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Geologic processes influence the effects of mining on aquatic ecosystems

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Abstract. Geologic processes strongly influence water and sediment quality in aquatic ecosystems but rarely are geologic principles incorporated into routine biomonitoring studies. We test if elevated concentrations of metals in water and sediment are restricted to streams downstream of mines or areas that may discharge mine wastes. We surveyed 198 catchments classified as "historically mined" or "unmined," and based on mineral-deposit criteria, to determine whether water and sediment quality were influenced by naturally occurring mineralized rock, by historical mining, or by a combination of both. By accounting for different geologic sources of metals to the environment, we were able to distinguish aquatic ecosystems limited by metals derived from natural processes from those due to mining. Elevated concentrations of metals in water and sediment were not restricted to mined catchments; depauperate aquatic communities were found in unmined catchments. The type and intensity of hydrothermal alteration and the mineral deposit type were important determinants of water and sediment quality as well as the aquatic community in both mined and unmined catchments. This study distinguished the effects of different rock types and geologic sources of metals on ecosystems by incorporating basic geologic processes into reference and baseline site selection, resulting in a refined assessment. Our results indicate that biomonitoring studies should account for natural sources of metals in some geologic environments as contributors to the effect of mines on aquatic ecosystems, recognizing that in mining-impacted drainages there may have been high pre-mining background metal concentrations.

Key words: aquatic communities; biomonitoring; geology; metals; mining; Rocky Mountain (USA) streams; sediment quality; water quality.

Introduction

Global anthropogenic metals inputs (atmospheric deposition and industrial discharge) to aquatic ecosystems exceed that due to natural processes (Nriagu and Pacyna 1988). At local and regional scales, the contributions of natural vs. anthropogenic metal loading into aquatic ecosystems are poorly constrained. In Colorado, USA, over 13 840 km of stream and river have been designated as impaired (Clean Water Act's section 303(d) list in 2008; *available online*)[5] because of elevated metals (aluminum, cadmium, copper, lead, iron, selenium, and zinc). Generally, this degradation is assumed to result from the mineral-extraction economy that began in central Colorado in 1859 (Chronic and Chronic 1972). However, central Colorado was heavily mineralized during the Laramide orogeny (75 to 45 million years ago), a period of mountain building in western North America that involved emplacement of plutons and associated sulfide mineral deposits of various types (e.g., Tweto and Sims 1963). Metals from these sulfide minerals have been released into aquatic ecosystems, but the relative contributions of weathering of unmined hydrothermally altered rock vs. historical mining is largely unknown.

Hydrothermal alteration can be an integral part of the ore-forming process in such a way that different suites of minerals are created (and locally extracted by mining) in areas with different types of hydrothermal alteration. Mines can be located in areas where hydrothermal alteration has resulted in a mineral deposit of sufficient metal concentration that it is economic to extract metals from the rock. However, mines or mineral deposits of certain deposit types are commonly surrounded by a more diffuse halo of altered rock that also contains concentrations of metals likely above crustal abundance. Because of these ore-formation processes it is possible that elevated concentrations of metals in bedrock influenced water and sediment quality in streams prior to mining (Tooker 1963, Tweto 1968, Wanty et al. 2002,

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2009, Verplanck et al. 2009), although it is difficult to estimate the pre-mining metal concentrations.

Biological assessment traditionally attempts to differentiate between the natural condition of a stream and the condition of a stream affected by metals. In general there are two approaches: those that compare stream condition at sites free of mining and metals contamination to sites that are mined or contaminated by a gradient of metal concentrations (e.g., Canfield et al. 1994, Schmidt et al. 2002), and those where sample locations are randomly selected throughout a watershed or region and used to generalize about the effects of metals (or abandoned mine lands) on stream condition throughout the study area (e.g., Clements et al. 2000). Biological assessments rarely resolve the differences between biological communities affected by natural vs. anthropogenic sources of metals. As a result, the degree (number of streams and extent of contamination within streams) to which natural geologic deposits cause elevated metal concentrations and adversely affect stream communities is largely unknown.

We evaluate the extent to which historic mining vs. natural sources of metals (hydrothermal alteration) influences the metal concentrations and aquatic communities in streams of central Colorado. We tested two hypotheses: (1) that elevated metal concentrations in water and sediment and depauperate aquatic invertebrate communities were restricted to historically mined catchments, and (2) that metals and aquatic insect communities in streams are controlled by geologic processes. These questions were evaluated by collecting a large database of water and sediment geochemistry and aquatic insect communities from catchments that include various ore deposit types and styles of hydrothermal alteration. To test the first hypothesis these data were classified based on disturbance (i.e., mined vs. unmined). To test the second hypothesis these same data were reclassified based on mineral-deposit criteria. This approach facilitated the development of lithologic-specific toxicological and ecological baselines. These baselines were used to better understand the role that geologic sources of metals play in structuring aquatic ecosystems in mineralized regions and to allow for a more quantitative assessment of the effect of historical mining on aquatic ecosystems.

