Aquatic Ecosystems in Central Colorado Are Influenced by Mineral Forming Processes and Historical Mining

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Abstract

Stream water and sediment toxicity to aquatic insects were quantified from central Colorado catchments to distinguish the effect of geologic processes which result in high background metals concentrations from historical mining. Our sampling design targeted small catchments underlain by rocks of a single lithology, which allowed the development of biological and geochemical baselines without the complication of multiple rock types exposed in the catchment. By accounting for geologic sources of metals to the environment, we were able to distinguish between the environmental effects caused by mining and the weathering of different mineralized areas. Elevated metal concentrations in water and sediment were not restricted to mined catchments. Impairment of aquatic communities also occurred in unmined catchments influenced by hydrothermal alteration. Hydrothermal alteration style, deposit type, and mining were important determinants of water and sediment quality and aquatic community structure. Weathering of unmined porphyry Cu-Mo occurrences resulted in water (median toxic unit (TU) = 108) and sediment quality (TU = 1.9) that exceeded concentrations thought to be safe for aquatic ecosystems (TU = 1). Metal-sensitive aquatic insects were virtually absent from streams draining catchments with porphyry Cu-Mo occurrences (1.1 individuals/0.1 m^2). However, water and sediment quality (TU = 0.1, 0.5 water and sediment, respectively) and presence of metal-sensitive aquatic insects (204 individuals/0.1 m^2) for unmined polymetallic vein occurrences were indistinguishable from that for unmined and unaltered streams (TU = 0.1, 0.5 water and sediment, respectively; 201 individuals/0.1 m^2). In catchments with mined quartz-sericite-pyrite altered polymetallic vein deposits, water (TU = 8.4) and sediment quality (TU = 3.1) were degraded and more toxic to aquatic insects (36 individuals/0.1 m^2) than water (TU = 0.4) and sediment quality (TU = 1.7) from mined propylitically altered polymetallic vein deposits. The sampling approach taken in this study distinguishes the effects of different mineral deposits on ecosystems and can be used to more accurately quantify the effect of mining on the environment.

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Introduction

Lithology, geologic processes, and time control the geochemistry and morphology of the Earth's surface and thus profoundly affect ecosystems (Hynes 1975, Vitousek et al. 1997, Cary et al. 2005). In combination with climate (i.e., precipitation and temperature) and vegetation (i.e., organic acids and anions), these processes determine the rate of mechanical and chemical weathering of bedrock, which influences the structure and function of terrestrial ecosystems (Drever 1994, Vitousek and Farmington 1997, Vitousek et al. 1997) and aquatic ecosystems (Wanty et al. 2002, Schmidt 2007).

In mineralized areas containing pyrite, degradation in water quality occurs when sulfide minerals are oxidized upon exposure to water and O_2 (Wanty et al. 2002), producing hydrogen ions. The acidic waters react with metal sulfides, forming metal hydroxides and locally high concentrations of dissolved metals, depending on the composition of rocks surrounding the mineral deposits (Plumlee et al. 1995). This natural redox cycle is enhanced by historical mining, which has exposed large volumes of unweathered, often pyritic rock with reactive surface areas enhanced in finely crushed rock.

Central Colorado was heavily mineralized during the Larimide orogeny by emplacement of plutons and associated sulfide mineral deposits of various types (Tweto and Simms 1963). Recent surveys of mountain streams in Colorado suggest that up to 25 percent are degraded by elevated metal concentrations (Clements et al. 2000). Generally, this degradation is assumed to result from the mineral extraction economy that began in central Colorado in 1859 (Chronic and Chronic 1972). It is largely unknown to what extent weathering has released metals that affect aquatic ecosystems in this region.

Hydrothermal alteration and ore deposit formation are complex enough that we must be precise about how we use terms describing these processes. **Hydrothermal alteration** is a geologic process that results from rock/fluid interactions causing cation/anion exchanges that fundamentally change the geochemistry of host rocks (Robb 2005). The type and extent of hydrothermal alteration is controlled by five factors: temperature, pressure, host rock composition, fluid composition, and the volume of fluid/rock interactions (Reed 1997). Hydrothermal alteration is a part of the ore-forming process such that one will rarely find a mineral deposit that has not been influenced by hydrothermal fluids (Robb 2005).

