

Geochemical Characterization of Mine Waste, Mine Drainage, and Stream Sediments at the Pike Hill Copper Mine Superfund Site, Orange County, Vermont

By Nadine M. Piatak, Robert R. Seal II, Jane M. Hammarstrom, Richard G. Kiah, Jeffrey R. Deacon, Monique Adams, Michael W. Anthony, Paul H. Briggs, and John C. Jackson

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Conversion Factors, Datums, and Abbreviations

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
Area		
hectare (ha)	2.471	acre
square kilometer (km ²)	247.1	acre
square meter (m ²)	10.76	square foot (ft ²)
hectare (ha)	0.003861	square mile (mi ²)
square kilometer (km ²)	0.3861	square mile (mi ²)
Volume		
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
Flow rate		
cubic meter per second (m ³ /s)	35.31	cubic foot per second (ft ³ /s)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
metric ton per day	1.102	ton per day (ton/d)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Horizontal coordinate information is referenced to the insert datum name (and abbreviation) here, for instance, "North American Datum of 1983 (NAD 83)"

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Abbreviations

ABA – Acid-base account

AP – Acid-generating potential

BC – Below confluence

DI – Deionized water

DO – Dissolved oxygen

DOC – Dissolved organic carbon

ESP – Eastern United States precipitation

HG-AAS – Continuous-flow hydride-generation atomic adsorption spectrometry

IC – Ion chromatography

ICP-AES or AES – Inductively coupled plasma-atomic emission spectrometry

ICP-MS or MS – Inductively coupled plasma-mass spectrometry

NIST – National Institute of Standards and Technology

NPL – National Priorities List

NP – Neutralizing potential

NNP – Net-neutralization potential

ORP – Oxidation-reduction potential

PRG – Preliminary Remediation Goals

SD – Stream sediment

USEPA – U.S. Environmental Protection Agency

VTDEC – Vermont Department of Environmental Conservation

XRD – X-ray diffraction analysis

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Abstract

The Pike Hill Copper Mine Superfund Site in the Vermont copper belt consists of the abandoned Smith, Eureka, and Union mines, all of which exploited Bessemer-type massive sulfide deposits. The site was listed on the U.S. Environmental Protection Agency (USEPA) National Priorities List in 2004 due to aquatic ecosystem impacts. This study was intended to be a precursor to a formal remedial investigation by the USEPA, and it focused on the characterization of mine waste, mine drainage, and stream sediments. A related study investigated the effects of the mine drainage on downstream surface waters. The potential for mine waste and drainage to have an adverse impact on aquatic ecosystems, on drinking-water supplies, and to human health was assessed on the basis of mineralogy, chemical concentrations, acid generation, and potential for metals to be leached from mine waste and soils. The results were compared to those from analyses of other Vermont copper belt Superfund sites, the Elizabeth Mine and Ely Copper Mine, to evaluate if the waste material at the Pike Hill Copper Mine was sufficiently similar to that of the other mine sites that USEPA can streamline the evaluation of remediation technologies. Mine-waste samples consisted of oxidized and unoxidized sulfidic ore and waste rock, and flotation-mill tailings. These samples contained as much as 16 weight percent sulfides that included chalcopyrite, pyrite, pyrrhotite, and sphalerite. During oxidation, sulfides weather and may release potentially toxic trace elements and may produce acid. In addition, soluble efflorescent sulfate salts were identified at the mines; during rain events, the dissolution of these salts contributes acid and metals to receiving waters. Mine waste contained concentrations of cadmium, copper, and iron that exceeded USEPA Preliminary Remediation Goals. The concentrations of selenium in mine waste were higher than the average composition of eastern United States soils. Most mine waste was potentially acid generating because of paste-pH values of less than 4 and negative net-neutralization potentials (NNP). The processed flotation-mill tailings, however, had a near neutral paste pH, positive NNP, and a few weight percent calcite. Leachate tests indicated that elements

and compounds such as Al, Cd, Cu, Fe, Mn, Se, SO_4 , and Zn were leached from mine waste in concentrations that exceeded aquatic ecosystem and drinking-water standards. Mine waste from the Pike Hill mines was chemically and mineralogically similar to that from the Elizabeth and Ely mines. In addition, metals were leached and acid was produced from mine waste from the Pike Hill mines in comparable concentrations to those from the Elizabeth and Ely mines, although the host rock of the Pike Hill deposits contains significant amounts of carbonate minerals and, thus, a greater acid-neutralizing capacity when compared to the host rocks of the Elizabeth and Ely deposits.

Water samples collected from unimpacted parts of the Waits River watershed generally contained lower amounts of metals compared to water samples from mine drainage, were alkaline, and had a neutral pH, which was likely because of calcareous bedrock. Seeps and mine pools at the mine site had acidic to neutral pH, ranged from oxic to anoxic, and generally contained concentrations of metals, for example, aluminum, cadmium, copper, iron, and zinc, that exceeded aquatic toxicity standards or drinking-water standards, or both. Surface waters directly downstream of the Eureka and Union mines were acidic, as indicated by pH values from 3.1 to 4.2, and contained high concentrations of some elements including as much as 11,400 micrograms per liter ($\mu\text{g/L}$) Al, as much as 22.9 $\mu\text{g/L}$ Cd, as much as 6,790 $\mu\text{g/L}$ Cu, as much as 23,300 $\mu\text{g/L}$ Fe, as much as 1,400 $\mu\text{g/L}$ Mn, and as much as 3,570 $\mu\text{g/L}$ Zn. The concentrations of these elements exceeded water-quality guidelines. Generally, in surface waters, the pH increased and the concentrations of these elements decreased downstream from the mines. The stream sediments also contained concentrations of trace elements such as cadmium, copper, selenium, and zinc that exceeded toxicity standards for aquatic life. The highest concentrations of metals were found directly downstream of the Eureka and Union mines, and concentrations decreased with increasing distance from the mines. The concentrations of metals in mine drainage and in stream sediments at the Pike Hill Superfund site were comparable to those found at the Elizabeth and Ely mines.

Introduction

Site Information

The Pike Hill Copper Mine was placed on the U.S. Environmental Protection Agency (USEPA) National Priorities List (NPL) in July of 2004 due to the impacts of mining-generated contaminants on nearby aquatic ecosystems. The Elizabeth Mine and the Ely Copper Mine also are listed on the NPL because of aquatic ecosystem and human-health impacts. All three abandoned mine sites worked Besshi-type massive sulfide deposits and are in the Vermont copper belt (fig. 1). This report focuses on the mines at the Pike Hill Copper Mine Superfund site, which includes the Smith (also known as Bicknell), Eureka (also known as Corinth), and Union mines. The Eureka and Union mines, each of which is larger than the Smith mine, are near the top and northeast slope of Pike Hill near the town of Corinth (figs. 2 and 3).

They are located approximately 300 meters (m) apart and are generally considered to be a single impacted landscape. The smaller Smith mine is on the southern flank of the hill (fig. 3). The entire site encompasses about 87.5 hectares and contains approximately 18,000 metric tons of mill and mine dumps that contain an average of 1.6 percent copper (USEPA, 2004a). The underground mines operated intermittently between 1847 and 1919, and this was the only site in the Vermont copper belt where magnetic ore separation was successful. The mines contributed an estimated 3,900,000 kilograms (kg) of copper, which constitutes about 6 percent of the known production from this copper belt (Kierstead, 2001). Past mining activity is evident by open mine cuts, trenches, shafts, adits, waste-rock piles including piles of mill tailings, and the foundations and remnants of an ore cobbing house, a blacksmith shop, the flotation/magnetic separation mill, and a tramway. The mine site landscape is a combination of barren open areas and patches of acid-tolerant deciduous and coniferous trees.

The northeast slope of Pike Hill Copper Mine, which contains most of the mine waste and the physical features associated with the Union and Eureka mines, is drained by a single small stream, which is the headwater to Pike Hill Brook (fig. 2). Pike Hill Brook has a stream reach of approximately 7 kilometers (km) and it enters a series of natural wetlands approximately 3.5 km downstream from the mine site; the outflow from the wetlands travels another 3 km before it enters the Waits River. Surface and ground waters from the area impacted by the Smith mine drain into a small unnamed tributary that flows south for approximately 1.6 km before it enters Cookville Brook (fig. 2). Approximately 4.5 km from this confluence, Cookville Brook and its tributaries form the South Branch of the Waits River. The South Branch then joins the main branch of the Waits River approximately 8 km downstream. The Waits River eventually flows into the Connecticut River. Both of these rivers are used for recreational purposes and contain fisheries.

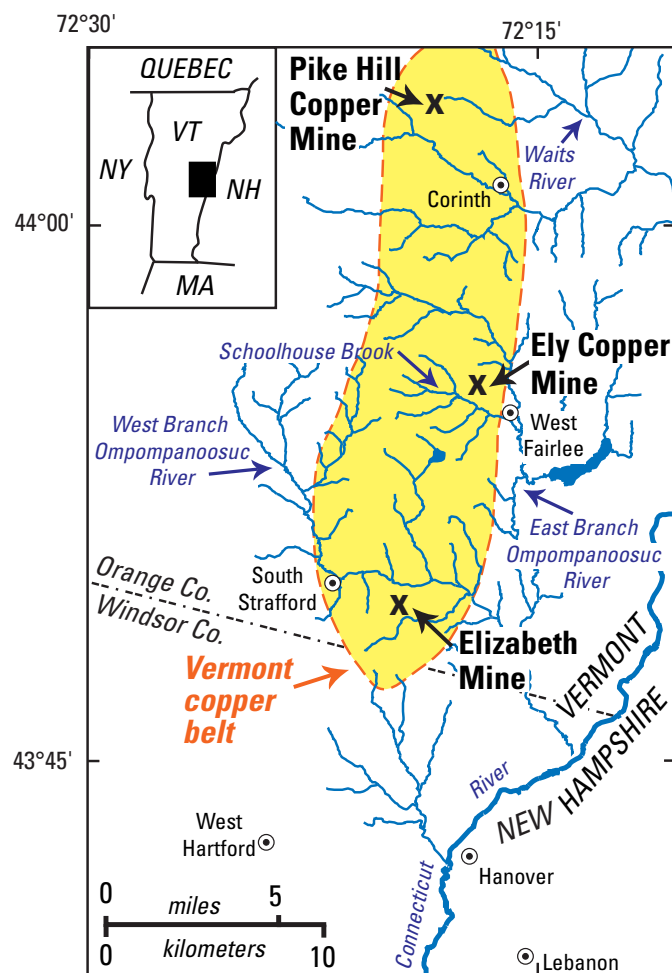


Figure 1. Regional locations of the Pike Hill Copper Mine, Ely Copper Mine, and the Elizabeth Mine. Modified from McKinstry and Mikkola (1954) and White and Eric (1944).

Previous Studies

Several preliminary geochemical investigations were made in the Pike Hill area. Slack and others (1984) found detectable gold in several stream-sediment samples from watersheds surrounding the mines. In addition, Slack and others (1990) reported anomalous concentrations of cobalt, copper, and zinc in stream sediments from drainages near the site. The massive sulfide ore was found to contain high Cd, Co, Cu, Mn, Se, and Zn (Slack and others, 2001). The leaves of several birch species were found to contain anomalous concentrations of several metals including copper and zinc, and airborne spectroradiometric data indicated anomalous spectral signatures for forest canopy surrounding the Eureka and Union mines (Power and Milton, 1990).