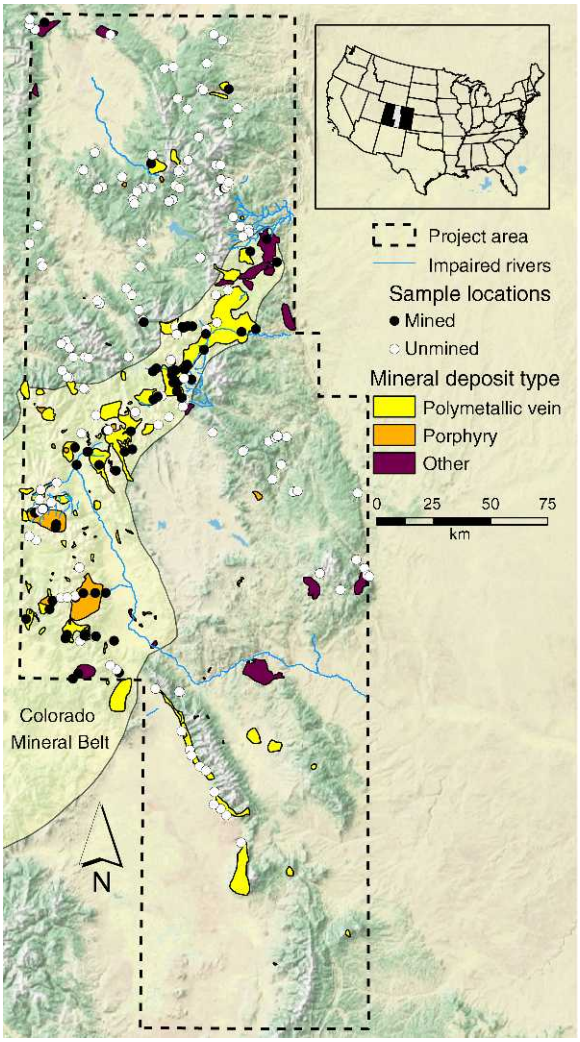

FIG. 1. Map of central Colorado (USA) study area showing sampled catchments. Catchments are classified on the basis of disturbance by historical mining and mineral deposit type. Rivers and streams (1165 km) depicted are on the Clean Water Act Section 303(d) list as impaired by aluminum, copper, cadmium, iron, lead, and/or zinc.

METHODS

Study area and design

The study area is central Colorado, USA, from Wyoming to New Mexico, an area of ~54 000 km^2 that includes most of the Southern Rocky Mountain Ecoregion, representing ~20% of the land area of Colorado (Fig. 1; Omernik 1987). This area includes a regional geologic feature, the Colorado Mineral Belt (Tweto and Sims 1963), that cuts diagonally across the study area. Mineral deposits in this zone have been exploited for base and precious metals for the past 150 years. Within this area, 1165 km of stream and river are classified as impaired (Clean Water Act section 303(d) list; see footnote 5) by metals commonly associated with mineralized areas and mined lands (aluminum, cadmium, copper, lead, iron, and zinc). The climate of the study area is temperate continental, with generally >50 cm of precipitation per year, especially at higher altitudes. Much of this precipitation occurs as snow in winter or as rain primarily between June and August. Vegetation ranges from deciduous cover at lower altitudes and in riparian zones, to conifer forests, and, at the highest altitudes, open tundra. Soils within the study area are thin (rarely greater than 10 cm thick) to nonexistent, the latter occurring in areas dominated by bedrock outcrops. Thicker (up to a meter or more)

immature soils, as well as unconsolidated overburden, are found intermixed at lower elevations and along streams.

The sample locations in this study are from small catchments (first- and second-order streams) at high altitude, ranging from 2330 to 3550 m above sea level. Catchments were selected that were underlain by a single predominant lithology (rocks of similar geochemistry and mode of formation). Drainage area boundaries (herein called "catchments") were defined with digital elevation models (DEM; 30×30 m resolution) using the ArcGIS 9.2 geographic information system software (ESRI 2006, Gesch 2007). Catchment boundaries along with geologic maps and databases of mine locations (see *Geologic mapping*, below) were used to classify each sample location (see *Site classification*, below) prior to going into the field (Fig. 1).

Geochemical and benthic macroinvertebrate samples were collected from these locations during base-flow conditions in the summers (July–August) of 2004–2007 (Fig. 1; Church et al. 2009, Wanty et al. 2009). Geochemical samples were collected from streams of various sizes (i.e., watershed area, site elevation, discharge), but biological data collection was confined to a narrower range of stream sizes to decrease the role variable habitat plays in structuring the aquatic invertebrate community. Although all field studies are influenced by confounding variables such as habitat, neither small-scale (i.e., percentage cover, substrate size) nor large-scale habitat factors (i.e., watershed area, elevation, percentage watershed vegetation) were strong predictors of mean biological responses in this data set (Schmidt et al. 2010). As a result, 198 locations were sampled for geochemistry ($n = 263$ samples for water and sediment) and 94 locations for benthic invertebrates ($n = 110$ samples, five replicates each) were included in this analysis. The differences between the number of samples and that of site locations are interannual replicates included to add annual variability of the benthic communities and geochemistry into the analysis. Duplicates of geochemical samples also were collected from ~10% of sample locations.