There is a continuum of hydrothermal alteration styles ranging from propylitic to quartz-sericite-pyrite alteration. Propylitic alteration results from low temperature fluids/rock interactions at low pore water/rock volumes and forms epidote, chlorite, and other minerals with acid neutralizing capacity. This is the most widespread form of alteration in the study area. Quartz-sericite-pyrite alteration occurs under higher temperature and pressure and transforms feldspars into other minerals such as quartz, sericite, and pyrite, which is the major acid generating sulfide mineral.

A **mineral deposit** is a mineral occurrence of sufficient size and concentration and is accessible such that under favorable circumstances it would be considered to have economic potential (Cox and Singer 1986). An **ore deposit** is a mineral deposit which has been tested and is known to be of sufficient size, concentration, and accessibility, and is deemed beneficial for economic reasons to exploit. The term **mined** is reserved here for areas that were exploited such that publically available data indicated that a commodity from the mine site was produced. As a result, there are many catchments where ore-forming processes have elevated concentrations of metals in catchment rocks, which likely influence water and sediment quality despite prior mining (Tooker 1963, Tweto 1968, Wanty et al. 2002, Bove et al. 2007, Mast et al. 2007).

The expected water quality due to weathering of specific minerals associated with these hydrothermal alteration and deposit types have implications for the understanding of the changes in metal toxicity across the landscape. The bioavailability of a dissolved free-ion metal is affected by a suite of constituents (e.g., HCO_3^-, CO_3^{2-}, Cl^- ,Ca^{2+}, Mg^{2+}) found in surface water (Meyer 2002). By applying geoenvironmental models (Cox and Singer 1986) descriptive of the distribution of minerals that affect water quality and toxicity of metals, we can improve our ability to understand the effects of mining on aquatic ecosystems.

We evaluate the extent to which mining exacerbates the influence of ore-forming processes on the toxicity of metals to aquatic insect communities in streams of central Colorado. Two hypotheses are tested: (1) that elevated metals in water and sediment that may impair aquatic insect communities are restricted to mined catchments (a presumption made in many ecological risk assessments of historical and abandoned mines), and (2) that ore-forming processes influence the effect of mining on water and sediment toxicity to aquatic insect communities. To test the first hypothesis, comparisons are made between catchments which were unmined and unaltered (referred to as reference), unmined and influenced by ore-forming processes identified as hydrothermal alteration (referred to as background), and mined catchments. To test the second hypothesis, it was necessary to reclassify our catchments (Church et al., this volume). Reference catchments were split into two mineral occurrence types: polymetallic vein (referred to as deposit type A) and porphyry Cu-Mo (copper-molybdenum) occurrences (deposit type B). Mined deposit type A catchments were broken down by the style of hydrothermal alteration associated with their formation: propylitic or quartz-sericite-pyrite alteration.

Methods

Study design

Stream water and sediment were collected from 198 catchments during base-flow conditions during the summers (July through August) of 2003–2007 (Figure 1) (Church et al., in press). In a subset of these catchments, aquatic insect communities were collected upstream from the site where water and sediment samples were collected (Church et al., in press). Aquatic insects were collected either simultaneous with or within a few days immediately following the collection of stream water and sediment. Digital elevation models (DEM, 30-m resolution) were used to define catchment boundaries using geographic information systems (ArcGIS 9.2). Small catchments (1st- and 2nd-order streams) predominantly underlain by a single lithology (rocks of similar geochemistry and mode of formation) were sampled. Catchments were characterized as unaltered, influenced by different styles of hydrothermal alteration, or historically mined (Figure 1). Field parameters, geochemical results, and quality assurance/quality control (QA/QC) data are reported in Church et al. (in press).

Hydrothermal alteration was mapped (Figure 1) and characterized across the study area primarily using mineral maps derived from analysis of advanced spaceborne thermal emission and reflection radiometer (ASTER) remote-sensing data. Such ASTER maps were supplemented and verified by published hydrothermal alteration data at local scales (generally from dissertations and wilderness studies) and more detailed mineral maps generated from airborne visible/infrared imaging spectrometer (AVIRIS) data. Hydrothermal alteration identified using the ASTER data was classified as advanced argillic, argillic ± ferric iron, quartz-pyrite-sericite (QSP), and propylitic on the basis of spectrally identified mineral assemblages. For example, the QSP alteration type was characterized by the occurrence of ferric iron + sericite ± kaolinite. Several minerals that are associated with alteration may also occur in unaltered sedimentary and metamorphic rocks. Hydrothermally altered areas were differentiated from unaltered areas by applying a 3-km buffer around intrusions and by excluding specific lithogeochemical units (Church et al. 2008) that contain abundant muscovite (e.g., shale and metapelite) and (or) carbonate minerals (limestone and dolomite). This process allowed for the inclusion of areas which were hydrothermally altered and the exclusion of areas that have mineral assemblages that formed under other geologic processes. The mapping of alteration using remote sensing data is possible only where the ground is not covered by vegetation, thus adding a degree of uncertainty to this level of catchment classification. It is unknown how much of the area is hydrothermally altered but so obscured by vegetation that we could not map it. Some catchments that have no evidence of historical mining activity are, nevertheless, hydrothermally altered.

