Polished blocks of selected samples of tailings
177 deposited soon after the 2014 spill, and of sediments and ochres remaining in the floodplain in
178 2016 (denoted as ‘tailings site’ in Fig. 1), were examined under low vacuum with the BSE detector
179 on the Mineral Liberation Analysis (MLA) 650 FEG ESEM at Queen’s University, Canada. SEM-
180 MLA has previously been used in environmental mineralogical studies to characterize and quantify
181 mine waste metal- and metalloid-bearing phases (Bromstad et al., 2017; DeSisto et al., 2016). A
182 Cu-bearing Fe oxide phase was added to the library of minerals included in the SEM-MLA
183 software, for which Fe oxides with c. >0.1 wt% Cu could be detected and mapped.
184

185 **3. Results and discussion**

186 **3.1 Water quality impacts**

187 Stream pH values were generally greater than 8.5 throughout the entire reach but ranged
188 between a high of 9.3 in Upper Hazeltine Creek (HC-5) and a low of 7.5 in Lower Hazeltine Creek
189 just upstream of the sedimentation pond (HC-9) (Supplementary Table S1). Prior to the dam spill,
190 the mean pH of Hazeltine Creek was reported as 8.2 (Minnow Environmental Inc, 2009). Diel
191 variation in stream pH (Supplementary Fig. S1) recorded opposite the TSF over a 4-day period
192 (30th July to 2nd August 2015) showed a range from 7.0 – 8.7 before and on the day of the synoptic
193 sampling (2nd August). Some variation on the day of synoptic sampling may reflect enhanced
194 photosynthesis due to clear skies (Gammons et al., 2015) and lower water levels due to the
195 operation of a streamflow control device (a weir was installed to control flow during stream
196 reconstruction). The pH values of sampled inflows (range: 7.8 – 8.7) were generally lower than
197 stream samples (range: 7.5 – 9.3) (Supplementary Table S1), particularly at sites in Upper
198 Hazeltine Creek, suggesting that the inflow waters pHs were buffered by mixing with the stream
199 water. The pH values of inflow and stream waters were more similar in Lower Hazeltine Creek
200 suggesting mixing of subsurface water and stream water in this reach. This result may explain the
201 spatial variation of stream pH with more buffering capacity existing in Upper Hazeltine Creek.
202 The high buffering capacity of stream water (range: 139 – 178 mg L⁻¹ CaCO₃) in Hazeltine Creek,
203 combined with the high calcite and low sulfur content of the spilled tailings (SRK Consulting
204 (Canada) Inc, 2015b), explains the alkaline pH of the stream water. Concentrations of most major
205 ions (filtered, mg L⁻¹: Ca, 44 – 357; K, 19 – 117; Mg, 8 – 77; Na, 8 – 120; Si, 3 – 11) were highest
206 in inflows in Upper Hazeltine Creek, and gradually decreased in the downstream direction
207 (Supplementary Table S1 and Supplementary Table S2).

208 Total and filtered (0.45 µm) concentrations of Cd, Mo, Ni, Pb, Se and Zn in Hazeltine
209 Creek stream water were found to be less than British Columbia Water Quality Guidelines
210 (BCWQGs – filtered concentrations, µg L⁻¹: Cd, 1; Mo, 500; Ni, 150; Pb, 170; Se, 2; Zn, 97).
211 Filtered As (range: 7 – 8 µg L⁻¹) and Cr (range: 2 – 5 µg L⁻¹) concentrations were slightly above
212 environmental standards (BCWQGs – µg L⁻¹: As, 5; Cr, 1) but Cr concentrations were comparable
213 with pre-event concentrations (range: <1 – 4 µg L⁻¹) (Golder Associates Ltd, 2015). Fe and Mn
214 (and Al) concentrations were within aquatic environmental standards and similar to pre-event
215 concentrations (Golder Associates Ltd, 2015). Filtered V concentrations (range: 7 – 12 µg L⁻¹)
216 were elevated compared to pre-event concentrations (median: 1 µg L⁻¹) (Golder Associates Ltd,
217 2015) suggesting further investigation into the fate and behaviour of this element is warranted.
218 However, the main element with elevated concentrations was found to be Cu; total (range: 7 – 28
219 µg L⁻¹) and filtered (range: 7 – 23 µg L⁻¹) concentrations were above environmental guidelines
220 (BCWQGs – µg L⁻¹: Cu, 6) throughout Hazeltine Creek and increased with distance downstream

221 (Supplementary Table S1 and Fig. 2a). In Upper Hazeltine Creek, around the area known as the
222 Polley Flats (0 – 3000 m below Polley Lake weir), Cu was higher in inflows than in the stream
223 water (Fig. 2b). This result suggests that the inflows were receiving Cu from residual tailings and
224 caused an increase in stream Cu in this part of the watershed. However, inflow Cu concentrations
225 farther downstream (3000 – 8500 m below Polley Lake weir) were more similar to, or lower than,
226 stream water concentrations in Lower Hazeltine Creek, suggesting surface inflow waters were not
227 the only source of Cu in the watershed.

228

229 **3.2 Sediment quality impacts**

230 pXRF survey of within channel sediments along the entire length of Hazeltine Creek
231 revealed elevated Cu concentrations throughout the river corridor at the time of our sampling in
232 2015 (Fig. 3). Copper concentrations in material present on the floodplain surface up to 50 m
233 distance from the channel ranged from 88 to 1020 mg kg⁻¹. These values exceeded both the
234 threshold effect level (TEL: 37.5 mg kg⁻¹) and predicted effect level (PEL: 197 mg kg⁻¹) for Cu
235 (British Columbia Ministry of Environment (BCMoE), 2015), and also the mean Cu
236 concentrations of Hazeltine Creek sediments before the breach (Minnow Environmental Inc,
237 2015). The Cu concentrations reported were comparable to other rivers affected by tailings spills
238 (Bird et al., 2008; Hudson-Edwards et al., 2003; Kossoff et al., 2014) and historical mining
239 operations (Gilchrist et al., 2009; Macklin et al., 2006). Cu concentrations were elevated in both
240 silt-sized material, believed to reflect tailings-dominated material (range 89 – 419 mg kg⁻¹) and
241 sand-sized material, believed to reflect magnetite-rich sands (range 72 – 800 mg kg⁻¹). The highest
242 concentrations occurred in the magnetite sands in the second canyon between 5700 and 6700 m
243 (Fig. 3).