Geologic mapping

Databases from the State of Colorado (Sares et al. 2008) and the Federal Government (Mineral Resource Data System, USGS 2005) were used to determine deposit type and disturbance by mining (Fig. 1). The number of mine openings and a qualitative estimate of the volume of mine tailing in a catchment were derived from these databases as a description of the extent of disturbance by mining within a catchment. Catchments were characterized as "mined" if publically available data indicated that a commodity from the site was produced. Catchments not mined but with disturbances such as adits and prospect pits were classified as "unmined" because no commodity was produced and it was likely the extent of disturbance was minimal.

Hydrothermal alteration was mapped and characterized using mineral maps derived from analysis of Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) remote-sensing data (e.g., Rockwell 2009) and verified at the local scale with Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) data. Hydrothermal alteration identified using the ASTER data was classified into quartz–sericite–pyrite (QSP) and propylitic on the basis of spectrally identified mineral assemblages. Ecologically these two types of alteration are important because they are descriptive of acid-generation potential. QSP alteration contains pyrite in host rock with little acid-neutralizing capacity resulting from the alteration process. As the pyrite weathers it releases sulfuric acid, and drainages from these areas often have pH values below 7. In contrast, propylitic alteration emplaces acid-neutralizing minerals (e.g., calcite, chlorite, and epidote) into host rocks that weather to release drainage that is often near-neutral in pH. The mapping of hydrothermal alteration using remote-sensing data is possible only where the ground is not covered by vegetation, so some watersheds in the study area are hydrothermally altered but not detected by these methods. For more detailed information on the geological mapping and for the characteristics of principal hydrothermal mineral-deposit types found in the study area see Church et al. (2009).

Geochemical analysis

Water samples were collected using methods described in Wilde et al. (1998) to meet the requirements of the biotic ligand model (HydroQual 2007). Routine water-quality parameters (temperature, conductivity, and pH) were measured in the field using a Horiba D-24 combination meter (Wilde et al. 1998). Meters were calibrated at the beginning of each day with certified standards, and checked periodically throughout the day. All water samples were filtered through an Acrodisc Premium 25-mm syringe filter with 0.45-μm nylon membrane (Pall Corporation, Port Washington, New York, USA) in the field and stored at 4°C until analyzed. Water samples for dissolved organic carbon (DOC) were filtered in the field through a 0.70-μm glass-fiber filter, acidified with concentrated hydrochloric acid (12 mol/L) to a pH < 2, and stored in baked amber-glass bottles. Dissolved trace-metal samples were acidified in the field with concentrated ultrapure nitric acid (13 mol/L) to a pH < 2 and stored in polyethylene bottles. Samples for anions were collected and stored under refrigeration in polyethylene bottles. Streambed sediment samples were collected from surfaces of fluvial sediment deposits in pool or low-velocity areas along the sampled reach using a plastic scoop. The samples were composited, wet-sieved through a 2-mm stainless-steel screen with ambient stream water, and collected into a plastic pan. In the laboratory these samples were prepared for chemical analysis by air-drying and dry-sieving them through a 150-μm stainless-steel screen.

Water analyses were conducted at the laboratories of the USGS Central Mineral and Environmental Science Center in Denver, Colorado, USA. A Shimadzu TOC-5000A organic carbon analyzer was used to measure DOC. Concentrations of major cations were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and ICP-mass spectrometry (ICP-MS) whereas trace-metal concentrations were measured by ICP-MS, and major anions were measured by ion chromatography (Taggart 2002). High concentrations of SO_4^{-2} (>25 mg/L) were determined by ICP-AES and alkalinity was determined by titration (Taggart 2002). Sediment samples were prepared using total digestion and EPA 3050B leach procedures (U.S. EPA 1996) and analyzed by both ICP-AES and ICP-MS.

Field blanks were prepared by analyzing doubly deionized water that was transported from the laboratory to the field, and treated as a sample at a field site. A similar set of field blank samples was collected as for regular samples. Results of analyses of the field blanks were generally below detection, although one blank showed slight contamination, particularly for iron. Field duplicate samples collected the same day as the suspect field blank showed good reproducibility. In most cases, reproducibility was within ±10%, although errors increased if elements were present near their lower determination limits. No duplicate samples were included in this evaluation.

Aquatic invertebrate sampling

At each site five replicate benthic samples were collected using a 0.1-m^2 Hess sampler (350-μm mesh net) from shallow riffle areas (<0.5 m deep). Representative sample localities were selected on the basis of the following criteria: location was a riffle or run habitat unit, depth was 0.10–0.25 m, and substrate was representative of the stream reach. Overlying substrate was scrubbed to dislodge and capture all algae, diatoms, and invertebrates, while inorganic debris was removed. Underlying substrate was disturbed to a depth of ~10 cm and the remaining material was sieved using a 350-μm mesh sieve. All organisms retained were preserved in 80% ethanol in the field.

In the laboratory the samples were processed to remove debris, and subsampled until 300 organisms (±10%) were removed from the sample (Moulton et al. 2000). Invertebrates were identified to the lowest practical taxonomic level—genus for most taxa (Merrit and Cummings 1996, Ward et al. 2002). Taxa observed at fewer than 20 sites were removed from the analysis to reduce the influence of rare taxa on study results. Taxonomic ambiguities—closely related specimens identified at different levels of taxonomic resolution for many reasons (i.e., inability to distinguish characteristics of early instars or damaged specimens)—were resolved by distributing individuals identified at coarser levels of taxonomic resolution to finer levels depending on their abundance (Cuffney et al. 2007). The five replicate benthic samples were averaged and used to calculate benthic macroinvertebrate community metrics.