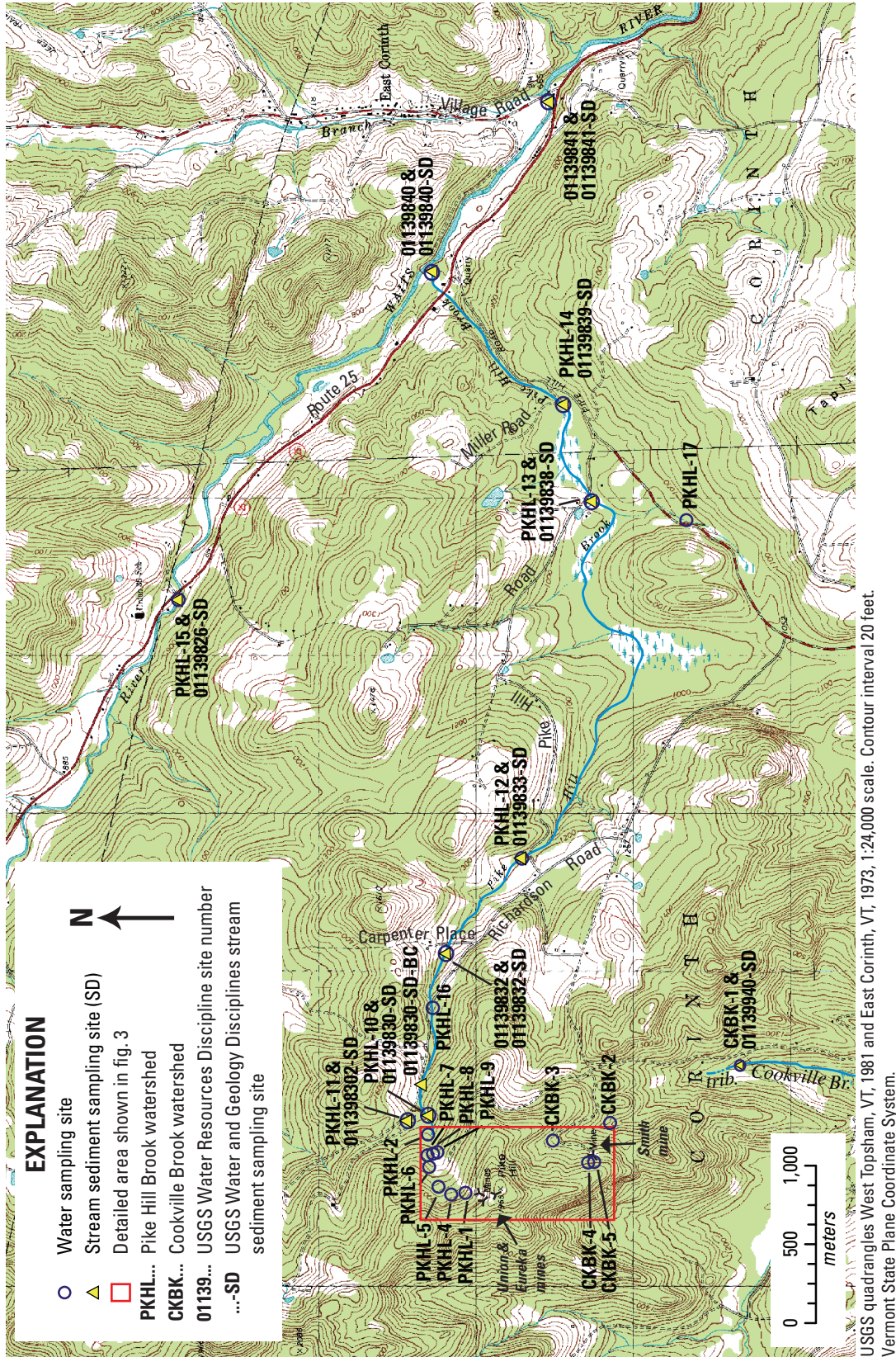


Figure 2. Locations of water and stream-sediment sampling sites at the Pike Hill mines study area.

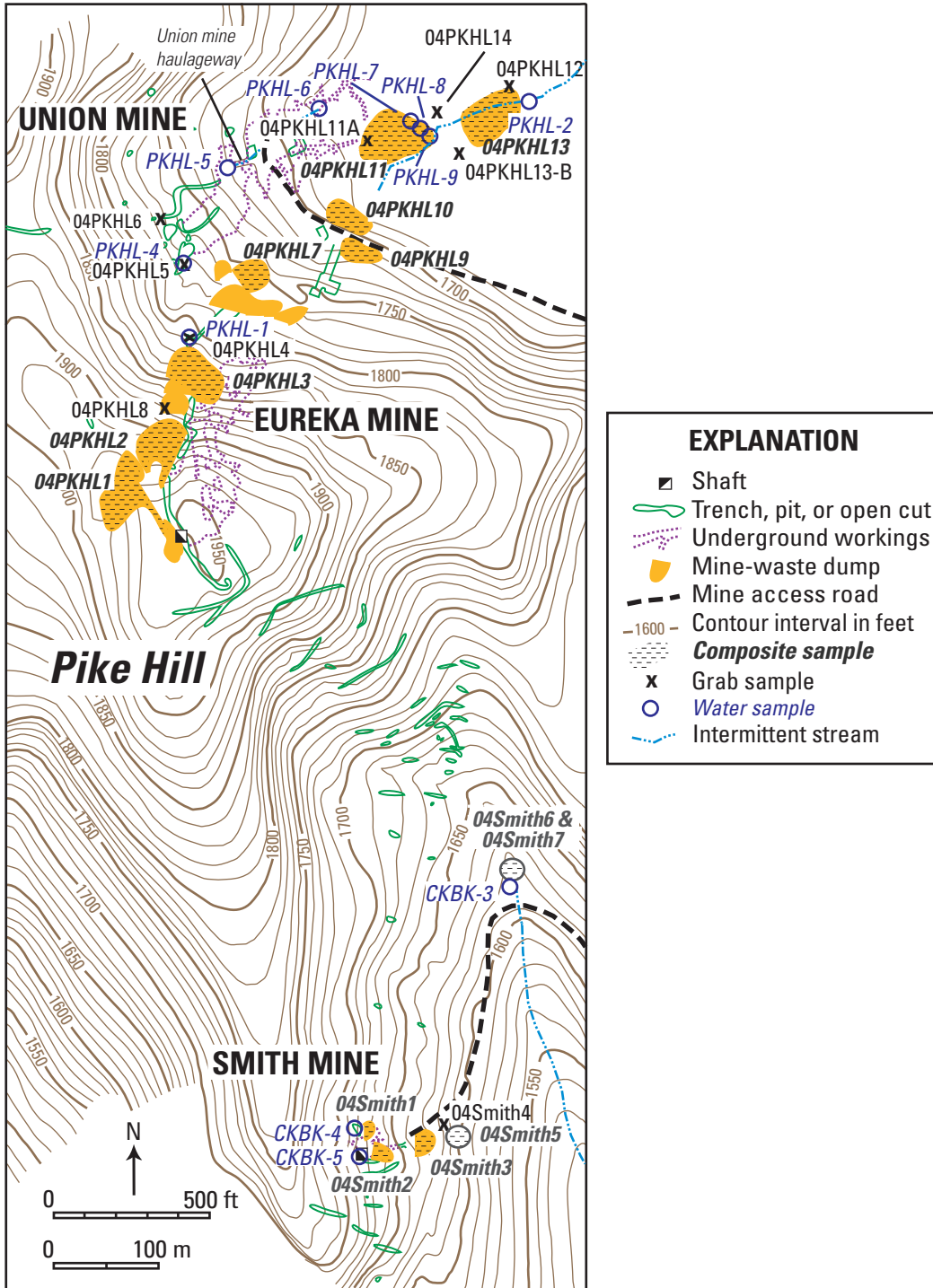


Figure 3. Locations of composite and grab solid-sample sites, water sampling sites, shafts, open cuts, underground workings, and mine-waste piles at the Pike Hill Copper Mine Superfund site. Modified from White and Eric (1944).

Thesis projects by two students from Middlebury College in Vermont included the geochemical and mineralogical analysis of waste-rock material (Wierscinski, 1999) and iron-oxide precipitates (Totten, 1999). Macroinvertebrate and fish populations in surface waters downstream of the site have been significantly impaired because of acidic mine drainage (U.S. Environmental Protection Agency, 2004a).

Objectives

The USEPA requested that the U.S. Geological Survey (USGS) conduct a preliminary study of mine waste, mine drainage, and stream sediments at the Pike Hill mines to provide a foundation for the design of a formal remedial investigation at the site. This study focused on mine waste, mine-drainage environments, and stream sediments. A companion study assessed the current water-quality conditions and element loads in and around the Pike Hill Brook watershed with an emphasis on the downstream effects of the mine drainage on biological organisms (Kiah and others, 2007).

This report describes the type of waste piles and their mineralogy, chemical composition, and acid-generating potential to clarify the role of the mine waste as a potential source of contamination. Leachate tests were also done to determine the potential mobility of various chemical constituents in runoff from individual waste piles. Initial characterization of the mine waste was reported in Piatak and others (2006a). The preliminary results of sequential extraction experiments for selenium on several mine-waste samples and a stream-sediment sample from Pike Hill were described in Piatak and others (2006b).

This report also characterizes the geochemistry of various mine-drainage environments and compares element and acid content with guidelines for aquatic ecosystems and drinking-water standards to understand the aqueous geochemical environments present in the area. The mineralogy and chemical composition of stream sediments in the impacted watershed were determined to provide information about the potential for adverse impacts on the aquatic ecosystem. Elemental content in the sediments was then compared to sediment-quality standards for freshwater ecosystems. The results from this study were then compared to similar studies of the Elizabeth and Ely mines.

Geologic Setting

The Vermont copper belt includes the Elizabeth, Ely, and Pike Hill mines, as well as several smaller mines and prospects (fig. 1). The massive sulfide deposits in the Vermont copper belt were likely formed on an ancient seafloor by submarine hydrothermal-exhalative and replacement processes (Slack and others, 1993). The deposits are stratabound and generally stratiform, and they contain massive ores composed of pyrrhotite, chalcopyrite, and minor sphalerite and pyrite within metasedimentary and minor mafic metavolcanic rocks of Silurian and

Devonian age. The massive sulfides are generally closely associated with amphibolite. The deposits and host rocks were deformed during several stages of folding and amphibolite-grade metamorphism (Slack and others, 1993).

The Pike Hill mines exploited a sheetlike ore zone that strikes a few degrees west of north and dips about 30° east (White and Eric, 1944). The deposits are in the Silurian Waits River Formation, which consists of calcareous pelite, pelite, minor quartzose metalimestone and metadolostone, and sparse calcite marble. In contrast, the Elizabeth and Ely deposits occur in the younger (Early Devonian) Gile Mountain Formation, which is characterized by siliciclastic rocks including graphitic pelite and quartzose granofels and lesser micaceous quartzite, calcareous pelite, hornblende schist, and amphibolite (Slack and others, 1993). The host rock of the Pike Hill deposits contains significant amounts of carbonate minerals, and, thus, has a greater acid-neutralizing capacity than the host rocks of the Elizabeth and Ely deposits.

Methods

Mine Waste

Sampling

Mine-waste piles at the Pike Hill mines site were divided on the basis of waste type, color, and geographic location. Eleven composites of soil-sized waste-pile material were collected having a minimum of 30-equal sample increments over a measured area divided into a stratified grid. Surface composites of background and downslope soils consisted of three-to-ten increments. Increments were homogenized, stored in plastic bags, air dried, and dry-sieved through a 10-mesh sieve so that the less than 2 millimeter (mm) soil-size fraction was collected, and then the material was split into aliquots by fractional shoveling (Pitard, 1993). The composite-sample protocol was developed by the USGS for the rapid screening and characterization of historical mine-waste piles (Smith and others, 2002). Samples of ferricrete and hardpan were also air-dried, sieved to less than 2 mm, and split. Grab samples collected for mineral-identification purposes were either stored in plastic bags or sealed plastic vials until analysis.