244

245 **3.3 Stream copper loading and source areas**

246 Synoptic sampling of streamflow and stream Cu concentrations is used here to identify and
247 quantify sources of Cu to Hazeltine Creek under low flow conditions. Flow measurements are
248 presented in Supplementary Fig. S2. Spatial profiles of filtered and total Cu loading show a general
249 increase downstream of the Polley Lake weir (Fig. 2c); the maximum filtered (453 g day⁻¹) and
250 total (549 g day⁻¹) loads were recorded at HC-8. The primary source of total (67%) and filtered
251 (68%) Cu loading in Hazeltine Creek was the reach from HC-1 to HC-6 (0 – 4000 m) which
252 comprised residual tailings in Upper Hazeltine Creek (Fig. 2c; source area #1). In this reach,
253 filtered Cu loads increased consistently and there was no difference between cumulative (the sum
254 of all loadings in the reaches where a positive change in loading was measured) and measured
255 filtered Cu loads (Supplementary Fig. S3), suggesting there was no chemical attenuation
256 (precipitation or adsorption) of Cu here. Total loads exhibit a similar profile to filtered loads in
257 this reach aside from a slight decrease in load between HC-3 and HC-4. The general increase in
258 Cu loading through this reach is most likely due to inflow waters with elevated filtered and
259 particulate Cu concentrations that are draining the residual tailings (Fig. 2b). The increase in
260 filtered and total loads between HC-5 and HC-6 was probably due to surface and/or subsurface
261 inflows that were not sampled. The secondary source of total (33%) and filtered (32%) Cu loading
262 was the reach from HC-6 to HC-10 which comprised the two bedrock canyons and Upper
263 Hazeltine Creek (Fig. 2c; source area #2). Copper loading through this reach was more variable
264 than further upstream but a notable increase in total and filtered loads occurred through Canyon 2
265 (HC-8) followed by similar magnitude decreases downstream of the canyon in Lower Hazeltine
266 Creek (HC-9). A slight increase in loads downstream of the sedimentation pond (HC-10) prior to

267 discharge into Quesnel Lake was probably due to elevated Cu concentrations in the sedimentation
268 pond (Fig. 2b). Considering stream Cu loading in the entire watershed, the differences between
269 cumulative and measured Cu loads suggests 18% and 39% of the total and filtered Cu, respectively,
270 added to Hazeltine Creek along its course was attenuated prior to discharge into Quesnel Lake
271 (Supplementary Fig. S3). The alkaline stream water and high calcite and low sulfur content of the
272 Mount Polley tailings undoubtedly limits mobilization and transport of Cu and other trace metals
273 in Hazeltine Creek (Nordstrom, 2011). Nevertheless, the gradual increase in Cu concentrations
274 and loads in the stream suggests aqueous and total Cu phases were influencing stream chemistry
275 (Fig. 2). The following sections present results and discussion aimed at elucidating the mechanisms
276 that may be responsible for the observed spatial pattern of Cu loading.
277

278 **3.4 Copper mobilization and transport**

279 The primary source of stream Cu loading identified in 2015 was the residual tailings (0 –
280 4000 m) in Upper Hazeltine Creek. Whilst on-going remediation activities in Hazeltine Creek have
281 removed much of the spilled tailings, substantial volumes remain in the river corridor (most
282 notably in the Polley Flats area opposite the TSF in Upper Hazeltine Creek) intermixed with
283 natural materials. Groundwater seeps and drainage ditches in Upper Hazeltine Creek that were
284 connected to Hazeltine Creek in 2015 contained elevated concentrations of filtered (up to $37 \mu\text{g L}^{-1}$
285 1) and total Cu (up to $148 \mu\text{g L}^{-1}$) (Fig. 2b, 4a). At the water pH values measured in these inflows,
286 Cu is predicted to have been present principally as Cu(II) hydroxide ($\text{Cu}(\text{OH})_2$), with Cu(II)
287 carbonate (CuCO_3) also present in some samples. Speciation modelling of inflow waters indicates
288 cuprite was saturated ($\text{SI} = -2$ to $+2$) (Supplementary Table S3), and minor amounts of cuprite and
289 chrysocolla were identified in SEM-MLA, suggesting these minerals exerted a solubility control
290 over Cu in these waters. The presence of elevated filtered Fe (up to $194 \mu\text{g L}^{-1}$), Cu (up to $38 \mu\text{g}$
291 L^{-1}) and SO_4 (up to 966mg L^{-1}) in these inflows (Fig. 4a, b, d) suggests weathering of chalcopyrite
292 (CuFeS_2) was occurring in the tailings in source area #1 (Fig. 2c). In addition, SEM-MLA
293 investigations provide evidence of chalcopyrite altering directly to Cu-bearing Fe oxides, possibly
294 ferrihydrite, in the tailings (Fig. 5a, b; Supplementary Figure S4). Such Cu-bearing Fe oxide is a
295 commonly-observed product for alkaline oxidation of chalcopyrite (Vaughan and Coker, 2017;
296 Yin et al., 2000). Weathering of Mn oxides was also indicated with elevated Mn (up to $7343 \mu\text{g L}^{-1}$
297 1) and saturation of rhodocrosite in inflow waters (Supplementary Table S3). Oxidation of
298 chalcopyrite in near-surface tailings followed by rainfall and infiltration of rainwater into the
299 tailings will dissolve the oxidation products and produce leachate with elevated dissolved Cu, Fe
300 and SO_4 . This leachate could be transported through the tailings to groundwater seeps and drainage
301 ditches through surface run-off and via subsurface flow paths along the tailings / glacial till
302 interface. The hydraulic residence time of mobilized Cu leachate within the tailings will play an
303 important role in Cu transport to groundwater seeps and drainage ditches and, ultimately, to stream
304 water (Fuller and Harvey, 2000; Gandy et al., 2007). Fine-grained material (such as the clay and
305 silt-sized ‘grey’ tailings) will increase residence time and limit the rate of oxygen diffusion,
306 thereby maintaining Cu in relatively insoluble forms (Gandy et al., 2007). Evidence from column
307 and humidity cell tests suggests mineral solubility controls (e.g. ferrihydrite) will limit Cu leaching
308 in fine-grained tailings where flow paths are longer than half a meter (SRK Consulting (Canada)
309 Inc, 2015a). Shorter flow paths, such as those that characterize sediments in the riparian zone, are
310 more likely to remain oxic which could explain the elevated Cu measured in riparian groundwater
311 seeps and drainage ditches during this study.

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

339 Whilst chalcopyrite weathering in riparian tailings may have been the primary source of
340 Cu loading in Hazeltine Creek, evidence from this study suggests another potential source of
341 aqueous Cu throughout the stream corridor at the time of sampling. Filtered concentrations of Cu
342 were found to be elevated (range: 43 – 1017 $\mu\text{g L}^{-1}$) in sediment pore waters (relative to stream
343 waters) recovered through in-situ sampling (Fig. 4a and Fig. 6a), suggesting a mechanism of Cu
344 release was operating in the stream sediments. Release of Cu in the streambed could be related to
345 either oxidation of chalcopyrite or reductive dissolution of Cu-bearing oxides. Whilst Cu sulfides
346 can be oxidized in subaqueous environments if the waters contain sufficient oxygen (Todd et al.,
347 2003), an increase in SO_4 in pore waters would have been expected to accompany the increase in
348 filtered Cu as evidence of Cu sulfide weathering, and this was not evident in Hazeltine Creek pore
349 waters (Fig. 4d and Fig. 6d). A more plausible mechanism for Cu release in the streambed is
350 reductive dissolution of Cu-bearing Fe oxides given the elevated filtered concentrations of Fe
351 (range: 63 – 3510 $\mu\text{g L}^{-1}$) and Mn (18 – 1468 $\mu\text{g L}^{-1}$) found in sediment pore waters (relative to
352 stream waters) (Fig. 4b,c and Fig. 6b,c). Filtered Fe and Mn was strongly and significantly
353 correlated with filtered Cu in the streambed pore waters (Supplementary Figure S4). In addition,
354 sequential extraction tests conducted on Hazeltine Creek sediment indicates that the reducible
355 geochemical phase is an important host for Cu (Minnow Environmental Inc, 2015; SRK
356 Consulting (Canada) Inc, 2015c) and several investigations have highlighted reductive dissolution
357 as an important mechanism driving aqueous Cu release in the streambed (Calmano et al., 1993).