Although many other metrics were evaluated, we only evaluated the total generic richness of Ephemeroptera, Plecoptera, Tricoptera (EPT); an EPT index is presented here for simplicity. Typically, five major groups (Ephemeroptera, Plecoptera, Tricoptera, Diptera, and Elmidae) comprise nearly 100% of the benthic fauna in Colorado streams (Ward et al. 2002). In fact, EPT (57%), Diptera (24%), and Elmidae (5%) comprise the majority (86%) of average total taxa richness at sites observed in this study. Members of those orders that comprise the EPT index are often cited as some of the taxa most sensitive to metals (Plafkin et al. 1989, Lenat and Barbour 1994), and the loss of these taxa can disrupt energy transfer through the stream food web (Carlisle and Clements 2005). EPT index has also been cited as a sensitive metric useful for regional-scale assessments of metal contamination (Clements et al. 2000).

Determination of toxic units

Because most metal-contaminated streams in Colorado are affected by mixtures of cadmium (Cd), copper (Cu), and zinc (Zn), we used a cumulative measure (assuming additive metal toxicity) of aqueous metal toxicity (Sprague 1970, Clements et al. 2000). The method relies on the biotic ligand model to account for site-specific influences of water quality on metal toxicity to aquatic organisms (HydroQual 2007, Schmidt et al. 2010). Toxic units for water (TU_{wat}) are defined as

$$TU_{water} = \sum_i \frac{m_i}{c_i}$$

a ratio where m_i is derived from the biotic ligand model and is the calculated metal accumulated on the biotic ligand, given the specific-site water conditions relative to that amount of metal accumulated on the biotic ligand in water of character specified by the U.S. EPA (2003, 2007) and criterion continuous concentration values, c_i, summed for Cd, Cu, and Zn (U.S. EPA 2009). Theoretically, at $TU_{wat} \leq 1$ all metal concentrations are below criterion continuous concentration, and are presumed to be protective of 95% of aquatic organisms (Stephan et al. 1985, Schmidt et al. 2010).

Because less is known about the mechanisms by which metals in sediment are accumulated and cause toxicity in aquatic organisms, an empirical model was used to estimate toxicity. Sediment toxicity due to metal mixtures was calculated as described above except where m_i is the total metal concentration and c_i is the criterion value for the (ith) metal in sediment, summed for Cd, Cu, and Zn. Criterion values used to calculate sediment toxic units (TU_{sed}) were derived from the probable-effects concentration, consensus-based sediment quality guidelines (PEC-CBSQG; MacDonald et al. 2000).

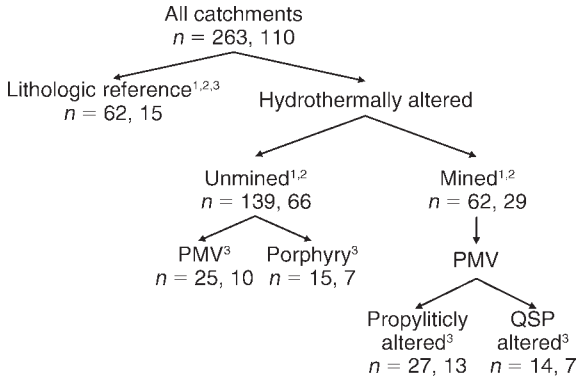

FIG. 2. Breakdown of the catchment classification, with sample size (n) given for the geochemical (first number) and aquatic invertebrate community (second number). Unmined catchments were subdivided into lithologic reference and those influenced by hydrothermal alteration. Hydrothermally altered catchments were further subdivided by mineral-deposit type. Mined sites from a single deposit type (polymetallic veins, PMV) were reclassified into two distinctly different styles of hydrothermal alteration: propylitic and QSP (quartz–sericite–pyrite). The superscript numbers define groups of data that were used to test different hypotheses: (1) Data used to test the hypothesis that elevated concentrations of metals in water and sediment and depauperate aquatic communities are restricted to historically mined catchments, with results presented in Fig. 3. (2) Data used to test the second hypothesis, that geologic processes (i.e., hydrothermal alteration and mineral deposit type) control stream geochemistry and aquatic communities, with results presented in Fig. 4. (3) Data used to test the second hypothesis, that geologic processes (i.e., hydrothermal alteration and mineral deposit type) control stream geochemistry and aquatic communities, with results presented in Fig. 5.

Probable-effects concentrations are empirically derived thresholds above which harmful effects are likely to be observed.