Databases from the State of Colorado (M.A. Sares, 2008, U.S. Forest Service Abandoned Mine Land Inventory, Colorado, Colorado Geological Survey, unpub. report) and the Federal Government (Mineral Resource Data System, U.S. Geological Survey) were used to determine disturbance by mining (Figure 1). Catchments were characterized as mined if publically available data indicated that a commodity from the mine site was produced. For all

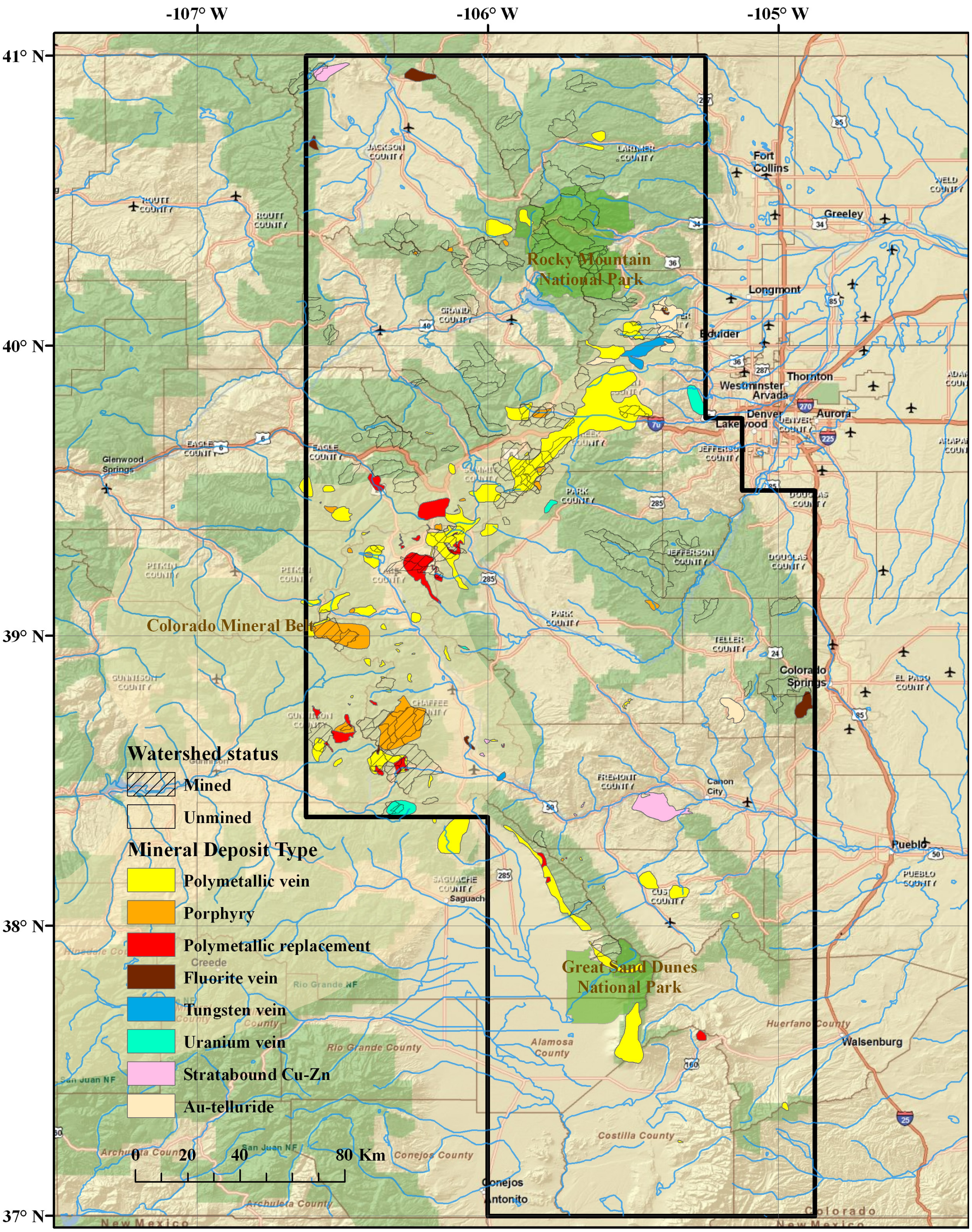

Figure 1. Map of central Colorado study area showing sampled catchments. In this figure, catchments are classified on the basis of disturbance by historical mining and deposit type.

other disturbances (such as adits, shafts, and prospect pits), for the deposit types considered here, we found few cases in which these disturbances were observed to increase sulfide mineral weathering to a degree we could distinguish from reference. As a result we lumped catchments influenced by adits, shafts, and prospect pits into the unmined group.

Geochemical analysis

Filtered (0.45 µm) and unfiltered water samples were analyzed using both inductively coupled plasma–atomic emission spectrometry (ICP-AES) and inductively coupled plasma–mass spectrometry (ICP-MS). Sediment samples were prepared using total digestion and EPA 3050B leach procedures. Analyses were done using both ICP-AES and ICP-MS. Detailed analytical methods; QA/QC data on duplicates, replicates, and standard reference materials; and analytical results are described in Church et al. (in press).

Previous work has shown that sediment geochemistry is dominated by colloids, which vary in proportion seasonally and with storm events (Fey et al. 2002, Church et al. 2007a). Thus, each sample was treated as a separate observation to determine a range of element concentrations from these disturbed catchments. Both filtered and unfiltered water and fine sediment samples (sieved to 177 µm) collected from 198 catchments over a 4-yr period (2003–2007) constitute the data set discussed in this paper. No duplicate samples were included in this evaluation.

Benthic macroinvertebrate sampling