Mineralogy

X-ray diffraction analysis (XRD) was used by USGS laboratories in Reston, Va., to identify minerals. XRD was done on samples pulverized in alcohol for 3 minutes in a McCrone micronizer equipped with agate grinding pellets. The powder patterns were collected with a Scintag X1 automated powder diffractometer equipped with a Peltier detector having

CuK α radiation. The XRD patterns were analyzed with the use of Material Data Inc.'s JADE software and standard reference patterns. The relative amount of phases in each pattern was estimated with the Siroquant computer program, which utilizes the full XRD profile in a Rietveld refinement (Taylor and Clapp, 1992). The accuracy of the Siroquant results is approximately ± 5 weight percent.

Evidence for readily soluble salts was evaluated by filtering mine-waste leachates (see below) that had been evaporated to dryness. In addition, 2.0 grams (g) of mine waste was mixed with 40 milliliters (mL) of deionized water (DI), shaken, and processed in a centrifuge. Water was then decanted, and the pH was measured. The procedure was repeated with fresh DI each day for 8 days. The decanted waters were evaporated. Leachate evaporates from both experiments were evaluated with the use of XRD.

Bulk Geochemical Composition

The bulk chemical composition of solid mine-waste samples was determined with the use of inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) following acid-digestion of the sample with a mixture of HCl-HNO₃-HClO₄-HF (Briggs, 2002a; Briggs and Meier, 2002). These analyses were conducted at USGS laboratories in Denver, Colo. For interpretation purposes, the ICP-AES results were used for the major elements (e.g., Al, Ca, Fe), whereas ICP-MS results were used for relevant trace elements such as As, Cd, Co, Cu, Mn, Ni, Pb, and Zn, although all of the results are reported in the appendices. The samples were digested with a mixture of HNO₃-HF-HClO₄ and analyzed for selenium with the use of continuous-flow hydride-generation atomic absorption spectrometry (HG-AAS) by SGS Laboratories (formerly XRAL) in Toronto, Canada (Hageman and others, 2002). The USGS job numbers and laboratory-sample numbers for entry into the National Geochemical Database (Smith, 2002) are listed in Appendices 1 to 5 for mine waste, leachates, reference waters and field-blank samples, waters, and stream sediments, respectively. Certified National Institute of Standards and Technology (NIST) reference materials were analyzed to evaluate accuracy and precision.

Acid-Base Accounting

Acid-base account (ABA) was originally designed to estimate the inherent capacity of coal-mine waste to produce or to neutralize acid (Sobek and others, 1978). Currently, this method is used to evaluate metal-mine waste as well as coal-mine waste, and it typically includes the determination of paste pH, which is a quick measure of relative acid generation or acid neutralization (White and others, 1999). The paste-pH method was based on Price and others (1997) and was determined in USGS laboratories in Reston, Va., and in the Vison SciTec, Inc., laboratories in Vancouver, British Colum-

bia. ABA is numerically quantified as the net-neutralization potential (NNP), which is the difference between the neutralization potential (NP) and the acid-generating potential (AP), and it was determined by Vison SciTec, Inc. with the use of a combination of the Sobek method to determine NP and the modified Sobek method to determine AP (Sobek and others, 1978; White and others, 1999). The AP, NP, and NNP were reported as kilograms of CaCO₃ per metric ton of mine waste. For this study, NNP of less than 0 and paste pH of less than 4.0 were considered potentially acid generating (Sobek and others, 1978).

Leachate Chemistry

A modification of the field-leach test developed by Hageman and Briggs (2000) was done on splits of the samples in USGS laboratories in Reston, Va. A split of the less than 2-mm size fraction was used because this represents the most chemically reactive material in weathered mine waste (Hageman and Briggs, 2000). This size fraction choice may slightly overestimate the leachability of the waste material, but it did not appear to miss any readily leachable phases (Smith and others, 2002). The sample was combined with a solution that approximates eastern United States precipitation (ESP) at a solution-to-sample ratio of 20:1 (mass basis) to provide an indication of the potential chemical composition of runoff. A mixture of sulfuric acid and nitric acid was added to deionized water to adjust the pH to 4.2 ± 0.1 (USEPA, 1994). The mixtures were shaken for 5 minutes, and, after 24 hours, the pH, specific conductance, dissolved oxygen (DO), temperature, and oxidation-reduction potential (ORP) were measured on unfiltered splits. The leachates were then filtered through 0.45-micrometer (μm) pore-size nitrocellulose filters and analyzed for cations by ICP-AES and ICP-MS and for the anions chloride, fluoride, nitrate, and sulfate by ion chromatography (IC) in USGS laboratories in Denver, Colo. The ICP-AES, ICP-MS, and IC analyses were done according to USGS methods outlined in Lamothe and others (2002), Briggs (2002b), and Theodorakos and others (2002). The ICP-AES results were used for major elements, the ICP-MS were used for trace elements, and the IC results were used for anions. Concentrations of dissolved total iron and ferrous iron were determined with the use of colorimetric kits containing 1, 10 phenanthroline indicator on a Hach DR/2000 spectrophotometer.

Water Sampling and Analysis

Field methods for aqueous samples were based on those described by Ficklin and Mosier (1999). Samples were collected in 1-liter high-density polyethylene bottles that were rinsed twice with sample water prior to collection. Splits were filtered through 0.45 μm pore-size nitrocellulose filters. Filtered and raw splits, which were acidified with ultra-pure nitric acid and stored in high-density polyethylene bottles that were acid-washed with 10 percent HCl, were analyzed for

dissolved and total acid soluble cations, respectively. Filtered and unacidified aliquots for anion and alkalinity analysis were stored in high-density polyethylene bottles that were not acid-washed and were refrigerated until they were analyzed. Unacidified splits for dissolved organic carbon (DOC) were filtered, stored in precombusted glass vials, and frozen upon return to the laboratory.

Water temperature, pH, specific conductance, DO, ORP, dissolved ferrous iron, and dissolved total iron were measured on site at the time of sample collection. The pH was measured with the use of an Orion 290A meter fitted with an Ag/AgCl epoxy electrode and temperature probe; specific conductance was measured with an Orion 135 specific conductance meter. DO was analyzed with the use of Chemetrix high-range ampoules, and ORP was determined with the use of an Orion 290A meter fitted with an ORP triode electrode (model 91-79) and calculated in reference to Orion ORP standard 967901. Concentrations of dissolved total iron and ferrous iron were determined with the use of colorimetric kits containing 1, 10 phenanthroline indicator on a Hach DR/2000 spectrophotometer. Alkalinity samples were analyzed by Gran titration with 0.18 N H₂SO₄.

Water samples were analyzed for cations by ICP-AES and ICP-MS and for the anions chloride, fluoride, nitrate, and sulfate by IC in USGS laboratories in Denver, Colo. The ICP-AES, ICP-MS, and IC analyses were performed according to USGS methods outlined in Lamothe and others (2002), Briggs (2002b), and Theodorakos and others (2002). The ICP-AES results were used for the interpretation of major elements, ICP-MS was used for trace elements, and IC was used for anions. Concentrations of DOC were determined by high temperature combustion and measurement of evolved CO₂ by infrared detections in the Marine Chemistry Laboratory at the University of Washington (Hedges and Stern, 1984).

Stream-Sediment Sampling and Analysis

Stream-sediment samples were composites of at least 30-sample increments, and they were wet-sieved in the field to remove material coarser than 2 mm. Homogenized samples were then air dried and dry-sieved to less than 80 mesh or the 177- μ m fraction (Peacock and others, 2002). Minerals were identified by use of XRD as described above for mine-waste samples. The relative amounts of phases were determined with the Siroquant computer program by the procedure outlined previously for mine-waste samples.

The bulk chemical composition of the stream-sediment samples was determined with the use of ICP-AES and ICP-MS following acid-digestion of the samples with a mixture of HNO₃-HCl-HClO₄-HF; this analysis was done by SGS Laboratories, Toronto, Canada. An aliquot of the digested sample was aspirated into the ICP-AES and ICP-MS, and optimal elements from each were determined. The samples also were analyzed for selenium with the use of HG-AAS after digestion of the samples with a mixture of HNO₃-HF-HClO₄; this was conducted by SGS Laboratories (Hageman and others, 2002).

Sample Descriptions and Locations

Mine-Waste Samples

Sampling site locations are shown on figure 3, and sample descriptions and sampling site locations are listed in tables 1 and 2. Three mine-waste composites and several other samples were collected from the Smith mine. Composite sample 04Smith1 was collected below the organic layer from the uppermost waste pile (fig. 4A). Sample 04Smith1-1 of weathered sulfidic ore coated with efflorescent sulfate salts was collected from this uppermost waste pile (fig. 4B). In addition, sample 04Smith1-2 was collected from jarosite-rich soil on the slopes of this waste dump. Composite sample 04Smith2 was collected from the waste pile that was near the Smith mine adit (fig. 4C). It consisted of sandy soil and oxidized ore boulders, and it contained less organic material (leaves and plants) than sample 04Smith1. The last composite mine-waste sample, 04Smith3, from the Smith mine was collected from the lowermost dump downslope of the adit; the soil from this dump was sandy and locally contained clots of jarosite and oxidized ore boulders (fig. 4D). Sample 04Smith4 from a hardpan layer below the organic layer was collected approximately 23 m downslope from the toe of the waste piles (fig. 4E). In addition, a 3-increment composite, sample 04Smith5, of a brown soil horizon beneath the leaf litter was collected in this area (fig. 3). Two composite background-soil samples, 04Smith6 and 04Smith7, were collected at locations that were not impacted by mining (fig. 3).

Most of the solid samples collected for this study were collected from the landscape surrounding the Eureka and Union mines near the top of Pike Hill (fig. 3; table 1). Composite sample 04PKHL1 was collected from the waste piles adjacent to the open cuts at the top of Pike Hill (fig. 4F). This area was barren and had boulders that locally contained clots of jarosite. Sample 04PKHL2 was a composite collected from a mine-waste pile approximately 10-m wide that contained a mound of ore, which is shown by an arrow in figure 5A. Sample 04PKHL2-1 of oxidized sulfidic ore also was collected in the same area. The series of north-south trending waste piles uphill of the main Eureka mine adit from which sample 04PKHL3 was compiled is shown in figure 5B. Yellowish-green coatings on rock chips were collected as sample 04PKHL3-1. Water sampling site PKHL-1 was located at the main Eureka mine adit (fig. 5C). At this adit, samples 04PKHL4-C and -D were collected from blue and white amorphous coatings on the wet rock face (fig. 5D) and samples 04PKHL4-A, ochre floc (fig. 5E), and 04PKHL4-E, tan precipitate, were both collected just above the waterline on the rock face. Sample 04PKHL4-B was collected from ochre stalactites in the adit entryway, and sample 04PKHL4-F was collected from host rock from the adit wall.

Table 1. Sample descriptions for mine-waste and solid-grab samples from the Pike Hill mines study area.