Site classification

To test our first working hypothesis, that elevated concentrations of metals in water and sediment and depauperate aquatic invertebrate communities are restricted to historically mined catchments, all samples were classified by the presence (n = 62 samples for geochemistry, $n = 29$ samples for biology) or absence (n = 201, 81 samples, respectively) of disturbance by mining. To test our second working hypothesis that geologic processes (i.e., hydrothermal alteration and mineral-deposit type) control stream geochemistry and aquatic communities, we reclassified our samples based on the presence of hydrothermal alteration, mineral-deposit type, and mining (Fig. 2, Table 1). Lithologic reference ($n = 62$, 15 samples, respectively) catchments are areas where hydrothermal alteration was not detected in the AVIRIS/ASTER images and were not mined. Hydrothermally altered (n = 139, 66 samples, respectively) catchments are areas with detectable hydrothermal alteration at the earth's surface, but were not mined. Because not all hydrothermal alteration results in the formation of a mineral deposit, not all hydrothermally altered sites were mined or classified into different mineral deposit types (Fig. 2, Table 1). The effects of different styles of hydrothermal alteration (propylitic vs. QSP) on unmined polymetallic vein deposits were indistinguishable and were lumped together into one category, background polymetallic vein deposits (n = 25, 10 samples, respectively). Porphyry mineralized sites, which were not mined, were classified as background porphyry deposits (n = 15, 7 samples, respectively). Because few mined and unremediated porphyry style deposits were found within the study area, the effect of mining and remediation on porphyry-style deposits was not evaluated.

Statistical analysis

Multiple working hypotheses were evaluated requiring tests between groups of data classified based on disturbance (i.e., presence or absence of mining), hydrothermal alteration (propylitic and QSP), and mineral-deposit type (polymetallic vein and porphyry). Because normality and homogeneity of variance could not be achieved in most log-transformed data, differences in means were tested using nonparametric procedures. A Wilcoxon ranked sum test ($P < 0.05$) or Kruskal-Wallis ANOVA by ranks and Dunn's multiple-comparison test were used to evaluate differences among groups (Siegel and Castellan 1988, Sokal and Rohlf 2003). Boxplots were used to depict the results for ease of interpretation. All statistical comparisons were developed using R software version 2.7.2 (R Development Core Team 2008).

RESULTS

Samples were collected from diverse lithologies resulting in a wide spectrum of aqueous and sediment geochemical characteristics (Table 2). Disturbance by mining was extensive, with up to 146 inactive mine openings (estimate of the number of mines within a catchment), and >700 000 m^3 of historic mine tailings (a qualitative visual estimate of the amount of earth disturbed and deposited on the surface) were observed in some catchments. The presence of mineralized rock and historic mining on stream water and sediment caused some streams to have very low pH (< 4), and concentrations of metals in water and sediment in excess of 200 and 50 times, respectively, the thresholds thought safe for aquatic organisms (Table 2).

Water (Fig. 3A) or sediment (Fig. 3B) from mined (n = 62) catchments were statistically more toxic than in unmined (n = 201) catchments. The average EPT (Ephemeroptera, Plecoptera, Tricoptera) index (Fig. 3C) in unmined catchments (n = 81) was statistically higher than in mined catchments (n = 29). However, water or sediment exceeded toxic thresholds in 31 of 201 unmined (Fig. 3A, B) catchments, and the lowest EPT index (0.2; Fig. 3C) was observed in an unmined catchment. Elevated metal concentrations in water and sediment likely created an environment that supported

TABLE 1. Definitions of the geologic classification scheme used to test the working hypotheses, and used in Figs. 2–5.

Classification	Definition
Lithologic reference	unmined catchments where hydrothermal alteration was not detected
Hydrothermally altered	unmined catchments with detectable mineralization or alteration
Propylitic alteration	style of hydrothermal alteration that emplaces acid-neutralizing minerals such as calcite ($CaCO_3$), epidote ($Ca_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$, and chlorite (variable formulae, cf. Hey 1954) into host rocks
Quartz–sericite–pyrite (QSP) alteration	style of hydrothermal alteration that emplaces acid-generating minerals such as pyrite (FeS_2) into host rocks, and consumes acid-neutralizing minerals as part of the alteration process
Polymetallic vein, PMV	mineral deposit composed of a mixture of minerals commonly containing copper, cadmium, and zinc and emplaced in host rocks as long fractures and vein structures
Porphyry	mineral deposit type that includes copper and molybdenum-sulfide minerals such as pyrite, chalcopyrite ($CuFeS_2$), and molybdenite (MoS_2), characterized by large volume and high sulfide content

few EPT taxa in both mined and unmined catchments, rejecting our first working hypothesis, that metals and depauperate benthic communities were confined to mined catchments.

Sites were reclassified to test if hydrothermal alteration was a determinant of metals in streams and depauperate benthic communities (Fig. 2, Table 1). Lithologic reference catchments had water (Fig. 4A) and sediment (Fig. 4B) concentrations ($n = 62$) that averaged below TU (toxic unit) = 1 and had a significantly higher EPT index (Fig. 4C, $n = 15$) as compared to either hydrothermally altered ($n = 139$, 66 geochemistry and EPT index, respectively) or mined catchments ($n = 62$, 29 geochemistry and EPT index respectively). Both unmined but hydrothermally altered catchments and mined catchments had numerous outliers, suggesting multiple groups were aggregated within each class based on the presence of hydrothermal alteration or mining alone. To reduce the observed within-group variation in both catchment types, unmined but hydrothermally altered and mined catchments were reclassified by deposit type (Fig. 2).