Five replicate benthic samples (n = 5) were collected using a 0.1-m^2 Hess sampler (minus 350-µm mesh net) from shallow riffle areas (<0.5 m). 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 of all algae and diatoms and inorganic debris was removed. Underlying substrate was disturbed to a depth of approximately 10 cm and the remaining material was sieved using a 350-µm mesh sieve. All organisms retained were preserved in 80 percent ethanol in the field.

In the laboratory, samples were processed to remove debris and sub-sampled until 300 organisms (±10 percent) were removed from the sample following methods described by Moulton et al. (2000). Invertebrates were identified to the lowest practical taxonomic level (genus or species for most taxa; subfamily for chironomids) (Merritt and Cummings 1996, Ward et al. 2002). Means of the five replicate benthic samples were used to calculate the density (number of individuals per 0.1 m^2) of taxa known to be sensitive to metals (i.e., mayflies, stoneflies + caddisflies) (Clements et al. 2000).

Determination of toxic units

Streams are often impaired by a mixture of trace metals at chronic concentrations that act additively to cause toxicity to aquatic organisms (Clements et al. 2000, Playle 2004). Toxic units (TUs) are the ratio of measured metal concentration for a given site (water or sediment) normalized by a benchmark protective of freshwater organisms. Toxicity due to multiple metals is accounted for by summing the toxic unit value for each metal observed at a site as follows:

$$\Sigma TU = \sum_i \frac{m_i}{c_i}$$

where m_i is the metal concentration and c_i is a benchmark value for the i^{th} metal (Table 1). Because cadmium, copper, and zinc (Cd, Cu, and Zn) are the primary metals of concern in the central Colorado Rocky Mountain region, all toxic units reported are the sum of all three metals.

The benchmark values for metals in water are derived from the U.S. Environmental Protection Agency Criterion Continuous Concentration (CCC) (National Academies of Sciences and Engineering 1973). The CCC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

Table 1. List of benchmarks used to derive toxic units (TU) for water and sediment.