Sample number	Mine	Sample type	Date	Location	Description
04Smith1	Smith	Mine-dump composite	10/19/04	Uppermost dump at the Smith mine. Adjacent to a small pond (water site CKBK-4).	Olive-yellow sandy soil with weathering sulfidic ore. Covered with leaves and organic material.
04Smith1-1	Smith	Rock	10/19/04	Location same as above.	Weathered sulfidic ore with coating of white salts.
04Smith 1-2	Smith	Mineral	10/19/04	Location same as above.	Sample of locally developed yellow soil on slopes of waste dump.
04Smith2	Smith	Mine-dump composite	10/19/04	Middle dump near main Smith mine adit (water site CKBK-5).	Olive-yellow sandy soil and oxidized ore boulders. More mine waste, less jarosite, and less organic material than noted for 04Smith1.
04Smith3	Smith	Mine-dump composite	10/19/04	Lowermost dump below main Smith mine adit.	Olive-yellow sandy soil and oxidized ore boulders, locally clots of jarosite.
04Smith4	Smith	Hardpan	10/19/04	Swampy area with ferns in woods 23 m down slope from toe of lowermost mine-waste dump.	Ochre hardpan below yellow jarositic layer. Hardpan encountered at 5-8 cm below organic debris horizon.
04Smith5	Smith	Soil	10/19/04	Series of holes dug at 30 m, 46 m, and 61 m downslope from lowermost mine-waste dump. Location given for 30 m hole.	Strong-brown soil samples 2.5-15 cm below organic horizon. Composite sample of this horizon from three holes. Note that O-layer thickness increases from 10 cm at 30 m downslope to 20 cm at 46 m downslope to 30 cm at 61 m downslope.
04Smith6	Smith	Soil	10/19/04	Background soil sample (water site CKBK-2).	Upslope background-soil sample away from mining-impacted area.
04Smith7	Smith	Soil	10/19/04	Background soil sample (water site CKBK-2).	Upslope background-soil sample away from mining-impacted area.
04PKHL1	Eureka	Mine-dump composite	10/20/04	Mine-waste dump adjacent to open cuts at top of Pike Hill.	Barren, sandy, brownish-yellow, mine-waste dump. No boulders; scattered pieces of weathered ore and country rock. No water. No erosion gullies. Clots of jarosite in soil. Part of pile drains to the west.
04PKHL2	Eureka	Mine-dump composite	10/20/04	Mine waste along all-terrain-vehicle trail just down slope from 04PKHL1. Mine waste spread along 10 m of hillside with ore mound at northeast end.	Same character as 04PKHL1 but locally contains an ore pile. More cobbles and boulders, and drains to the east. Ore is fresh.
04PKHL2-1	Eureka	Rock	10/20/04	Location same as above.	Oxidized sulfidic ore from small ore pile.

Table 1. Sample descriptions for mine-waste and solid-grab samples from the Pike Hill mines study area.—Continued

Sample number	Mine	Sample type	Date	Location	Description
04PKHL3	Eureka	Mine-dump composite	10/20/04	Series of north-south trending mine-waste piles just above main Eureka mine adit.	Sandy yellow soil with jarosite clots. Many fist-size cobbles of oxidized ore and country rock. Yellow-green coating on some pebbles. No fresh ore. Some shallow erosion gullies indicative of surface runoff.
04PKHL3-1	Eureka	Mineral	10/20/04	Location same as above.	Rock chips with yellow-green coating.
04PKHL4-A	Eureka	Mineral	10/20/04	Main Eureka mine adit.	Ochre floc in mine pool at adit.
04PKHL4-B	Eureka	Mineral	10/20/04	Location same as above.	Ochre stalactites growing from drips along adit entryway.
04PKHL4-C	Eureka	Mineral	10/20/04	Location same as above.	Bright blue precipitate on wet rock face at adit.
04PKHL4-D	Eureka	Mineral	10/20/04	Location same as above.	White precipitate on wet rock face at adit.
04PKHL4-E	Eureka	Mineral	10/20/04	Location same as above.	Tan floc just above waterline of adit pool.
04PKHL4-F	Eureka	Mineral	10/20/04	Location same as above.	Chips of host rock to white precipitate.
04PKHL5-A	Union	Mineral	10/20/04	Adit in wooded area north of Eureka main adit. Western-most adit for the Union mine.	White foam floating on top of mine pool. Note that white material forms a paint-like stripe of precipitate closest to the wallrock and adjacent to a blue stripe of precipitate. White precipitate also lines the bottom of the pool.
04PKHL5-B	Union	Mineral	10/20/04	Location same as above.	Thick blue precipitate coating organic material along decline to adit pool.
04PKHL5-C	Union	Mineral	10/20/04	Location same as above.	Vial of pure blue precipitate.
04PKHL6	Union	Mineral	10/20/04	Adit in wooded area adjacent to long, narrow engineered haulageway. Remnants of brick structure on site.	Starburst sprays of delicate white gypsum crystals growing from adit ceiling. No other salts observed.
04PKHL7	Eureka and Union	Mine-dump composite	10/20/04	Large unvegetated area of mine-waste dumps below the Eureka and Union mine adits and above the road and foundation of a terraced building (possibly the flotation mill plant).	Sandy, brownish-yellow, mine-waste soil with cobbles and locally, boulders up to 0.5 m across of weathering ore. Note deep erosion gullies on dump surfaces are much more pronounced than on dumps at higher elevations.
04PKHL8	Eureka	Mineral	10/20/04	Adit directly above the Eureka adit.	Bright blue salts growing on sprays of white gypsum on adit ceiling.
04PKHL9	Eureka and Union	Mine-dump composite	10/20/04	Partly burned flotation-tailings pile above the mine road.	Locally red where burned. Deep gullies expose black tailings. Top of pile is about 18 m across and the pile rises about 15 m above the road. Depth to bedrock less than 1 m in gullies.

[cm, centimeters; m, meters; °C, degrees Celsius; Dup, field replicate sample]

Table 1. Sample descriptions for mine-waste and solid-grab samples from the Pike Hill mines study area.—Continued

Sample number	Mine	Sample type	Date	Location	Description
04PKHL9-A	Eureka and Union	Tailings	10/20/04	Partly burned flotation-tailings pile above the mine road.	Red, hematite-rich tailings.
04PKHL9-B	Eureka and Union	Tailings	10/20/04	Location same as above.	Gray tailings dug from gully area.
04PKHL9-C	Eureka and Union	Tailings	10/20/04	Location same as above.	Jarosite-rich material above gray tailings.
04PKHL10	Eureka and Union	Mine-dump composite	10/20/04	Tailings piles below the road. Note material from pile 04PKHL9 present in road and drapes over slope below the road to just above 04PKHL10.	Sandy, quartz-rich processed flotation-mill tailings in several piles. No vegetation or ore.
04PKHL11	Eureka and Union	Mine-dump composite	10/20/04	Large area of barren mine waste below the mine access road.	Mine-waste dumps with local concentrations of weathering ore boulders and cobbles. Efflorescent sulfate salts observed.
05PKHL11-Dup	Eureka and Union	Mine-dump composite	8/3/05	Large area of barren mine waste below the mine access road. Replicate.	Mine-waste dumps with local concentrations of weathering ore boulders and cobbles. Efflorescent sulfate salts observed.
04PKHL11-A	Eureka and Union	Tailings	10/20/04	Location same as above.	Local concentration of dark-gray flotation tailings.
04PKHL11-1 snowballs	Eureka and Union	Rock	10/20/04	Location same as above.	Weathered ore cobbles coated with white salts on mine-waste dump. Air temperature recorded as 8.8° C and relative humidity as 59.4 percent.
04PKHL12	Eureka and Union	Ferricrete	10/20/04	Seep area below mine-waste piles 04PKHL11 (water site PKHL-7).	Flat ferricrete terrace forming at seeps from base of mine-waste pile. Ferricrete is semi-hard, incorporates leaves. Note Ulothrix in seeps.
04PKHL13	Eureka and Union	Mine-dump composite	10/20/04	Lowermost mine-waste piles at Pike Hill.	Mine-waste piles with clots of yellow jarosite, cobbles and boulders of weathered ore and country rock.
04PKHL13-A	Eureka and Union	Rock	10/20/04	Location same as above.	Thin, yellow-green coatings locally developed on rock chips on mine waste in dry seep area at base of large dump.
04PKHL13-B	Eureka and Union	Ferricrete	10/20/04	Location same as above.	Ferricrete developed in dry seep area at base of lowermost large mine-waste dump.
04PKHL14	Eureka and Union	Mineral	10/20/04	Mine waste below the mine access road.	Jarosite-rich clot in mine waste.

Table 2. Locations and Munsell soil color for select solid samples from the Pike Hill mines study area.

[n.d., not determined; latitude and longitude in decimal degrees and referenced to WGS 84, corners of sampling grid (1 to 4) given for composites; Dup, field replicate sample]

Sample number	Munsell soil color	Munsell soil color							
		Latitude 1	Longitude 1	Latitude 2	Longitude 2	Latitude 3	Longitude 3	Latitude 4	Longitude 4
04Smith1	Olive yellow	44.054694	-72.305528	44.054722	-72.305722	44.054861	-72.305778	44.054889	-72.305500
04Smith2	Olive yellow	44.054528	-72.305639	44.054528	-72.305472	44.054472	-72.305528	44.054528	-72.305667
04Smith3	Olive yellow	44.054639	-72.305167	44.054556	-72.305028	44.054583	-72.304944	44.054722	-72.304722
04Smith4	Dark yellowish brown	44.054639	-72.304528						
04Smith 5	Strong brown	44.054556	-72.304417						
04Smith6	Yellowish brown	44.057217	-72.303336						
04Smith7	Yellowish brown	44.056972	-72.303442						
04PKHL1	Brownish yellow	44.060611	-72.308222	44.060500	-72.308972	44.060833	-72.308583	44.060889	-72.308139
04PKHL2	Yellow	44.060889	-72.308139	44.061028	-72.308056	44.060972	-72.307972		
04PKHL3	Yellow	44.061806	-72.307417	44.061444	-72.307556	44.061639	-72.307889	44.061750	-72.307917
04PKHL4-A thru F	n.d.	44.061944	-72.307806						
04PKHL5-A thru C	n.d.	44.062583	-72.307917						
04PKHL6	n.d.	44.062972	-72.307806						
04PKHL7	Brownish yellow	44.062583	-72.307056	44.062694	-72.306694	44.062583	-72.306500	44.062389	-72.307000
04PKHL8	n.d.	44.061194	-72.307861						
04PKHL9	Yellowish brown	44.062583	-72.305194	44.062500	-72.305583	44.062583	-72.305667	44.062722	-72.305611
04PKHL9-A	Red	n.d.	n.d.						
04PKHL9-B	Gray	n.d.	n.d.						
04PKHL9-C	n.d.	n.d.	n.d.						
04PKHL10	Brown	44.062917	-72.305917	44.063111	-72.305778	44.062806	-72.305250	44.062750	-72.305306
04PKHL11	Yellow	44.063528	-72.305111	44.063889	-72.305278	44.064056	-72.304694	44.063639	-72.304472
05PKHL11-Dup	Yellow	44.063528	-72.305111	44.063889	-72.305278	44.064056	-72.304694	44.063639	-72.304472
04PKHL11-A	Dark gray	n.d.	n.d.						
04PKHL11-1	n.d.	44.064056	-72.304694						
04PKHL12	Strong brown	44.063750	-72.304417						
04PKHL13	Yellow	44.063861	-72.303944	44.063944	-72.303333	44.063806	-72.303333	44.063694	-72.303722
04PKHL13-A	n.d.	44.063944	-72.303333						
04PKHL13-B	Strong brown	44.063944	-72.303333						
04PKHL14	n.d.	44.063450	-72.304192						



Figure 4. Sampling sites at the Pike Hill Copper Mine Superfund site. **A.** Site of composite mine-waste sample 04Smith1. Pounded water is water sampling site CKBK-4. **B.** Sample 04Smith1-1 was collected from white salts on weathered ore. **C.** Site of composite mine-waste sample 04Smith2. **D.** Site of composite mine-waste sample 04Smith3. **E.** Site of hardpan sample 04Smith4. **F.** Site of composite mine-waste sample 04PKHL1. (Sample and site numbers are shown in white boxes.)