358 Although positive ORP values were recorded in pore waters in this study (Fig. 4f), potentially
359 suggesting an oxic system, in the absence of low pH (acidic) streambed pore waters, the only
360 mechanism capable of producing the high filtered Fe and Mn concentrations found in Hazeltine
361 Creek pore waters was reductive dissolution (Kimball et al., 2016). The highest pore water Cu and
362 Fe concentrations were generally recorded at 10 cm depth but then declined at 0 cm depth (surface
363 water) suggesting that diffusion of the released Cu to stream water was mediated by
364 (co)precipitation and / or sorption reactions (Fig. 6). Cuprite was saturated at the sediment-water
365 interface (0 – 10 cm) (Supplementary Table S3), however ferrihydrite was supersaturated and
366 sorption of Cu(II) to Fe oxides is well documented in neutral and alkaline systems (Kimball et al.,
367 2016; Koski et al., 2008). Furthermore, evidence from SEM-MLA analysis indicates the presence
368 of Cu-bearing Fe oxides in the stream sediments (Fig. 5c, d; Supplementary Figure S4). Oxidation
369 of the tailings chalcopyrite to Cu-bearing Fe oxide could have occurred either before (in the TSF)
370 or after the 2014 tailings spill (in Hazeltine Creek). However, textural evidence strongly suggests
371 that some of the Cu-bearing Fe oxides formed as discrete phases following deposition in Hazeltine
372 Creek; this pattern is particularly evident in the Fe ochre sample collected from a seep mid-way
373 down Hazeltine Creek (Fig. 5c, d). Also, the chalcopyrite: Cu-bearing Fe oxide ratio decreases
374 from 0.36 – 0.57 in the 2014 deposited tailings, to 0.19 – 0.24 in the upper part of the Polley Flats,
375 and to 0.00 – 0.06 in the lower part of the Polley Flats and further down Hazeltine Creek
376 (Supplementary Table S4). This suggests that chalcopyrite oxidation and/or formation of discrete
377 Cu-bearing Fe oxides increased in Hazeltine Creek between 2014 and 2016 and with distance
378 downstream of the TSF.

379 The secondary source of Cu loading in Hazeltine Creek occurred from HC-6 to HC-10.
380 The highest loading within this reach appeared to be Canyon 2 (5700 – 6700 m) in Upper Hazeltine
381 Creek, most likely as a consequence of high water velocities and turbulence that eroded and
382 suspended streamside and streambed sediments with high Cu concentrations (Fig. 3). Through this
383 reach, there was a decrease in the relative contribution of filtered Cu to the overall Cu load from
384 0.9 (at HC-6) to 0.6 (at HC-10), suggesting (co)precipitation and / or sorption of filtered Cu species
385 may have occurred. It appears that although Cu precipitation from HC-1 to HC-6 was limited by
386 kinetic constraints, an approach towards thermodynamic equilibrium occurred from HC-6 to HC-
387 10. Evidence for this can be seen in the shift from under saturation (HC-1 to HC-6) to saturation
388 (HC-6 to HC-10) for cuprite (Supplementary Table S3) and could reflect the reduced number of
389 inflows in the lower reach that could alter stream chemistry. As well as precipitation of secondary
390 Cu minerals, Cu sorption to particulate Fe phases (ferrihydrite) could also have been important for
391 removing filtered Cu (Fig. 5; Supplementary Table S4) (Kimball et al., 2016). Elevated Cu
392 concentrations in the sedimentation pond at the time of sampling probably caused the slight
393 increase in Cu loads between HC-9 and HC-10.

394 Consideration of the evidence presented in this study allows us to derive a conceptual
395 model of Cu cycling in the Hazeltine Creek watershed (Fig. 7). Oxygen diffusion in streamside
396 tailings in Upper Hazeltine Creek could drive oxidation of chalcopyrite in near-surface tailings
397 with reductive dissolution of Cu-bearing Fe oxides potentially occurring in deeper, anoxic tailings
398 (Fig. 7a). Rainfall and infiltration in the tailings could dissolve the oxidation by-products which
399 could be transported to drainage ditches and Hazeltine Creek water through surface runoff and /
400 or subsurface flow. Any free ionic Cu present would probably form aqueous organic complexes
401 and / or sorb to particulate Fe oxides. Copper mobilization in stream sediments could occur by
402 reductive dissolution of Cu-bearing Fe oxides (Fig. 7b). The released Cu could form insoluble Cu
403 sulfides in the stream sediment or diffuse through the sediment-water interface where it would be

404 complexed with organic matter and / or sorb to particulate Fe oxides. Finally, physical mobilization
405 of particulate Cu through Canyon 2 could occur through erosion / suspension of Cu-rich sediments
406 and streamside tailings in this high-gradient, turbulent and constrained reach.
407

408 **3.5 Long-term implications**

409 Following the accident, Mount Polley Mining Corporation acted swiftly and removed most
410 of the spilled tailings in Lower Hazeltine Creek within a few months of the accident. This strategy
411 has undoubtedly reduced the short- to long-term chemical impacts in the watershed. Since this
412 study, further tailings have been removed in Upper Hazeltine Creek, though some tailings still
413 remain intermixed with natural soil and sediment along parts of the stream corridor. Removal of
414 spilled tailings is the most common remedial measure taken for tailings dam spills (Kossoff et al.,
415 2014) and has been shown to considerably reduce long-term impacts on ecosystems (Hudson-
416 Edwards et al., 2003). However, despite the relatively low chemical impacts of the Mount Polley
417 spill, mobilization of particulate and aqueous Cu phases was evident in Hazeltine Creek at the time
418 of this study and could influence stream chemistry into the future. The processes driving Cu
419 mobilization are hypothesized to be (in order of decreasing importance): (i) chemical mobilization
420 in streamside tailings through primary sulfide oxidation, (ii) physical erosion / suspension of
421 particulate and colloidal phases in residual streamside and streambed tailings, and (iii) chemical
422 mobilization in streambed sediments through reductive dissolution of Cu-bearing Fe oxides. The
423 following sections discuss how these processes may evolve in the future and how the chemical
424 perturbation in Hazeltine Creek compares to pre-event conditions and other mine waste-impacted
425 watersheds around the world.