	Water (nmol/g of gill tissue wet weight)[1]	Sediment (mg/kg dry weight)[2]
Cd	0.341	4.98
Cu	0.106	49
Zn	1.356	459

[1]Major cations, anions, and organic ligands influence the toxicity of aqueous metals to aquatic organisms, and the Biotic Ligand Model is capable of predicating toxicity to aquatic organisms (HydroQual 2007). Benchmarks for water calculated using the Biotic Ligand Model to determine the amount of metal available to bind at the biotic ligand at U.S. EPA continuous chronic criteria metal concentrations using methods described in Schmidt (2007).
[2]Benchmarks for sediment are the probable effect concentration consensus-based sediment quality guideline derived from MacDonald et al. (2000).

However, these are values applied to water regardless of other characteristics of the water body. Dissolved organic carbon, major cations, anions, pH, and alkalinity are known to modify the toxicity of dissolved metals to aquatic organisms (Tipping 1994, Santore and Driscoll 1995). The Biotic Ligand Model is a computer model that, for a single metal, predicts acute toxicity to aquatic organisms while accounting for the influences of water quality on metal toxicity to aquatic organisms (HydroQual 2007). Schmidt (2007) developed a method which modifies the Biotic Ligand Model to derive m_i and c_i for water, while accounting for difference in water quality between sample locations and predicting the toxicity of multiple metals to aquatic insect communities. Here we used the method developed by Schmidt to derive the benchmark values for metals in water found in Table 1.

The benchmark values for sediment were derived from the consensus-based sediment quality guidelines Probable effect concentrations (PECs) (CBSQG; MacDonald et al. 2000). The PECs are those metal concentrations above which adverse effects on aquatic ecosystems are expected to occur more often than not. Because much less is known as to how sediment quality influences the availability of metals to aquatic organisms, no modifying factors are accounted for in determining the toxicity of sediment metal to aquatic organisms. Sediment benchmark values are in Table 1.

Data analysis

For simplicity and ease of interpretation, all data are presented as box-plots. The sample population is depicted as boxes where the tops and bottoms represent the 75th and 25th percentiles, respectively, 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. The dots report the largest outlier. Differences in samples are easily determined by comparing locations (medians) and data distributions between different sample populations.

Results

All water and sediment samples collected from reference catchments were found to be well below the toxic threshold of 1 TU (median TU = 0.1 for water and 0.5 for sediment; Figure 2). In contrast, water and sediment from background catchments often exceeded TU = 1 with median values for water (0.2) and for sediment (0.9). Fourteen of the 39 water samples (36 percent of the samples) in the background category exceeded a TU = 1, whereas 19 of 39 sediment samples (48 percent) exceeded this threshold. Most water (median TU = 1.4) and sediment (median TU = 2.3) samples from mined catchments exceed the toxic threshold with 51 percent of the water and 68 percent of the sediment samples exceeding a TU = 1.

Responses of metal-sensitive aquatic insects mirrored the finding that background catchments and mined catchments can produce both water and sediment that are toxic to aquatic insect communities (Figure 2). Reference catchments produced a community of metal-sensitive aquatic insects with a median value of 201 individuals/0.1 m^2, as