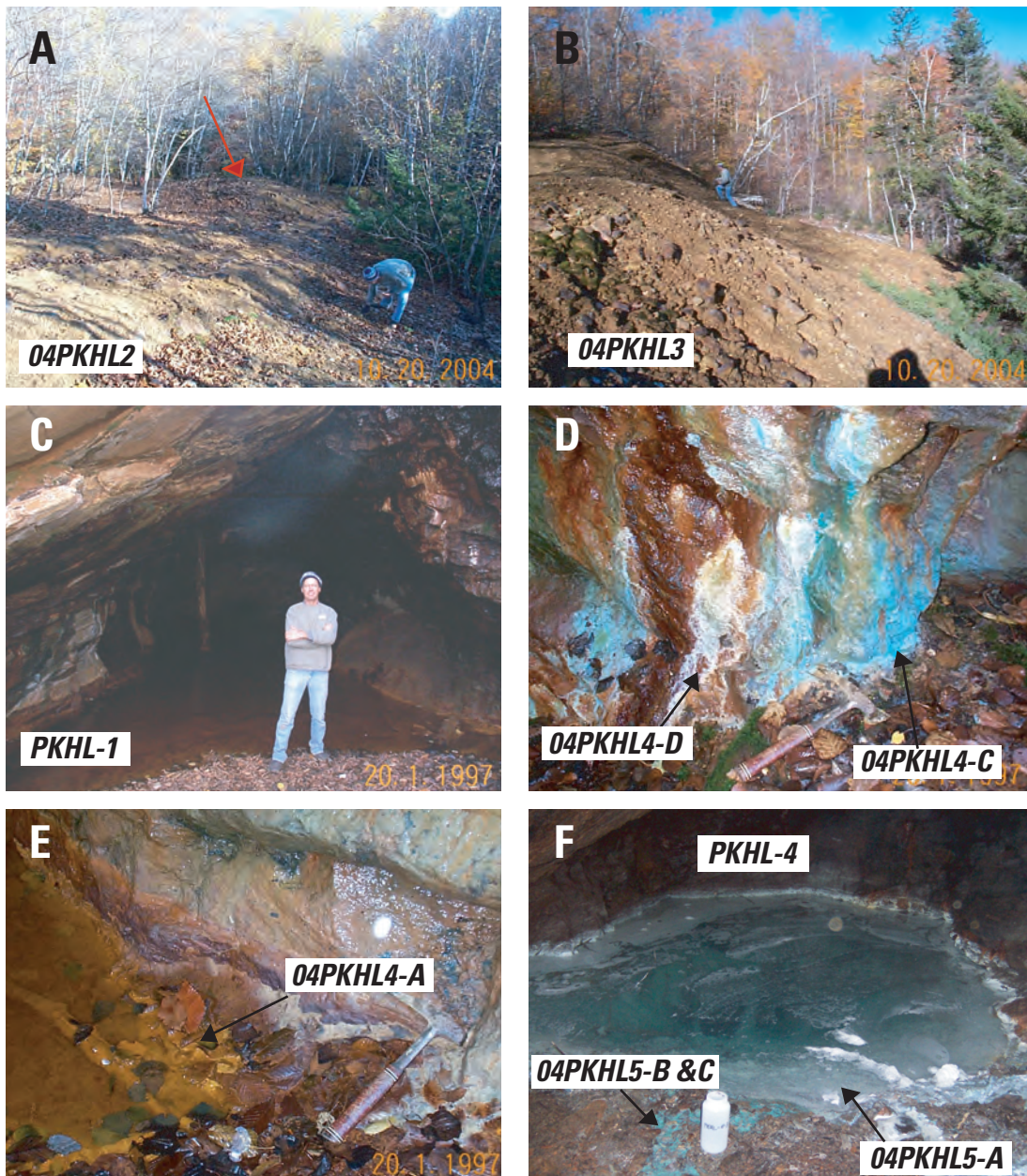


Figure 5. Sampling sites at the Eureka and Union mines at the Pike Hill Copper Mine Superfund site. **A.** Site of composite mine-waste sample 04PKHL2. The arrow indicates fresh sulfidic ore. **B.** Site of composite mine-waste sample 04PKHL3. **C.** The main Eureka mine adit, where water site PKHL-1 was located. **D.** Samples 04PKHL4-C of blue precipitate and 04PKHL4-D of white precipitate were collected from the wall of the Eureka mine adit. **E.** Sample 04PKHL4-A was collected from ochre floc just above waterline of the Eureka adit mine pool. **F.** Samples 04PKHL5-A of white foam, 04PKHL5-B of blue precipitate, and 04PKHL5-C of blue precipitate were collected from the adit. Water sampling site PKHL-4 was located at the mine pool. (Sample and site numbers are shown in white boxes.)

Water samples for site PKHL-4 and several solid grab samples were collected from an adit, which likely had been part of the Union mine workings, north of the Eureka mine adit (fig. 5F). Sample 04PKHL5-A was collected from white, foamy material that was floating on the surface and coating the bottom of the mine pool, and samples 04PKHL5-B and -C were collected from blue precipitate-coated rock at the entrance to the adit (fig. 5F); organic materials and white precipitate-coated rock also were present. To the northeast, sample 04PKHL6 was collected from starburst sprays of delicate white gypsum crystals coating the ceiling of an adit in a wooded area (fig. 3). A composite mine-waste sample, 04PKHL7, was collected from the unvegetated area downslope of the Eureka and Union mine workings and upslope of the mine access road (figs. 3 and 6A). These waste piles had deep, eroded gullies and contained cobbles and boulders of weathered ore as much as 0.5 m in diameter. Sample 04PKHL8 was collected from bright blue, efflorescent salts grown on gypsum sprays (fig. 6B). Samples collected upslope from the mine access road included composite sample 04PKHL9, from the partially burned flotation-mill tailings (fig. 6C), and grab samples 04PKHL9-A of the red burnt material, sample 04PKHL9-B of gray material that was exposed in erosional gullies (fig. 6D), and sample 04PKHL9-C of jarositic soil above the gray material (fig. 6D). In 1993, the Corinth Fire Department was informed that smoke was emanating from the mine. Spontaneous oxidation and combustion of reactive sulfides apparently caused this section of mine waste to smolder (U.S. Environmental Protection Agency, 2004a).

Downslope from the mine access road, sandy, quartz-rich, processed flotation-mill tailings are distinctive visually in contrast to the surrounding mine-waste piles (fig. 6E); composite sample 04PKHL10 was collected from this material. A large area of barren mine waste below the mine access road was sampled as composite 04PKHL11 (fig. 6F), and it was resampled as a field replicate in 2005 as 05PKHL11-Dup. Weathering sulfidic ore boulders and cobbles were observed, and sample 04PKHL11-1 was collected from some that had efflorescent sulfate salts. Nearby, sample 04PKHL11-A was collected from a localized concentration of dark-gray flotation tailings (fig. 7A). Water sampling sites PKHL-7 and PKHL-8 were located at two seeps that emerged from the base of waste pile 04PKHL11, and sample 04PKHL12 was collected from the ferricrete terrace forming around these seeps (fig. 7B). Composite mine-waste sample 04PKHL13 was collected from the lowermost waste piles at Pike Hill (fig. 7C). These waste piles contained cobbles and boulders of weathered ore and country rock and clots of jarosite; jarositic clots were collected as sample 04PKHL14. Sample 04PKHL13-A from rocks with thin yellowish-green coatings (fig. 7D) and sample 04PKHL13-B of a ferricrete were collected from a dry seep at the base of the lowermost mine dump.

Water and Stream-Sediment Samples

Mine-drainage environments were characterized by the collection and analysis of samples of surface-mine drainage, mine pools, seeps, downstream waters, and background waters. These samples were collected in October 2004 and August 2005 (figs. 2 and 3; table 3). In conjunction with this study, a regional watershed study that was conducted from October 2004 to December 2005 assessed the hydrology and quality of surface waters in and around the Pike Hill Brook watershed (Kiah and others, 2007). During that study, synoptic water-quality samples were collected at 10 sites in November 2004, June 2005, and August 2005 and at 9 sites in April 2005. In addition, monthly water-quality samples and continuous data for streamflow, water temperature, pH, and specific conductance were collected at several of these sites from December 2004 to September 2006.

The August 2005 synoptic sampling results of 10 watershed samples collected during the regional assessment (Kiah and others, 2007) are included in this report. These samples are designated with the Water Resources Discipline station number given in table 3 ("0113...") followed by "Aug." Stream-sediment samples also were collected and are designated with the Water Resources Discipline station number ("0113...") followed by "-SD" (table 3).

Five water sites and one stream-sediment site were sampled from the Smith mine area (figs. 2 and 3). Waters from this mine drain into an unnamed tributary to Cookville Brook. Site CKBK-1, which includes water samples CKBK-1-2 and 01139940Aug and stream-sediment sample 01139940-SD, was located in this unnamed tributary downstream of the impacted area (fig. 2). An acidic seep downslope of the mine site enters the tributary, and water samples CKBK-2-2 and CKBK-2-3 were collected from that site (fig. 8A). In the mixing zone of the seep with the tributary, white precipitate coated the streambed. The tributary upstream of the Smith mine was chosen for the site of background samples CKBK-3-2, collected in October 2004, and CKBK-3-3, collected in August 2005 (fig. 8B). Site CKBK-4 was ponded water located in a shallow pit at the site (fig. 4A) and site CKBK-5 was the mine-pool water at the Smith mine adit (fig. 8C).

Samples of surface, seep, and mine-pool waters and stream sediments were collected from areas directly impacted by the Eureka and Union mines. As shown in figure 3, mine-pool waters included water from the Eureka mine adit where site PKHL-1 was located (fig. 5C), perched mine-pool water from an adit on the western edge of the Union mine where site PKHL-4 was located (fig. 5F), and mine-pool water from the Union mine haulageway where site PKHL-5 was located.