Statistical differences were not observed between lithologic reference catchments and unmined polymetallic vein deposits for water (Fig. 5A) or sediment toxicity (Fig. 5B) or EPT index (Fig. 5C), but were significantly different from background porphyry deposits. Sediments from background polymetallic vein (PMV) catchments rarely exceed TU = 1, while background porphyry-deposit waters and sediments had average concentrations in excess of this threshold. The EPT index at background PMV catchments averaged lower than that observed at lithologic reference sites, but this difference was not statistically significant. However, background porphyry deposits were observed to nearly exclude aquatic life, with a median EPT index < 2, and were significantly different from both lithologic reference and background PMV sites.

The effect of mining and hydrothermal alteration type was found to be distinguishable for PMV deposits. Water (Fig. 5A) and sediment (Fig. 5B) from mined and propylitically altered catchments containing PMV deposits were less toxic than those from catchments containing mined and QSP-altered sites. No water samples and only a few sediment samples from the QSP-altered and mined class were found to be less than TU = 1 while propylitically altered and mined PMV deposits averaged TU < 1 for water and sediment averaged TU > 1, but both were less than those found for QSP-altered mined catchments. Although it appears that all QSP-altered catchments produce very toxic waters and sediments, it should be noted that unmined, PMV deposits that are QSP altered did not exceed TU = 1.

EPT index (Fig. 5C) for lithologic reference, unmined PMV deposits, and mined propylitically altered PMV deposits were statistically indistinguishable. Catchments containing background porphyry deposits were nearly devoid of EPT taxa, while mined QSP-altered PMV deposits also had a low average EPT index, as compared to lithologic reference and unmined PMV deposits. Mined QSP-altered PMV deposits were indistinguishable from unmined porphyry or mined propylitically altered PMV deposits.

DISCUSSION AND CONCLUSIONS

Historically, ecological risk assessments of abandoned mined lands have presumed that the presence of historical mining in a catchment was the primary cause of elevated concentrations of metals in water and

TABLE 2. Median and range of physicochemical parameters measured in this study.

Parameter	Median	Measured range
Mine openings	0	0–146
Volume of mine tailings (m^3)	0	0–540 000
Discharge (m^3/s)	0.1	>1–1.5
Temperature (°C)	10.2	0.8–24.1
pH (standard units)	7	3.5–8.5
Hardness (mg/L)	33.8	5–163
Cd^{2+} (μg/L)	0.01	>0.02–561
Cu^{2+} (μg/L)	0.25	>0.5–170,00
Zn^{2+} (μg/L)	1.5	>0.5–118 000
Toxic units for water, TU_{wat}	0.12	0.01–268
Cd in sediment (mg/kg)	1	1–63
Cu in sediment (mg/kg)	12	0.5–7 270
Zn in sediment (mg/kg)	107	19–13 100
Toxic units for sediment, TU_{sed}	0.57	0.26–52

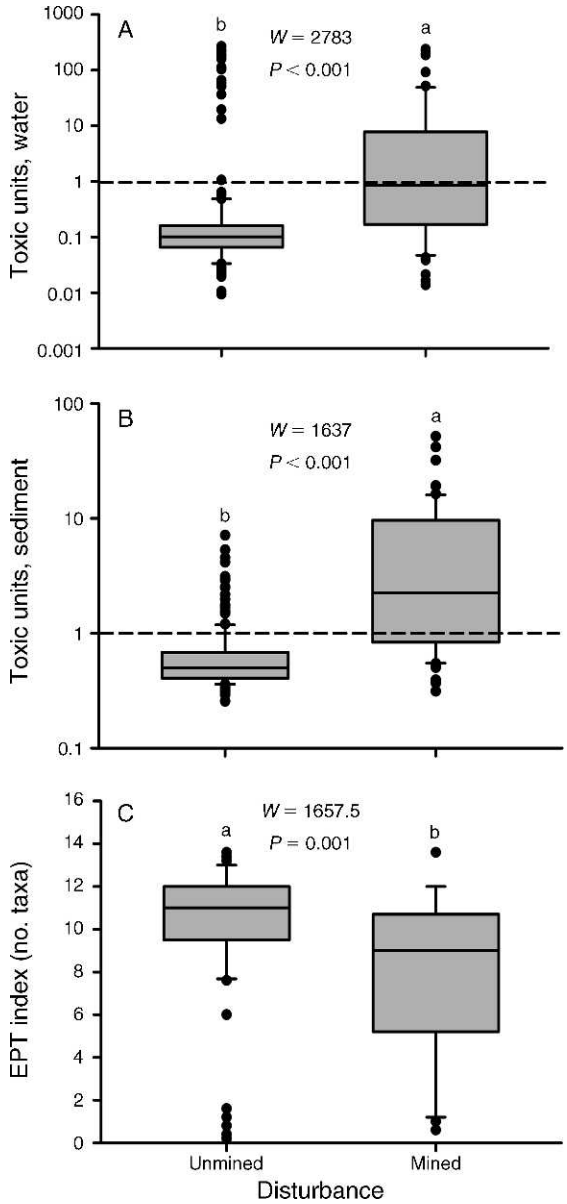

FIG. 3. Effect of mining on water and sediment toxicity and metal-sensitive aquatic invertebrate communities. Different lowercase letters indicate significant differences at $P \leq 0.05$ based on the Wilcoxon rank-sum statistic (W). Toxic units are the summed concentrations of Cd, Cu, and Zn, normalized by procedures described in *Methods: Determination of toxicity units* for water and sediment. The EPT (Ephemeroptera, Plecoptera, and Tricoptera) index is the total number of mayfly + stonefly + caddisfly taxa observed at a site. Boxplots depict the data distributions where the top and bottom represent the 75th and 25th percentiles and the dividing line is the 50th percentile or the median value. The whiskers extend to the 5th percentile (bottom) and 95th percentile (top) of the data distribution. Dots represent outliers beyond the 5th and 95th percentiles.