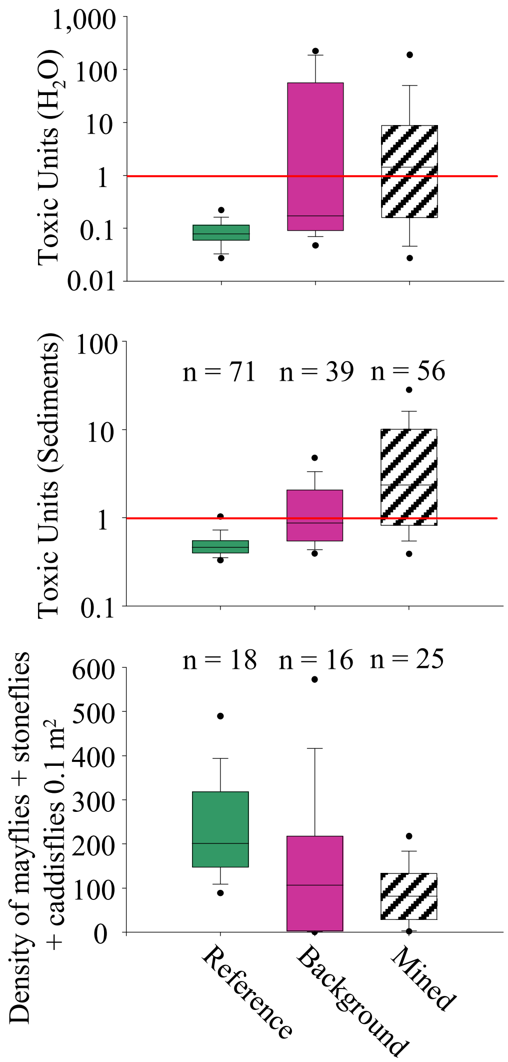

Figure 2. Effect of hydrothermal alteration and mining on water and sediment toxicity to metal sensitive aquatic insect communities. Sample size for water and sediment are identical. Solid colored box plots are unmined. Striped box plots are mined. Green colored (reference) box plots are data from unmined and not hydrothermally altered catchments. Purple colored (background) box plots are data from hydrothermally altered but unmined catchments. Green (reference) box plot is found in Figure 3, while the purple (background) box plot is split into two groups in Figure 3, based on deposit type.

compared to altered and mined catchments (107 individuals/0.1 m^2) with 63 percent of the samples falling below the median value for referenced catchments. Mined catchments were found to have a median value of 90 individuals/0.1 m^2, with 95 percent of the samples falling below the reference median.

The effect of mining, hydrothermal alteration, and mineral deposit type on water and sediment toxicity to aquatic insects is depicted in Figure 3. The effect of hydrothermal alteration (propylitic vs QSP) on background type A deposits was indistinguishable, so both styles of hydrothermal alteration were lumped together to compose this category. The median values for water (0.1 TU) and sediment (0.52 TU) from background type A deposits were not different from reference. In contrast, catchments containing background type B deposits (all of which are QSP altered) produced toxic water (median TU = 108) and sediment (median TU = 1.9). All the water sampled from background type B deposits exceeded the toxic threshold of 1, whereas 2 of the 14 sediment samples did not.

The effect of mining and hydrothermal alteration was distinguishable for type A deposits (Figure 3). Water from streams draining mined propylitically altered type A deposits were less toxic (median water = 0.4 TU, sediment = 1.7 TU) than those from mined QSP altered type A deposits (water = 8.4 TU, sediment = 3.1 TU). Only 1 water sample from the mined QSP altered type A deposits was found to be less than TU = 1. Only 1 sediment sample from a mined and propylitically altered type A deposit was found to be less than the median background value for type A deposits.

Metal-sensitive aquatic insect communities from background type A deposits (median 204 individuals/0.1m^2) were indistinguishable from those from reference sites. However, background type B deposits were so toxic that aquatic insects were nearly absent from these streams (median value of only 1.1 individuals/0.1 m^2). Mining in catchments containing type A deposits resulted in lower densities of metal-sensitive taxa, but the effect was also dependent on the type of hydrothermal alteration present in the catchment. Mined QSP altered type A deposits only averaged 36 individuals/0.1 m^2, as compared to mined propylitically altered type A deposits, which had an average population density of 128 individuals/0.1 m^2.