426 Restoration of the Hazeltine Creek river corridor was aimed at limiting further erosion of
427 tailings and turbidity in the stream. As a result, significant reductions in element concentrations
428 and turbidity were achieved in the weeks and months after the spill (Golder Associates Ltd, 2015;
429 MPMC, 2015). However, increases in particulate loading observed in this study suggests physical
430 erosion and suspension is a mechanism for Cu mobilization even at low flows. This was most
431 evident in the reach comprising the two canyons, possibly due to higher stream turbulence in this
432 constricted reach and greater connectivity between the stream and deposited tailings. In the future,
433 as river flow and water levels rise in response to rainfall or snowmelt, it will come into contact
434 with, and possibly erode, streamside tailings (intermixed with native materials) that remain dry
435 during lower flow conditions. This process has been shown to result in order of magnitude
436 increases in both filtered and total metal loads in mining-affected watersheds (Byrne et al., 2013;
437 Canovas et al., 2008; Gozzard et al., 2011; Nordstrom, 2011; Runkel et al., 2016) and is evident
438 in the water samples taken in July 2016 under high flow conditions (Fig. 8 and Supplementary
439 Figure S2). While transport of Cu was predominantly as filtered load at low flow (64% at HC-9),
440 particulate-bound load was clearly dominant at high flow (85% at HC-9), probably due to the
441 erosion of streamside tailings. Construction of fish habitat was underway during the high flow
442 sampling in 2016 which may also partially explain the observed increases in particulate
443 concentrations and loads. However, it is not unrealistic to hypothesize that construction activities
444 in the stream could have a similar effect on particulate transport as high flow events in the future.
445 Streams in the Quesnel River Basin follow a nival hydrological regime driven by spring snowmelt.
446 The high flow data for Hazeltine Creek, although based on a limited number of samples, and
447 collected during construction of fish habitat, suggest that elevated Cu loads due to physical
448 mobilization of residual tailings could be problematic during the spring months due to snowmelt.

449 Chemical mobilization of Cu in streamside tailings should be expected to decrease in the
450 future due to the gradual exhaustion of reactive materials. This decrease may be superimposed on
451 by short periods of increased mobilization driven by seasonal oxidation of chalcopyrite under
452 snow/ice cover and during prolonged dry periods. Subsequent flushing of accumulated weathering
453 products by snow melt (in spring) and precipitation events (in fall) may drive temporary increases
454 in Cu concentrations in Hazeltine Creek during these times (Canovas et al., 2008; SRK Consulting
455 (Canada) Inc, 2016). The important role of reductive dissolution in metal mobilization in
456 streambed environments has been known for some time (Fuller and Bargar, 2014; Fuller and
457 Harvey, 2000; Gandy et al., 2007), although it has never been studied in a river system whose
458 channel morphology was re-set by a tailings spill and subsequent river restoration. Tailings
459 material is now intermixed with natural sediment in the restored river channel and elevated Cu
460 concentrations are present in the sediment and pore waters. It is unknown how the actively
461 evolving hydrogeomorphic environment may affect hyporheic exchange and biogeochemical
462 processing in the streambed. The future evolution of the geomorphic environment, in response to
463 high magnitude flow events, will control the functioning of hyporheic processes, including those
464 that affect Cu cycling (Krause et al., 2011). For example, changes in stream gradient, morphology
465 and suspended sediment transport, could modify patterns of hyporheic exchange leading to oxic
466 environments favorable for the oxidation of Cu sulfides (chalcopyrite) (Heppell et al., 2013),
467 which are the primary host for Cu in Hazeltine Creek sediments (SRK Consulting (Canada) Inc,
468 2016). Based on the findings of this study, it is recommended that pore water chemistry in
469 Hazeltine Creek is monitored to chart changes in response to the changing hydrogeomorphic
470 environment. More widely, hyporheic processes should be included in conceptual models of
471 element cycling in watersheds affected by mine tailings spills.

472 There have been a number of recent high-profile mine tailings and mine waste spills (Minas
473 Gerais, Brazil, 2015; Gold Creek Mine, 2015, USA; Ajka, Hungary, 2010) that highlight the
474 increasing global environmental risk of such events (Hudson-Edwards, 2016; Mayes et al., 2011).
475 Many, but not all, examples of mine tailings spills are characterized by acid-generating and
476 metalliferous materials that can produce severe and long-lasting chemical impacts in receiving
477 watercourses (Kossoff et al., 2014; Kraus and Wiegand, 2006). This is because acid generating
478 tailings increase the solubility of metals leading to high stream metal concentrations and loads and,
479 frequently, negative biological impacts (Taggart et al., 2006). The data reported here suggest the
480 Mount Polley tailings spill has left a chemical footprint in Hazeltine Creek. However, water and
481 sediment quality impacts are primarily limited to Cu due to the relatively low metal and metalloid
482 content of the spilled tailings. It is important to stress that though chemical mobilization of Cu was
483 apparent in Hazeltine Creek at the time of this study, natural attenuation mechanisms of sorption,
484 precipitation and complexation in the alkaline stream water limit stream Cu concentrations to
485 levels only marginally above BCWQGs. Equilibrium modelling of Cu concentration in Hazeltine
486 Creek suggest an upper limit of $20 \mu\text{g L}^{-1}$ (SRK Consulting (Canada) Inc, 2015a) and this figure
487 is consistent with stream water concentrations (filtered) found in this study (range: $7 - 23 \mu\text{g L}^{-1}$).
488 It is also possible that further removal of tailings since this study may have reduced stream Cu
489 loading and concentrations below what was recorded in this study. A useful exercise to
490 contextualize the effects of the tailings spill on water quality and Cu transport is to compare
491 computed flux (kg yr^{-1}) and yield ($\text{kg km}^2 \text{ yr}^{-1}$) values for Hazeltine Creek (low and high flow
492 data) with values from unaffected regional watersheds and other mining-affected watercourses
493 around the world (low flow data only) (Fig. 8). Data for Hazeltine Creek are from sample point
494 HC-9 to consider watershed flux without the influence of the sedimentation pond that will not

495 operate in the long-term. Considering the low flow data, watershed Cu flux is elevated when
496 compared with the regional background values. However, the Cu yield (volume of Cu weighted
497 by watershed area) in Hazeltine Creek is only slightly higher than values from Edney Creek
498 (unaffected tributary of Hazeltine Creek) and similar to Cub Creek (unaffected smaller regional
499 watershed) which suggests a relatively minor departure from background Cu yield. Comparison
500 of low flow data with some mining-affected watersheds around the world reveals Cu loads and
501 yields are generally several orders of magnitude greater than in Hazeltine Creek.
502