sediment. We demonstrate here that hydrothermally altered rock alone in a catchment also may result in elevated concentrations of metals in water and sediment (Church et al. 2009, Verplanck et al. 2009, Wanty et al. 2009). Novel to our work is that risks to aquatic life were quantified and it was determined that metals released naturally from weathering of the hydrothermally altered rock limit the EPT (Ephemeroptera, Plecoptera, Tricoptera) index. Because historical mines

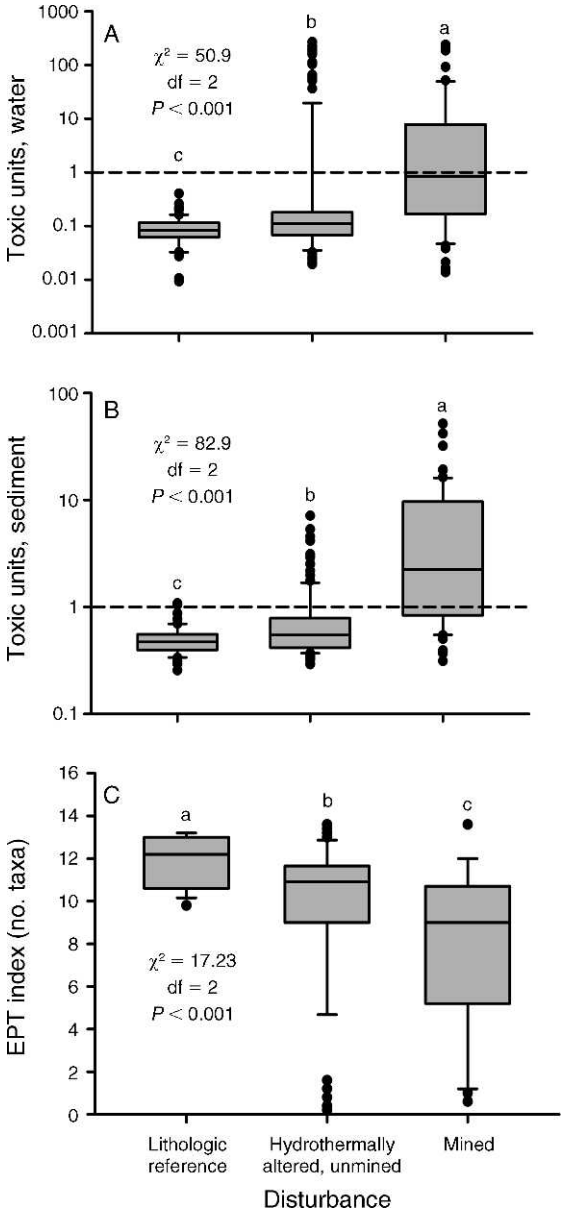

FIG. 4. Effect of hydrothermal alteration and mining on water and sediment toxicity and metal-sensitive aquatic invertebrate communities. Chi-square statistics are the result of a Kruskal-Wallis one-way ANOVA by ranks. Different lowercase letters indicate significant differences based on Dunn's multiple-comparison test ($P \leq 0.05$). See Fig. 3 for boxplot descriptions.

in our study area are located in catchments that were hydrothermally altered, not all the metals in water and sediment from streams draining mined catchments are attributable to the mining process. However, mining appears to increase metal concentration and the toxicity of water and sediment to EPT taxa in these catchments.

The effect of hydrothermal alteration on the toxicity of water and sediment is not the same for all mineral-deposit types. Water and sediment from catchments that have unmined polymetallic vein (PMV) deposits were indistinguishable from lithologic reference catchments, likely due to carbonate minerals associated with this type of deposit that can neutralize acids and minimize the export of metals to aquatic ecosystems (du Bray 1996). In contrast, water and sediment from catchments containing unmined porphyry deposits were toxic, so that EPT taxa are essentially absent from these catchments. As a result, the style and intensity of hydrothermal alteration and the mineral-deposit type must be considered when assessing the environmental state of mined areas.

Locally derived geochemical and biological baselines can lead to an accurate assessment of the effects of mining on aquatic ecosystems. For example, in our study area mined PMV deposits hosted by propylitically altered rocks resulted in elevated water and sediment toxicity and a modest reduction of EPT index as compared to lithologic reference. However, mined QSP (quartz–sericite–pyrite)-hosted PMV deposits resulted in an 80% reduction of EPT index. Had we compared the median EPT index found at lithologic reference sites (11.8) to that observed at all mined sites (7.8), we would estimate that mining had caused a 34% decline in EPT index. However, mined propylitically altered PMV deposits decreased EPT index by only 6% compared to that observed at unmined PMV deposits. The use of unmined catchments with similar geologic characteristics (lithology and alteration) as a potential analog for pre-mining baselines allowed us to qualitatively distinguish between the influence on aquatic ecosystems of natural geologic processes and mining.