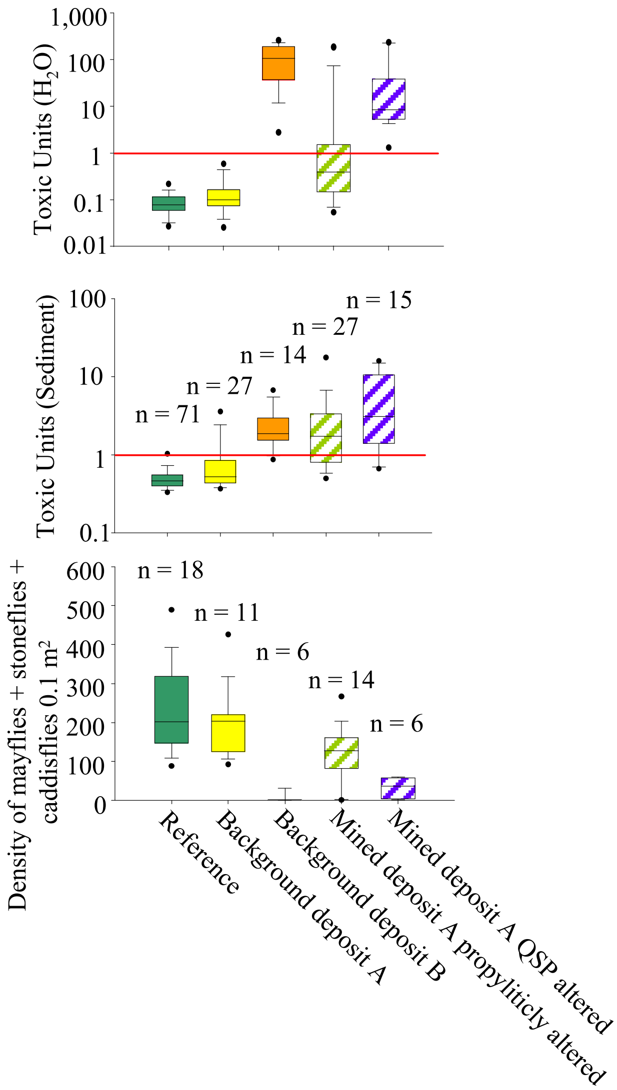

Figure 3. Effects of hydrothermal alteration (background sites), mining, and deposit type (A or B) on water and sediment toxicity to metal sensitive aquatic insect communities. Solid color box plots are unmined, and striped box plots are mined. Deposit A—polymentallic vein occurrences and deposits. Deposit B—porphyry Cu-Mo occurrences and deposits. QSP—quartz-sericite-pyrite.

Conclusions

We evaluated the extent to which mining verses ore-forming processes influenced the toxicity of water and sediment to metal sensitive aquatic insects. We found that elevated metals in water and sediment are not restricted to mined catchments. Impairment of aquatic communities also occurred in catchments that were unmined but had rocks that were hydrothermally altered (background). The effect of mining on the toxicity of water and sediment is dependent on the style of hydrothermal alteration. Some streams draining catchments influenced by ore-forming processes likely never supported a robust aquatic community (e.g., Church et al. 2007b).

Historically, ecological risk assessments of abandoned mine lands have presumed that the presence of historical mining in a catchment caused elevated concentrations of metals in water and sediment that impaired aquatic communities. We demonstrated that this presumption in many cases is incorrect. Hydrothermally altered rock also causes elevated concentrations of metals in water and sediment that impaired aquatic communities prior to or in the absence of mining. Ecological communities in these catchments are impaired by metals released during weathering of the hydrothermally altered rock. Because historical mines are located in catchments that have been hydrothermally altered, not all the elevated metal concentrations in water and sediment from streams draining mined catchments can be attributed to increased weathering of mineral sulfides extracted during the mining process. However, mining was found to increase the toxicity of water and sediment to aquatic insects from catchments influenced by ore-forming processes.

The effect of hydrothermal alteration on the toxicity of water and sediment is not the same for all deposit types. Water and sediment from catchments that have background type A deposits were indistinguishable from reference catchments, suggesting no significant release of metals by weathering of mineral sulfides emplaced through the alteration process. In contrast, water and sediment from catchments containing background type B deposits were toxic, so much so that aquatic insects are essentially absent from these catchments. As a result, hydrothermal alteration and mineral deposit type must be considered in the evaluation of background sites when conducting environmental assessments of mined sites.

The influence of mining on the same deposit type is dependent on the style of hydrothermal alteration. Mining of propylitically altered type A deposits resulted in elevated water and sediment toxicity and a modest reduction of metal-sensitive aquatic insects as compared to reference sites. However, mining of a QSP type A deposits resulted in an 80 percent reduction of the metal-sensitive aquatic insects. Previous assessments would not have distinguished these differences. Had we compared the median number of metal-sensitive aquatic insects found at reference catchments (201 individuals/0.1 m^2) to that observed at mined sites (90 individuals/0.1 m^2), we would estimate that mining had caused a 55 percent decrease in the aquatic insect community. However, mined propylitically altered type A deposits were found to only decrease metal-sensitive aquatic insects by 36 percent. An even greater overestimation of the effect of mining on aquatic communities may occur if comparisons between reference sites and type B deposits are made without considering the fact that background type B deposits are so toxic that they nearly exclude aquatic insects.

Not quantifying the amount of weathered metals in streams from ore-forming processes may result in the overestimation of the number of streams impaired by historical mining. Our study determined that less than 5 percent of the study area is influenced by hydrothermally altered mineral occurrences and deposits (Church et al., this volume). As a result, it is likely that much of the streams thought to be impaired by metals are in fact influenced by drainage from hydrothermally altered rocks. A better understanding of the spatial distribution and ecological effects of mineral deposits in Colorado and the United States would greatly increase our ability to prioritize remediation of abandoned mines. Through the application of the principles learned here, the likelihood of successful mined land restoration can be greatly improved.

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