503 **4. Conclusions**

504 The Mount Polley mine tailings spill in August 2014 was one of the largest on record
505 (estimated 25 Mm³ of tailings and supernatant water). Valley morphology was significantly altered
506 in the main receiving watercourse, Hazeltine Creek, through erosion of natural materials and then
507 deposition of tailings intermixed with natural materials. Although physical disturbance of
508 Hazeltine Creek was significant, this study has found the chemical impact of the spill to be
509 relatively low and restricted primarily to particulate and aqueous Cu, which was found to be
510 marginally above BCWQGs. Although the high calcite and low sulfur content of the mine tailings,
511 and the alkaline stream water of Hazeltine Creek, limit the potentially mobility of Cu in this
512 watershed, evidence from this study suggests chemical and physical Cu mobilization were
513 occurring throughout the watershed at the time of our sampling in 2015 and 2016. Copper sulfide
514 weathering in streamside tailings was hypothesized to cause elevated stream Cu loads in Upper
515 Hazeltine Creek. In addition, reductive dissolution of Cu-bearing Fe oxides is thought to have
516 caused elevated filtered Cu in streambed pore waters, though diffusion of this Cu to surface water
517 was probably mediated by sorption to Fe oxides at the sediment-water interface. Physical
518 mobilization was apparently associated with high water velocities and turbulences encountered in
519 a high gradient, bedrock canyon with elevated stream sediment Cu concentrations. River
520 restoration focused on the removal of most deposited tailings, re-introduction of riparian
521 vegetation and the construction of a new stream corridor should, in time, reduce the physical and
522 chemical mobilization of Cu from residual tailings in Hazeltine Creek. However, this long-term
523 decrease in Cu transport will be superimposed on by variability driven by: (i) seasonal oxidation
524 of tailings and flushing of Cu and (ii) high flow events associated with snowmelt and precipitation
525 in spring and fall, respectively. In the meantime, transport of Cu from Hazeltine Creek to Quesnel
526 Lake may be slightly higher than before the tailings dam spill. However, given the size of Quesnel
527 Lake, and the relatively low Cu flux from Hazeltine Creek, this additional Cu load should have a
528 negligible impact on lake water quality and ecosystem processes. Our data highlights how swift
529 removal of spilled tailings and river corridor stabilization can limit chemical impacts in affected
530 watersheds but also how chemical mobilization (of Cu) can still occur when the spilled tailings
531 and the receiving environment are alkaline. This data can be utilized to help design and implement
532 future post-spill restoration schemes.
533

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672

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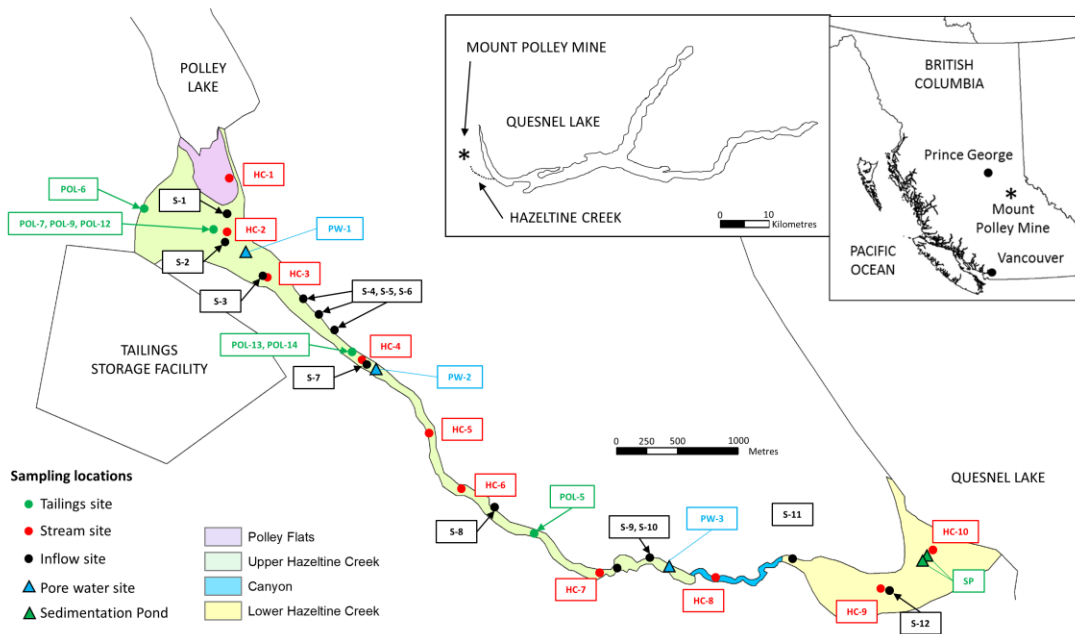
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 692 **Figure 1.** Location of study area showing tailings, stream (streamflow and water quality) and
 693 inflow (water quality only) sample sites.