In certain deposit types there is potential for streams to be misclassified as impaired due to mining if these geologic processes are not considered in biological assessments of abandoned-mine lands. A spatially randomized sampling design used to determine the number of kilometers of impaired streams found that 67% of the mountain streams in Colorado (USA) exceeded concentrations thought safe for aquatic life (Clements et al. 2000); while 1165 km of stream within our study area are listed as impaired (Clean Water Act [CWA] section 303(d) list in 2008; see footnote 5). Of the sample locations we investigated that are listed on the CWA section 303(d) list, 25% of them were unmined and influenced by natural sources of metals.

There are uncertainties associated with our methods. For example, the ASTER/AVIRIS data (Rockwell 2009) used to detect hydrothermal alteration can only determine the areal extent of alteration in areas that are not vegetated. The degree to which the vegetated surface and more importantly the subsurface (where groundwater systems and soils can be influenced by these mineralized systems) are affected by hydrothermal alteration cannot be assessed with these methods. As a result, there are streams subjected to hydrothermal alteration and mineral deposits that are not detectable.

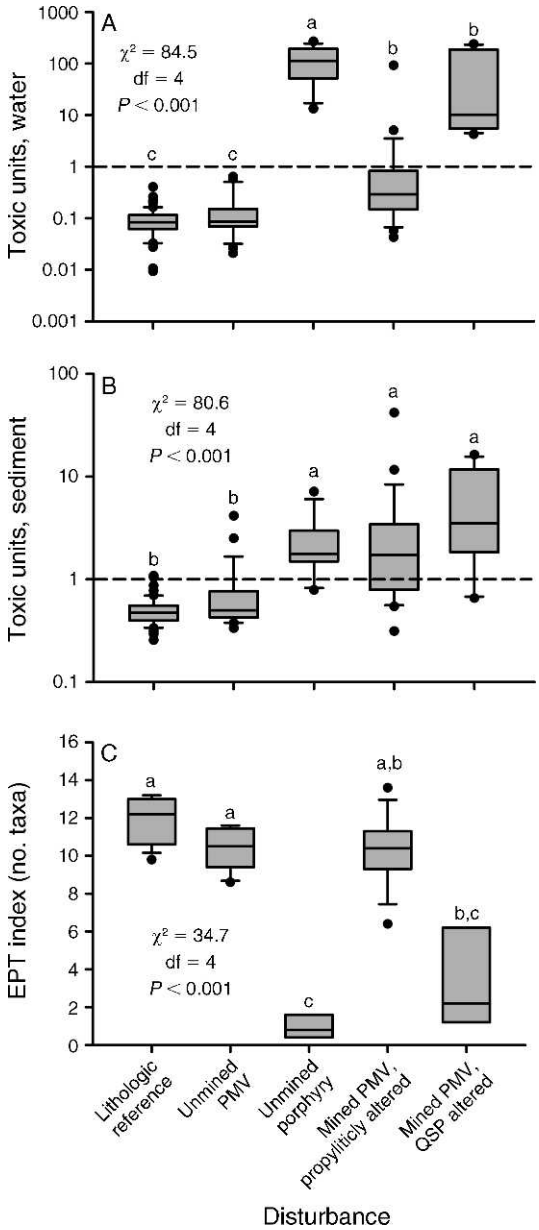

FIG. 5. Effect of hydrothermal alteration, mineral-deposit type, and mining on water and sediment toxicity and metal-sensitive aquatic invertebrate communities. Chi-square statistics are the result of a Kruskal-Wallis one-way ANOVA by ranks. Different lowercase letters indicate significant differences based on Dunn's multiple-comparison test ($P \leq 0.05$). See Fig. 3 for boxplot descriptions.

For example, five sample locations could not be classified based on mineral-deposit criteria and were not included in comparisons of mineral-deposit type or style of alteration. This inability to classify sites is likely less problematic as compared to our inability to determine the total extent of hydrothermal alteration and mineral deposit on the surface and subsurface of catchments. This latter limitation could explain a substantial amount of the variance in the sediment and water chemistry observed within rock type.

The influence of hydrothermal alteration, mineral deposits, and mining on aquatic ecosystems in the United States and the world is significant. Over 200 000 abandoned mines are located in the contiguous 48 U.S. states (there is no count of the number of abandoned mines globally), one half of which are hard rock mines like those investigated here (Ferderer 1996). Ludington et al. (1996) estimated that only half of the extractable mineral commodities found domestically are exploited, while estimating that 50% of the unexploited resources may influence surface ecosystems. Mineral deposits similar to those studied here can be found all over the world, with a substantial fraction of the U.S. polymetallic vein and porphyry deposits found in Arizona, Colorado, Montana, Nevada, and New Mexico (USGS 2009, Verplanck et al. 2009). Although many of these deposits are unmined, future exploitation of these types of mineral deposits could have implications for the health of regional ecosystems (Ludington et al. 1996). Because unmined hydrothermally altered areas are poorly documented in the literature, a better understanding of the spatial distribution and ecological effects of mineral deposits would greatly increase our ability to evaluate ecological risks associated with mining globally.

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