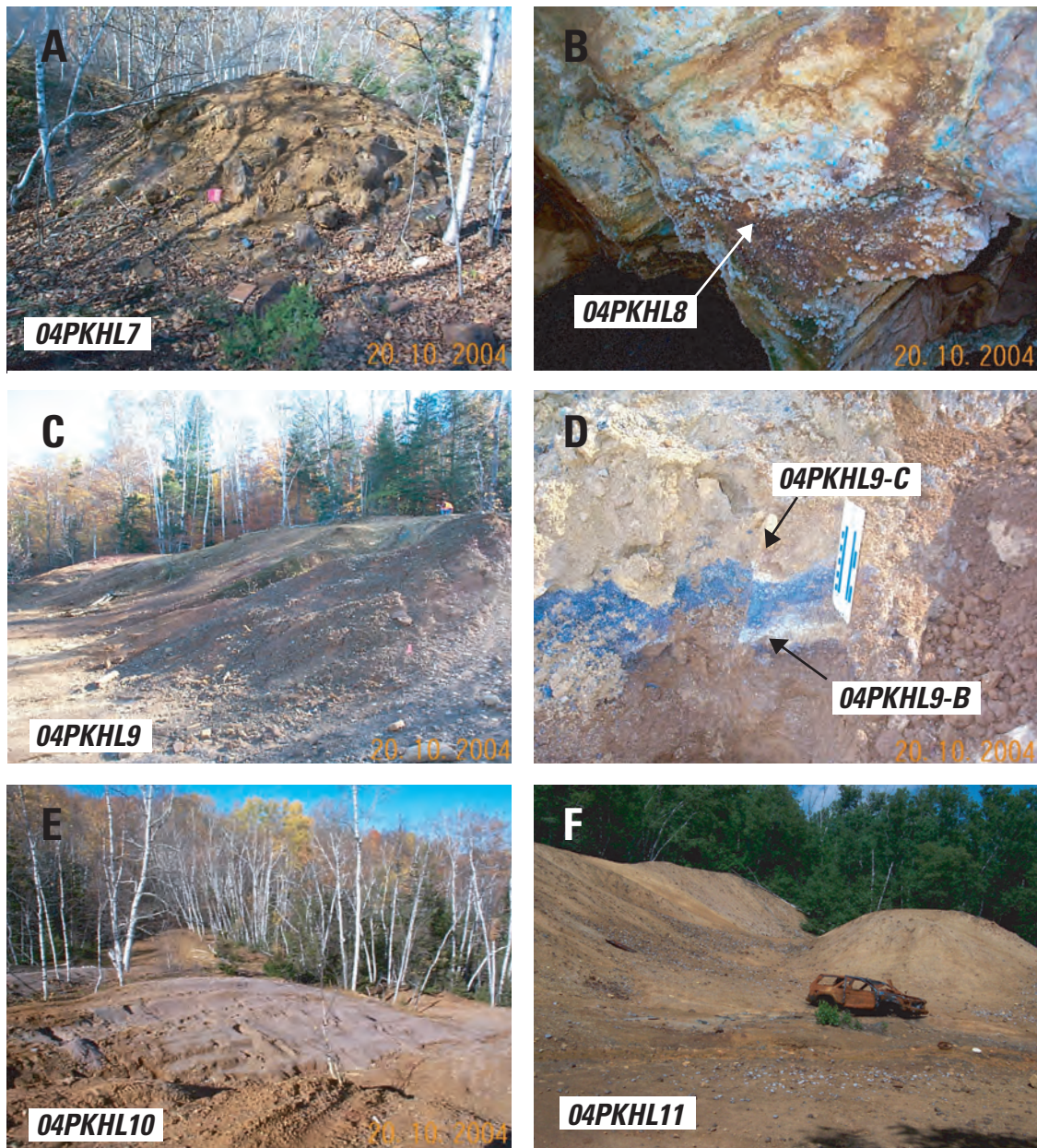


Figure 6. Sampling sites at the Pike Hill Copper Mine Superfund site. **A.** Site of composite mine-waste sample 04PKHL7. **B.** Sample 04PKHL8 was collected from blue chalcantite and white gypsum crystals on the ceiling of an adit near the main Eureka mine adit. **C.** Composite sample 04PKHL9 was collected from partly burned tailing. **D.** Sample 04PKHL9-B was collected from gray material exposed in a gully. The overlying yellow layer was the site of sample 04PKHL9-C. **E.** Site of composite processed tailings sample 04PKHL10. **F.** Site of composite mine-waste sample 04PKHL11. (Sample numbers are shown in white boxes.)

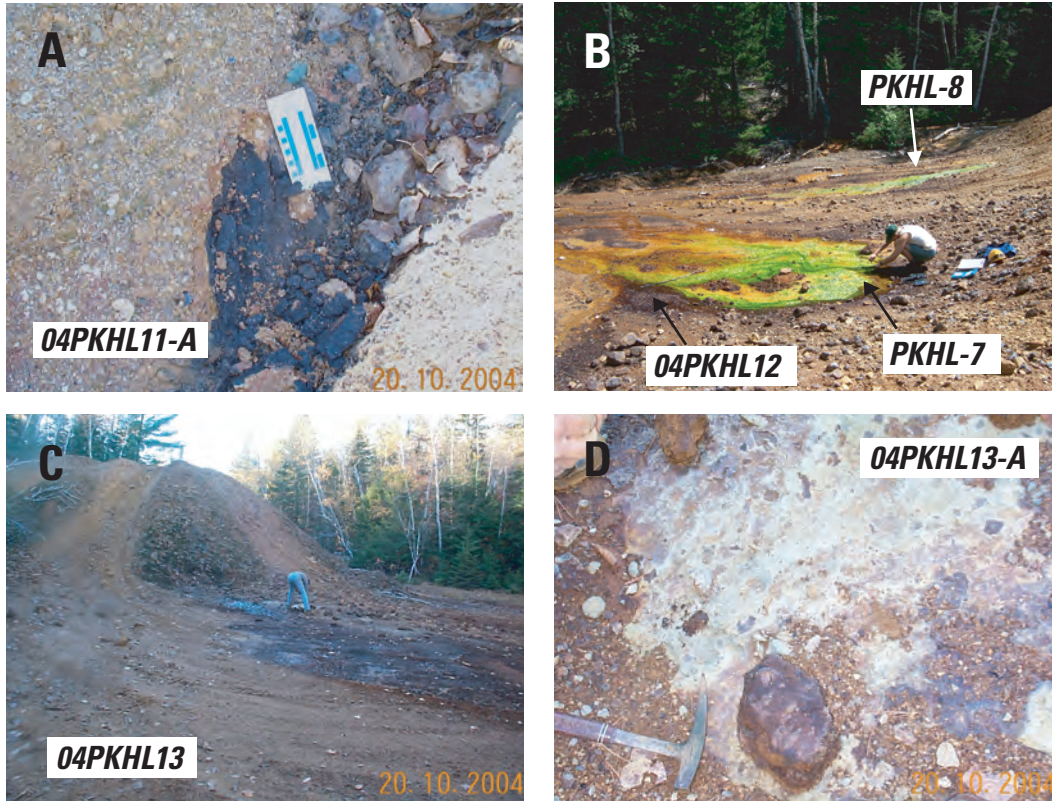


Figure 7. Sampling sites at the Pike Hill Copper Mine Superfund site. **A.** Dark-gray unoxidized flotation-mill tailings where sample 04PKHL11-A was collected. **B.** Water sampling sites PKHL-7 and PKHL-8 were located at the seeps at the base of waste pile 04PKHL11. Sample 04PKHL12 was collected from a ferricrete deposit. **C.** Composite sample 04PKHL13 was collected from the lowermost mine-waste piles. **D.** Sample 04PKHL13-A was collected from yellowish-green coatings on dry seep ferricrete. (Sample and site numbers are shown in white boxes.)

Figure 8. Water-quality sampling sites at the Pike Hill Copper Mine Superfund site. **A.** Site CKBK-2 was a seep to unnamed tributary to Cookville Brook. **B.** A background-water sample was collected upstream of Smith mine at site CKBK-3. **C.** Site CKBK-5 was the Smith mine adit, where mine-pool water was collected underneath the collapsed roof. **D.** Site PKHL-9 was the Eureka and Union mines drainage. (Site numbers are shown in white boxes.)

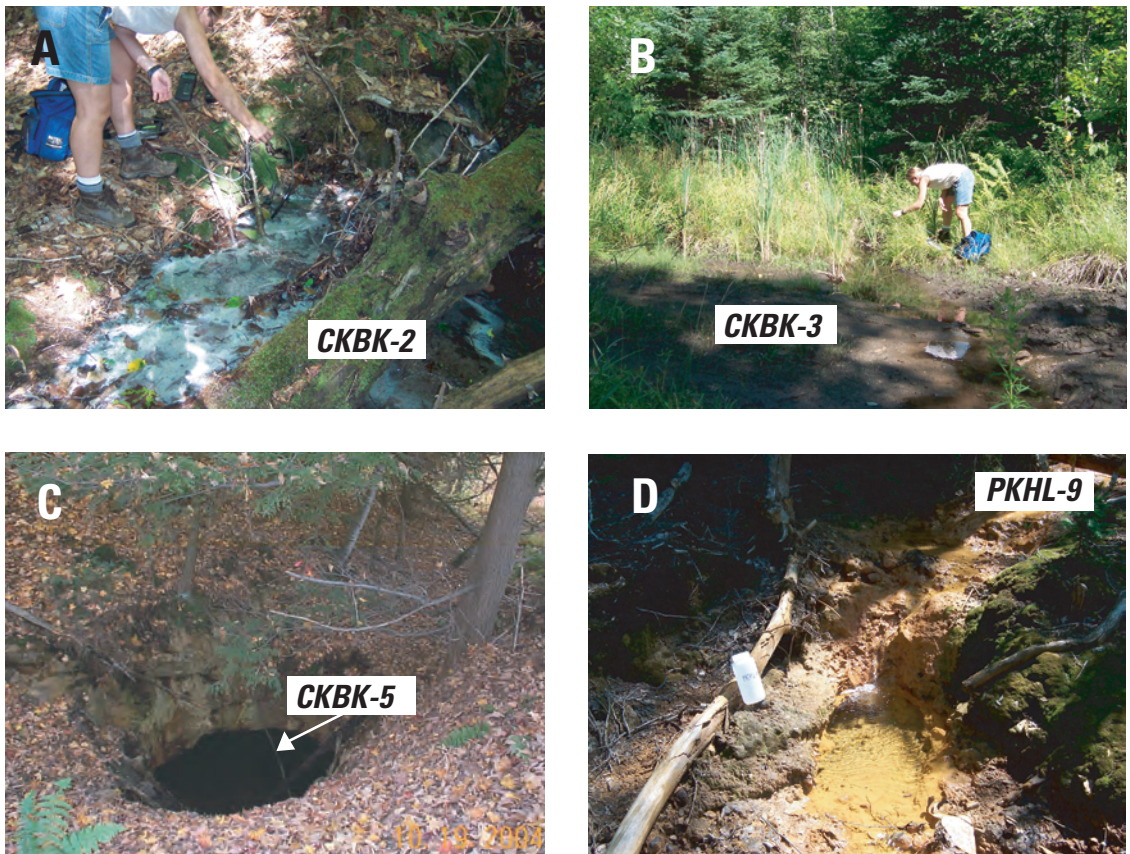


Table 3. Locations of water and stream-sediment samples collected from the Pike Hill mines study area.
 [GD, Geologic Discipline; WRD, Water Resource Discipline; n.a., not applicable because no sample was collected]

Water site number (GD)	Water site number (WRD) ¹	Station number (WRD)	Stream-sediment sample number (GD)	Latitude	Longitude	Water type	Location description
CKBK-1	10	01139940	01139940-SD	44.046000	-72.298400	Downstream surface	Unnamed tributary to Cookville Brook. Downstream of impacted area.
CKBK-2	n.a.	n.a.	n.a.	44.053800	-72.302850	Seep	Seep entering unnamed tributary to Cookville Brook from west side at base of bend in stream. Aluminum precipitate near Smith mine.
CKBK-3	n.a.	n.a.	n.a.	44.056817	-72.303833	Background	Headwaters of unnamed tributary to Cookville Brook upstream of Smith mine at road.
CKBK-4	n.a.	n.a.	n.a.	44.054800	-72.305750	Surface mine drainage	Smith mine stagnant ponded water north of main shaft. Abundant leaf litter and bacterial film.
CKBK-5	n.a.	n.a.	n.a.	44.054567	-72.305700	Mine pool	Mine pool water at Smith mine adit.
PKHL-1	n.a.	n.a.	n.a.	44.061933	-72.307750	Mine pool	Eureka main adit mine pool.
PKHL-2	n.a.	n.a.	n.a.	44.063917	-72.303067	Surface mine drainage	Headwaters of Pike Hill Brook downstream of Pike Hill mines, downstream of waste pile, on edge of wooded area.
PKHL-4	n.a.	n.a.	n.a.	44.062733	-72.307833	Mine pool	Perched Union mine pool, top of Union mine ore body, just north of Eureka mine adit. White and green precipitate seeping from hill next to stope. Pool has thick white precipitate on bottom, frothy white on top.
PKHL-5	n.a.	n.a.	n.a.	44.063433	-72.307217	Mine pool	Union mine haulage way. Bluish white precipitate on bottom, water is clear.
PKHL-6	n.a.	n.a.	n.a.	44.063933	-72.305667	Surface mine drainage	Stream draining Union mine haulage way area, just prior to infiltrating lower waste piles.
PKHL-7	n.a.	n.a.	n.a.	44.063783	-72.304500	Seep	Seep 1 at base of lower mine waste dump, northwestern-most seep.
PKHL-8	n.a.	n.a.	n.a.	44.063717	-72.304450	Seep	Seep 2 at base of lower mine waste dump, seep between seep 1 and surface flow.
PKHL-9	n.a.	n.a.	n.a.	44.063650	-72.304383	Surface mine drainage	Surface water from Eureka mine area downstream of lower mine dump adjacent to seeps.
PKHL-10	1	01139830	01139830-SD	44.063889	-72.299100	Surface mine drainage	Pike Hill Brook above Richardson Road. Drainage from Eureka and Unions mines upstream from first clean tributary. Eighteen meters upstream of confluence with neutral "clean" stream (PKHL-11) where white precipitates form. Orange precipitate on rocks. Field duplicates of water samples and lab replicate of stream sediment analyzed for chemistry.