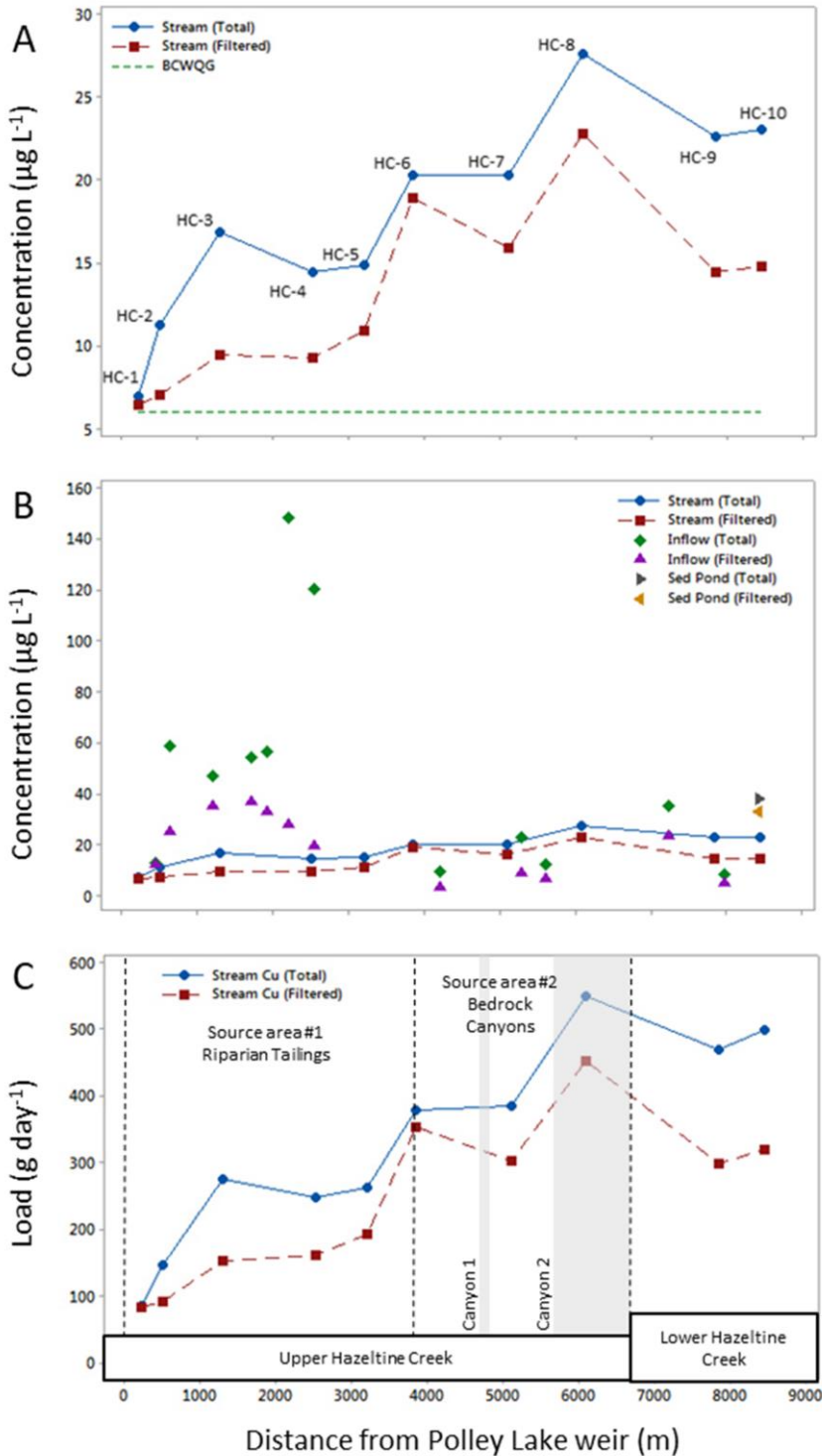
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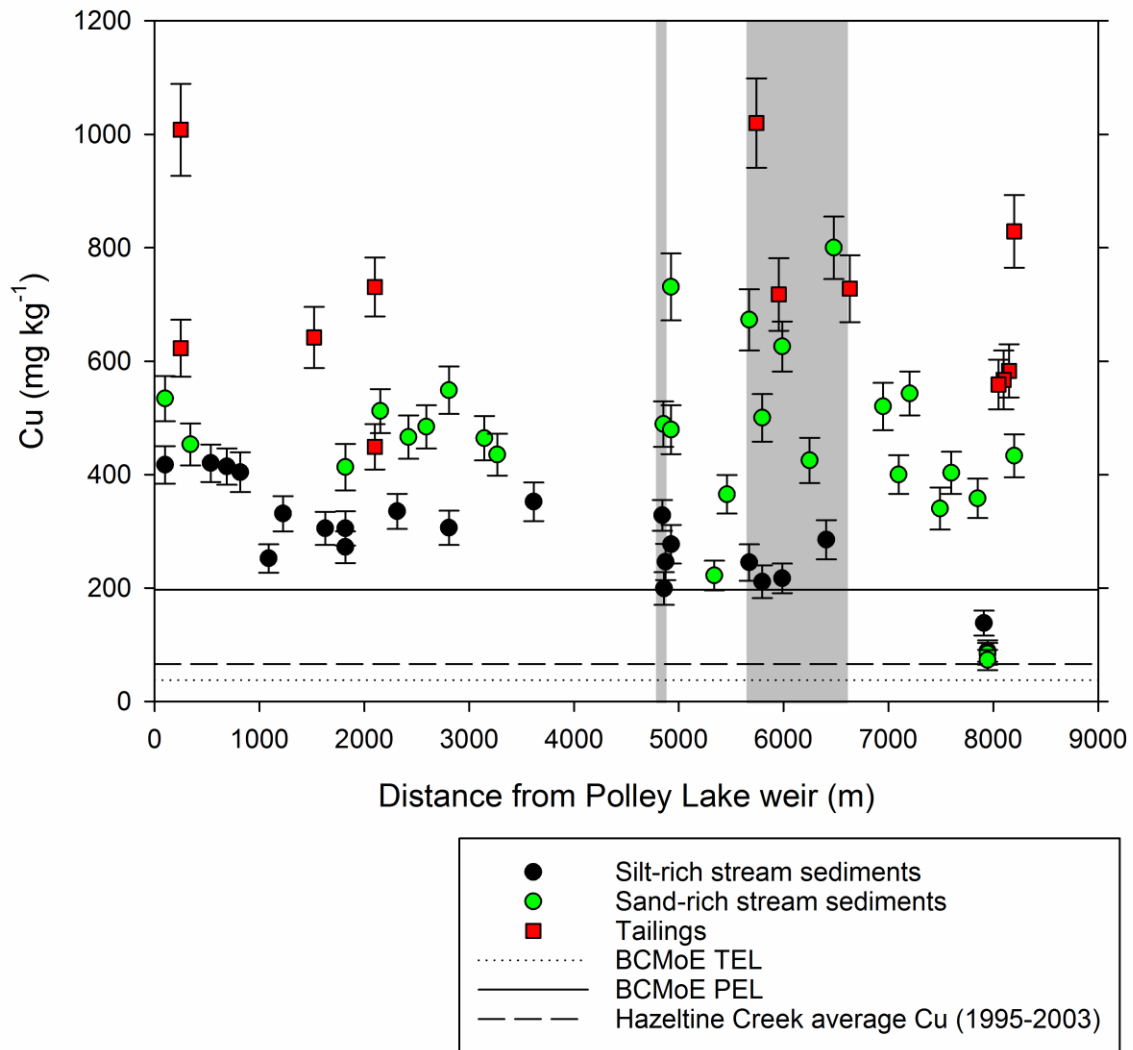
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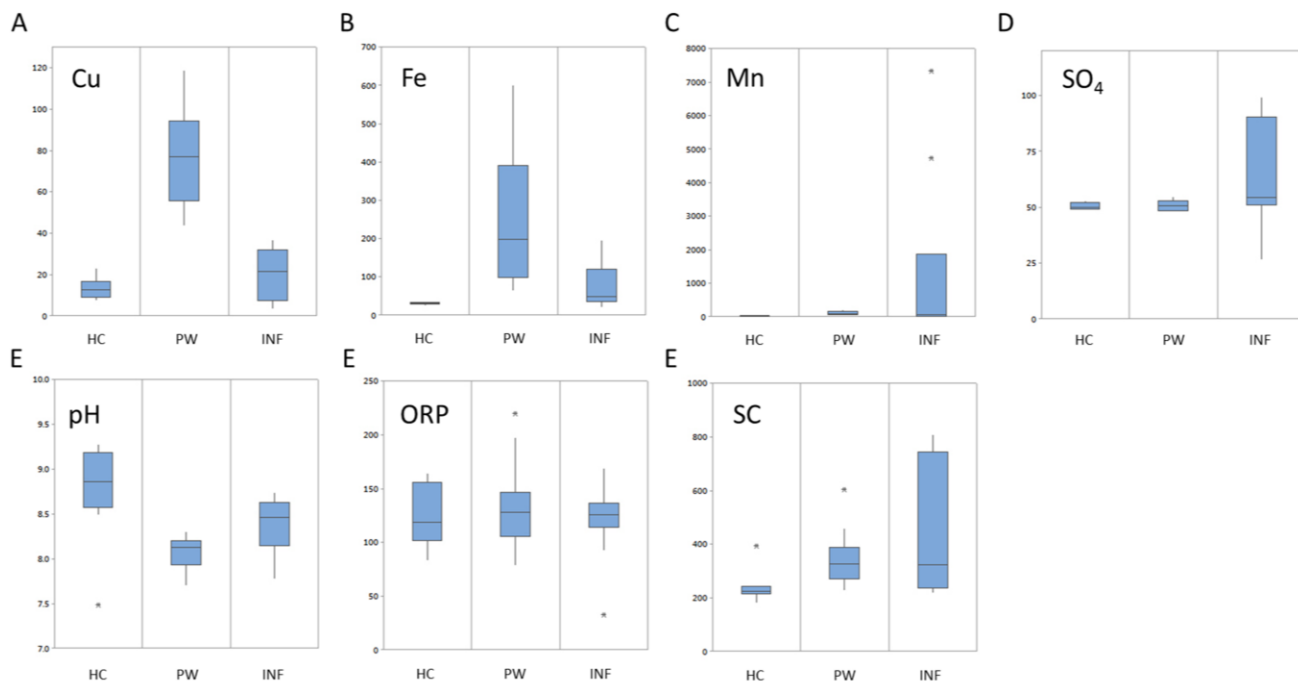
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700 **Figure 2.** (A) Spatial profiles of stream total and filtered Cu concentrations with British Columbia
 701 Water Quality Guideline (BCWQG). (B) Spatial profile of stream filtered Cu concentration and
 702 inflow (total and filtered) Cu concentrations.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