Table 3. Locations of water and stream-sediment samples collected from the Pike Hill mines study area.—Continued

[GD, Geologic Discipline; WRD, Water Resource Discipline; n.a., not applicable because no sample was collected]

Water site number (GD)	Water site number (WRD) ¹	Station number (WRD)	Stream-sediment sample number (GD)	Latitude	Longitude	Water type	Location description
n.a.	n.a.	n.a.	01139830-SD-BC	44.063889	-72.301944	Downstream surface	Pike Hill Brook several meters downstream of confluence with first clean tributary where white and orange flocc precipitates.
PKHL-11	2	011398302	011398302-SD	44.064867	-72.301600	Background	Clean tributary to Pike Hill Brook at Richardson Road. Flows into drainage from mines. At confluence, white precipitate forming.
PKHL-12	4	01139833	01139833-SD	44.057667	-72.280900	Downstream surface	Pike Hill Brook at Pike Hill Road, West Crossing. Downstream from confluence with unimpacted tributary.
PKHL-13	5	01139838	01139838-SD	44.053333	-72.253333	Downstream surface	Pike Hill Brook at bridge on Pike Hill Road between wetlands.
PKHL-14	6	01139839	01139839-SD	44.054867	-72.245117	Downstream surface	Pike Hill Brook downstream of wetlands at Miller Road.
PKHL-15	8	01139826	01139826-SD	44.077283	-72.259667	Background	Waits River upstream of confluence with Pike Hill Brook at Rt. 25 bridge crossing, near school.
PKHL-16	n.a.	n.a.	n.a.	44.063667	-72.292694	Downstream surface	Pike Hill Brook downstream of PKHL-10 and PKHL-11 confluence where road crosses the brook. Located between PKHL-10 and WR 1139832.
PKHL-17	n.a.	n.a.	n.a.	44.048222	-72.255250	Background	Tributary to Pike Hill Brook upstream of lower wetland.
01139832	3	01139832	01139832-SD	44.062500	-72.288611	Downstream surface	Pike Hill Brook at Carpenter Place.
01139840	7	01139840	01139840-SD	44.062222	-72.235000	Downstream surface	Pike Hill Brook at mouth.
01139841	9	01139841	01139841-SD	44.055278	-72.221667	Downstream surface	Waits River at Village Road downstream of confluence with Pike Hill Brook.

¹WRD site number used in Kiah and others (2007). Water-sample numbers are the Geologic Discipline site number with the suffix ".2" for samples collected in October 2004 or with the suffix ".3" or "Aug" for samples collected in August 2005. Stream-sediment samples are designated with the suffix ".SD" and the Water Resources Discipline station number.

As discussed above, samples from white and blue precipitates were collected from the perched Union mine adit, and samples were not collected from bluish-white precipitate that coated the bottom of the Union mine haulageway. Downhill from the mine access road, water samples PKHL-7-2, PIKHL-7-3 and PKHL-8-2 were collected from two seeps that emanated from the base of the mine-waste dump where solid sample 04PKHL11 was collected (figs. 2, 3, and 7B). Seep PKHL-8 was dry during the second sampling in August 2005. Surface-water site PKHL-6 was located at a stream that drains the Union mine haulageway area, after it disappears underground for approximately 80 m and then reappears, prior to infiltrating mine dump 04PKHL11 (fig. 3). Site PKHL-9 was drainage from the Eureka mine area downstream of the mine dump adjacent to the two seeps (fig. 8D), and site PKHL-2 was the headwaters of Pike Hill Brook, downstream of the Pike Hill mines. Farther downstream, a second sampling site, PKHL-10, was located at the headwaters of Pike Hill Brook near Richardson Road (fig. 9A), and site PKHL-11 was upstream from the confluence with an unimpacted tributary. (See figs. 2 and 3 for map locations.) Stream-sediment samples also were

collected from two of these water sampling locations and are 01139830-SD, located at site PKHL-10, and 011398302-SD, located at site PKHL-11. Stream-sediment sample 01139830-SD-BC was collected a few meters downstream of the confluence of Pike Hill Brook and the first unimpacted tributary, where white and orange precipitates coated the streambed; the abbreviation “BC” in the sample name was added to indicate “below confluence.” Approximately 600 m downstream of the confluence, water sample PKHL16-3 was collected. In addition, water and stream-sediment samples were collected approximately 400 m downstream of site PKHL-16 at site number 01139832 (fig. 2).

A series of three natural wetlands, which potentially could affect the geochemical cycles of sulfur and other elements from mine drainage, are approximately 3.6 km downstream from the mine site in Pike Hill Brook (fig. 2). Water samples PKHL-12-2, collected October 2004, and 01139833Aug, collected August 2005, and stream-sediment sample 01139833-SD, collected August 2005, were from Pike Hill Brook upstream of the wetlands where Pike Hill Road crosses the brook (fig. 9B). Water samples

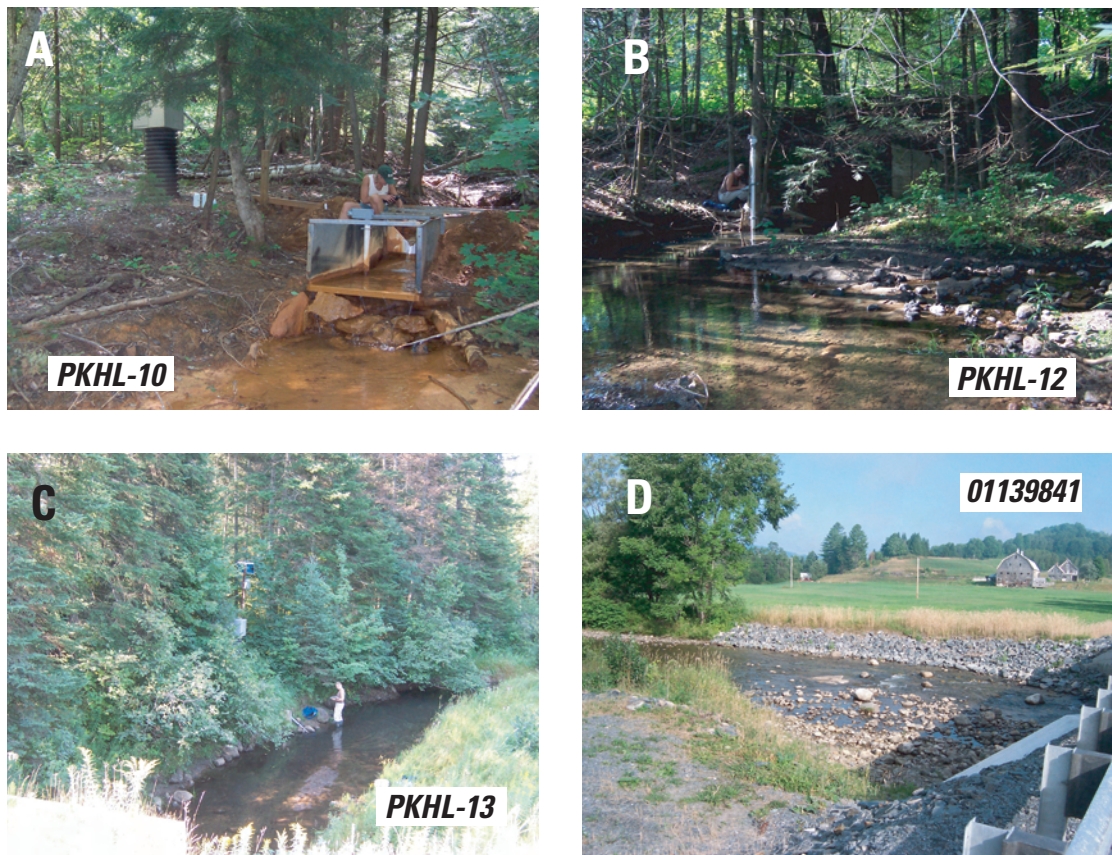


Figure 9. Water-quality sampling sites at the Pike Hill mines study area. **A.** Mine drainage downstream of the Eureka and Union mines at gaging station. **B.** Water sampling site PKHL-12 was located downstream of the confluence with a clean tributary. **C.** Site of Pike Hill Brook sample PKHL-13. **D.** Site of Waits River water sample 01139841. (Site numbers are shown in white boxes.)

PKHL-13-2 and 01139838Aug, and stream-sediment sample 01139838-SD were collected between two of the wetlands where the road again crosses the brook (fig. 9C), and water samples PKHL-14-2 and 01139839Aug, and stream-sediment sample 01139839-SD were collected downstream of the wetlands at Miller Road. Water site PKHL-17 was located at an unimpacted tributary to Pike Hill Brook upstream of the lower wetland (fig. 2). Water samples PKHL-15-2 and 01139826Aug, and stream-sediment sample 01139826-SD were collected from the Waits River upstream of the confluence with Pike Hill Brook. In addition, Pike Hill Brook was sampled at its mouth, where water sample 01139840Aug and stream-sediment sample 01139840-SD were collected, and the Waits River was sampled downstream of the confluence with Pike Hill Brook, where water sample 01139841Aug and stream-sediment sample 01139841-SD were collected (figs. 2 and 9D).

Results and Discussion

Mine Waste

Mineralogy

Semiquantitative mineralogy results for composites and several grab samples from Siroquant analysis of XRD patterns are shown in table 4 and figure 10. In table 4, primary minerals are listed first, followed by secondary minerals. Primary minerals formed at the same time as the rock enclosing them; secondary minerals formed later than the rock enclosing them (Neuendorf and others, 2005). The primary and secondary mineral percentages sum to 100 weight percent and are for the crystalline part of the sample. Table 5 lists the mineralogy for mine-waste and grab samples that were not analyzed by Siroquant and that, therefore, are not listed in table 4. The primary purpose of these samples was mineral identification rather than quantification.