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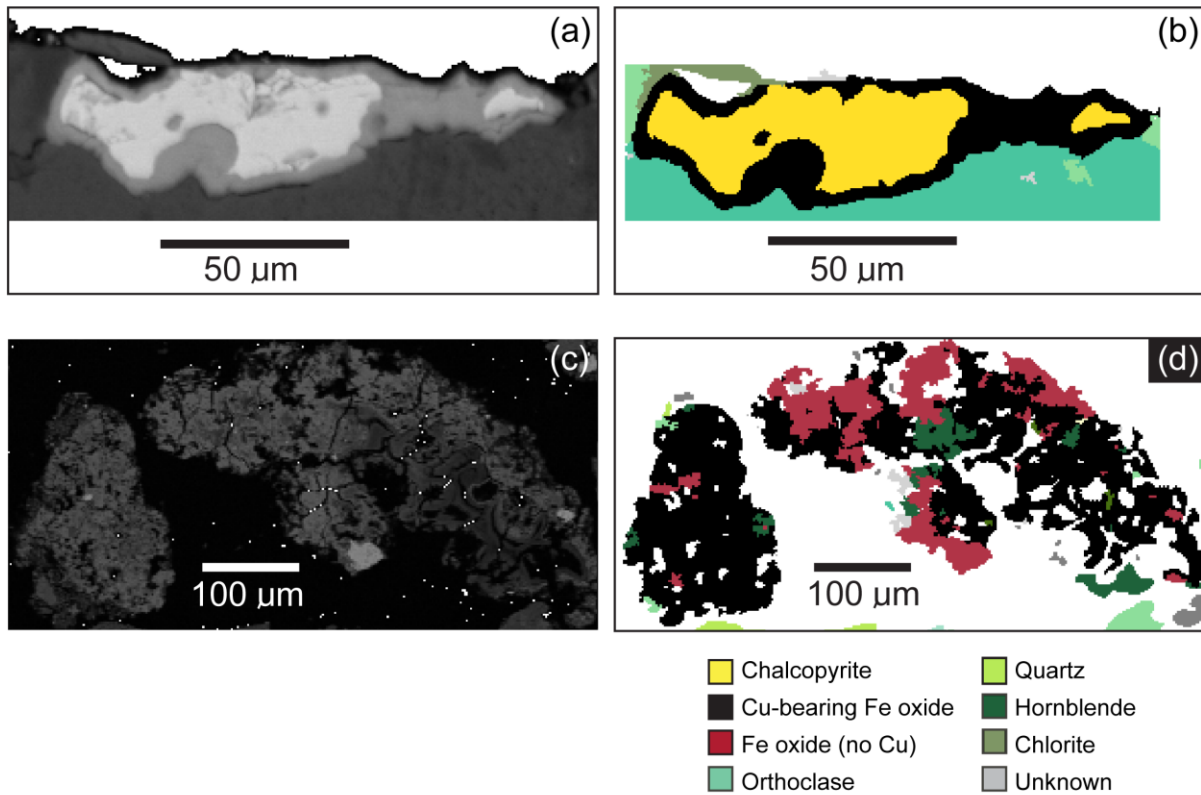
705 **Figure 3.** pXRF-derived Cu concentrations of sediments in Hazeltine Creek sampled on August
 706 1st 2014. Dotted line and solid line represent British Columbia Ministry of Environment (BCMoE)
 707 Threshold Effect Limits (TEL) and Predicted Effect Limits (PEL), respectively (British Columbia
 708 Ministry of Environment (BCMoE), 2015). The dashed line represents the Hazeltine Creek
 709 average Cu concentration from 1995 – 2003 (Golder Associates Ltd, 2015). Grey vertical bars
 710 represent the locations of two bedrock canyons at 4800 – 4900 m and 5600 – 6600 m below Polley
 711 Lake weir.



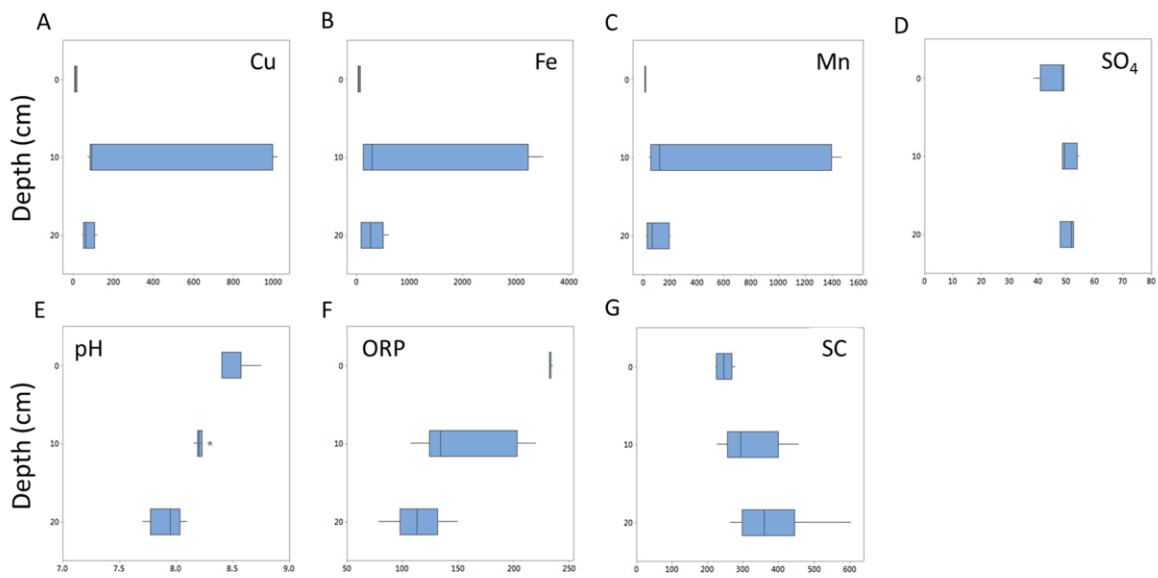
712

713 **Figure 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
 714
 715 (HC), streambed pore waters (PW) and watershed inflows (INF).

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717
 718 **Figure 5.** (a) Backscatter SEM image showing chalcopyrite (white) altered to Cu-bearing Fe oxide
 719 (medium gray) in sample POL5; (b) MLA mineral apportionment of (a); (c) backscatter SEM
 720 image of Fe ochre sample POL13; (d) MLA mineral apportionment of (c) showing abundance of
 721 Cu-bearing Fe oxide.



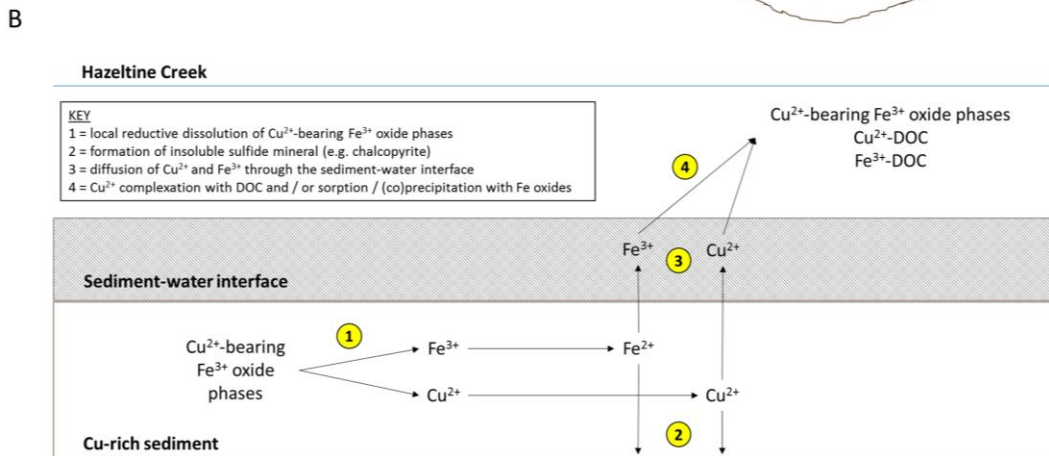
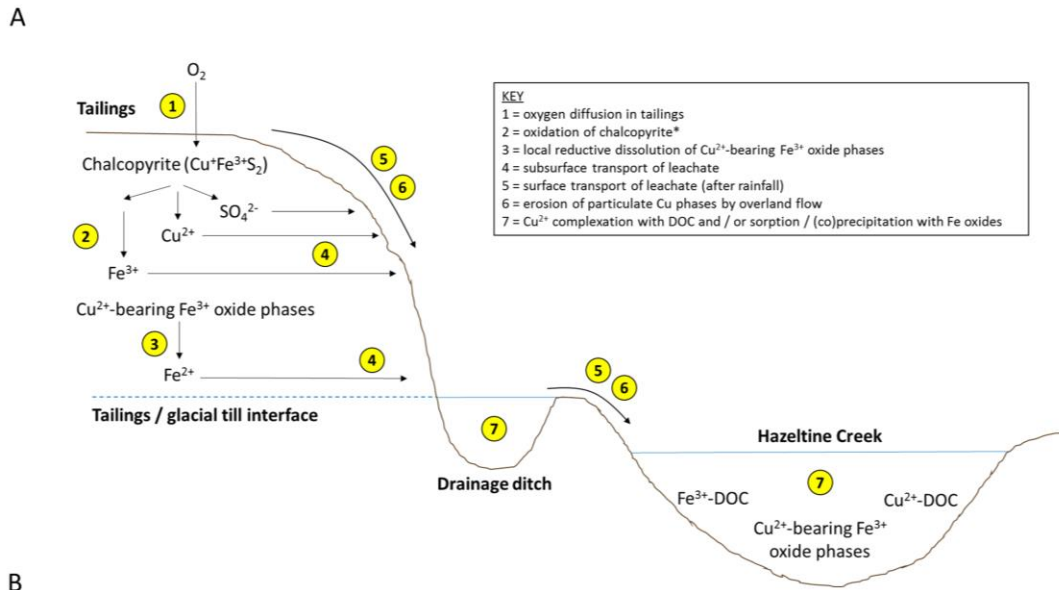
722

723 **Figure 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
 724 pore waters (0 cm = surface water).
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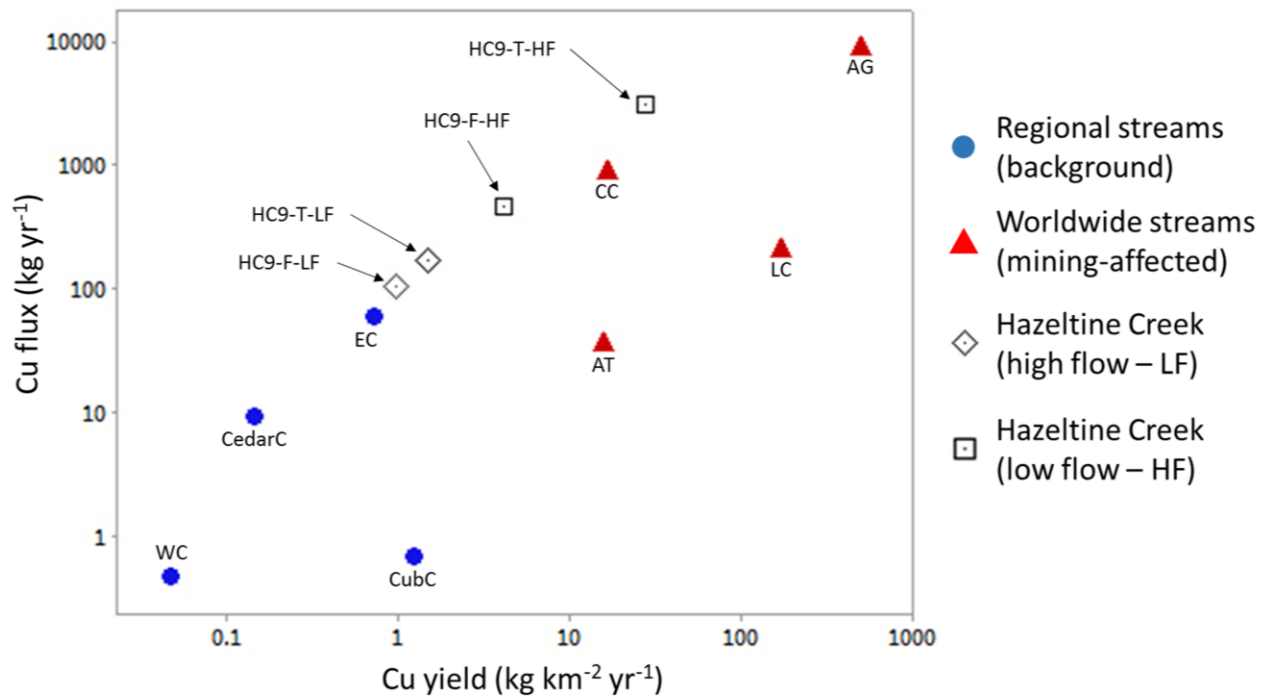


729

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

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