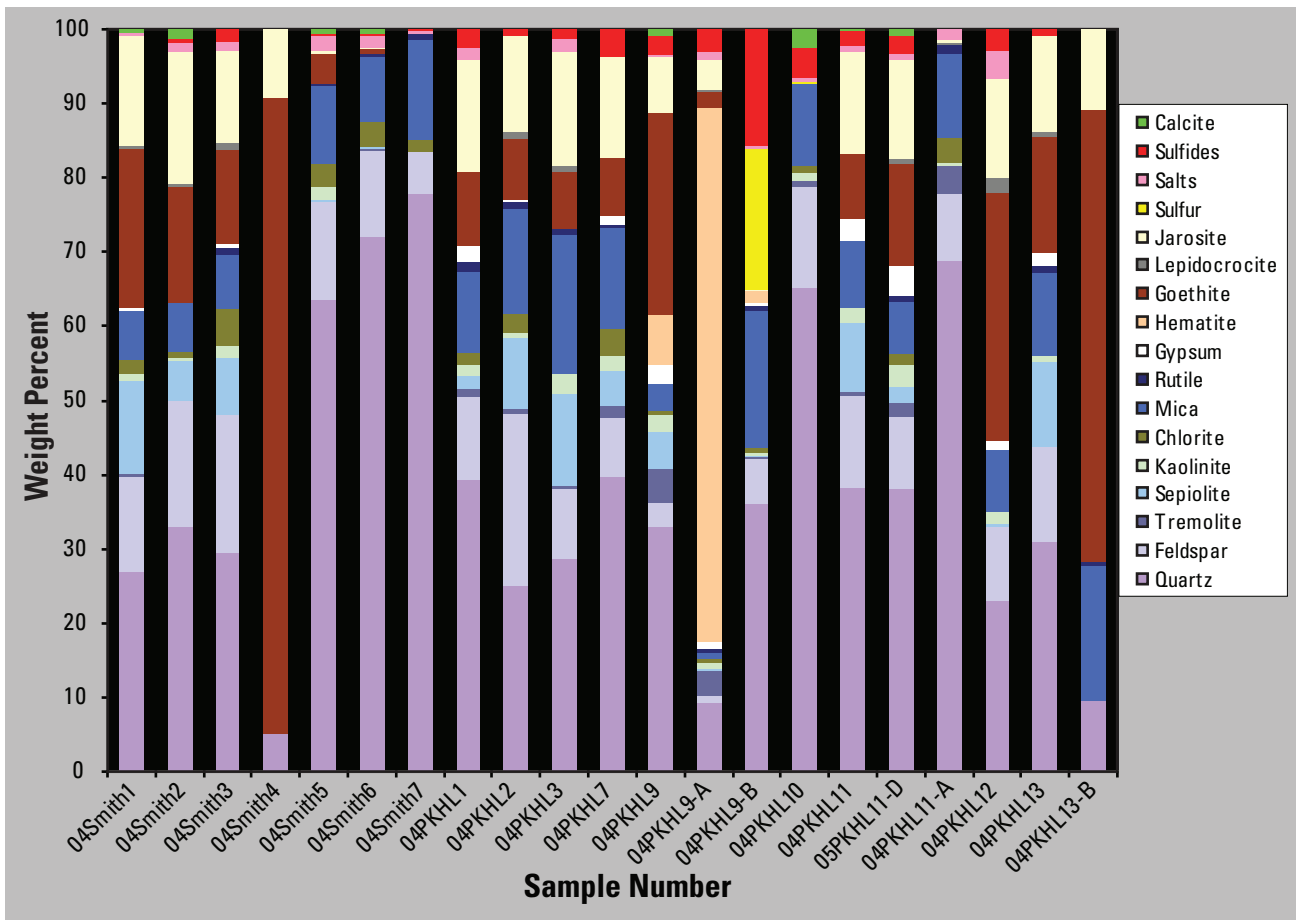


Figure 10. The relative weight percentages of minerals in mine waste from the Pike Hill mines study area; efflorescent sulfate minerals are “salts,” and chalcopyrite, pyrrhotite, pyrite, and sphalerite are “sulfides.”

Table 4. Estimates of the amounts of minerals in mine-waste samples from the Pike Hill mines study area.

Mineral	Ideal formula	Error ¹	Sample number								
			04Smith1	04Smith2	04Smith3	04Smith4	04Smith5	04Smith6	04Smith7	04PKHL1	04PKHL2
Primary minerals (weight percent)											
Albite	NaAlSi ₃ O ₈	0.9	7.2	7.7	8.6	n.d.	5.7	3.7	5.5	6.3	14.3
Anorthite	CaAl ₂ Si ₂ O ₈	1.2	0.0	0.0	0.0	n.d.	0.0	0.0	0.0	0.9	2.3
Biotite	K(Mg, Fe) ₃ (AlSi ₃ O ₁₀)(OH) ₂	0.4	0.5	0.0	0.0	n.d.	0.0	0.0	0.0	0.0	0.0
Calcite	CaCO ₃	0.5	0.4	1.2	0.0	n.d.	0.6	0.7	0.1	0.0	0.0
Chalcopyrite	CuFeS ₂	0.2	0.0	0.0	0.1	n.d.	0.0	0.0	0.0	1.5	0.3
Chlorite	(Mg, Fe ²⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	0.6	1.7	0.8	4.9	n.d.	3.2	3.5	1.6	1.6	2.6
Labradorite	(Ca, Na)(Si, Al) ₈ O ₈	1.1	5.6	9.1	9.9	n.d.	7.5	8.0	0.3	3.9	6.6
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	0.6	6.2	6.6	7.4	n.d.	10.4	8.8	13.3	11.0	14.1
Pyrite	FeS ₂	0.2	0.0	0.4	1.4	n.d.	0.1	0.0	0.0	0.8	0.5
Pyrrhotite	Fe _{1-x} S	0.2	0.0	0.0	0.0	n.d.	0.1	0.2	0.2	0.0	0.0
Quartz	SiO ₂	1.2	26.8	33.0	29.5	5.1	63.4	72.0	77.8	39.4	25.0
Rutile	TiO ₂	0.2	n.d.	0.0	1.0	n.d.	0.3	0.4	0.8	1.4	1.0
Sphalerite	ZnS	0.1	0.0	0.2	0.1	n.d.	0.1	0.0	0.0	0.1	0.0
Tremolite	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	0.9	0.5	0.0	0.0	n.d.	0.0	0.2	0.0	1.1	0.5
Secondary minerals (weight percent)											
Alunogen	Al ₂ (SO ₄) ₃ •17H ₂ O	0.8	0.0	0.0	0.0	n.d.	0.0	0.5	0.0	0.7	0.0
Copiapite	Fe ²⁺ Fe ³⁺ (SO ₄) ₆ (OH) ₂ •20H ₂ O	0.4	0.4	1.1	0.4	n.d.	0.6	0.0	0.0	0.2	0.0
Goethite	FeO(OH)	0.5	21.4	15.7	12.6	85.8	4.1	0.5	0.0	10.0	8.4
Gypsum	CaSO ₄ •2H ₂ O	0.3	0.4	0.0	0.3	n.d.	0.0	0.0	0.0	2.2	0.1
Hematite	Fe ₂ O ₃	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jarosite	K ₂ Fe ₆ ³⁺ (SO ₄) ₄ (OH) ₁₂	0.4	14.9	17.7	12.5	9.1	0.3	0.2	0.1	15.1	13.1
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	0.6	1.0	0.4	1.6	n.d.	1.7	0.0	0.0	1.3	0.7
Lepidocrocite	FeO(OH)	0.2	0.4	0.3	1.0	n.d.	0.0	0.0	0.0	0.0	0.7
Melanterite	FeSO ₄ •7H ₂ O	0.4	0.0	0.2	0.8	n.d.	1.4	1.0	0.3	0.7	0.0
Rozenite	FeSO ₄ •4H ₂ O	0.5	0.0	0.0	0.0	n.d.	0.0	0.1	0.0	0.0	0.0
Sepiolite	Mg ₄ Si ₆ O ₁₅ (OH) ₂ •6H ₂ O	0.5	12.5	5.5	7.6	n.d.	0.2	0.1	0.0	1.9	9.6
Sulfur	S	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fit of refinement											
Chi-square ²			4.24	4.2	4.22	3.08	4.55	5.44	5.17	4.48	5.48

[n.d., not determined]

Table 4. Estimates of the amounts of minerals in mine-waste samples from the Pike Hill mines study area.—Continued
[n.d., not determined]

Mineral	Sample number											
	04PKHL3	04PKHL7	04PKHL9	04PKHL9A	04PKHL9B	04PKHL10	04PKHL11	05PKHL11-D	04PKHL11A	04PKHL12	04PKHL13	04PKHL13B
	Primary minerals (weight percent)											
Albite	4.2	2.9	2.2	0.0	1.9	0.0	4.5	7.3	6.2	0.0	6.7	0.5
Anorthite	0.0	1.3	0.9	0.1	0.0	2.3	0.0	0.3	0.0	6.2	0.0	n.d.
Biotite	0.0	2.7	0.0	0.0	3.0	3.8	0.0	0	0.0	0.0	0.0	n.d.
Calcite	0.0	0.0	0.8	0.0	0.0	2.4	0.2	0.8	0.0	0.0	0.0	n.d.
Chalcopyrite	0.8	3.0	1.8	1.3	14.7	0.8	1.8	1.9	0.0	2.5	0.6	n.d.
Chlorite	0.0	3.5	0.6	0.6	0.5	1.1	0.0	1.3	3.3	0.0	0.0	n.d.
Labradorite	5.1	3.7	0.0	0.8	4.2	11.4	7.8	2.1	2.8	3.7	6.1	n.d.
Muscovite	18.8	11.1	3.6	0.8	15.7	7.1	8.8	7.3	11.5	8.3	11.2	18.0
Pyrite	0.4	0.6	0.0	1.2	0.7	1.8	0.1	0.5	0.0	0.0	0.0	n.d.
Pyrrhotite	0.0	0.0	0.0	0.5	0.1	0.5	0.0	0	0.0	0.3	0.0	n.d.
Quartz	28.8	39.8	33.0	9.3	36.1	65.2	38.2	38	68.7	23.1	30.9	9.5
Rutile	0.8	0.3	0.0	0.4	0.5	0.1	0.1	0.8	1.2	0.0	1.0	0.7
Sphalerite	0.1	0.0	0.8	0.0	0.3	1.0	0.2	n.d.	0.0	0.0	0.3	n.d.
Tremolite	0.4	1.6	4.6	3.4	0.3	0.8	0.4	1.8	3.9	n.d.	0.0	n.d.
	Secondary minerals (weight percent)											
Alunogen	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0	0.0	0.5	0.0	n.d.
Copiapite	1.4	0.0	0.2	0.5	0.3	0.0	0.6	0.4	0.2	0.6	0.0	n.d.
Goethite	7.6	7.7	27.3	2.2	0.0	0.0	8.7	13.6	0.0	33.5	15.6	60.5
Gypsum	0.1	1.3	2.4	1.0	0.5	0.0	3.0	4	0.0	1.2	1.7	n.d.
Hematite	n.d.	n.d.	6.8	72.1	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jarosite	15.4	13.6	7.5	4.0	0.1	0.0	13.6	13.4	0.3	13.1	13.0	10.7
Kaolinite	2.5	2.1	2.3	0.9	0.5	0.9	2.1	2.8	0.3	1.8	0.7	n.d.
Lepidocrocite	0.8	0.0	0.0	0.2	0.0	0.0	0.0	0.6	0.2	2.0	0.6	n.d.
Melanterite	0.3	0.1	0.0	0.0	0.0	0.7	0.2	0.5	1.2	1.9	0.0	n.d.
Rozenite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0.0	1.0	0.0	n.d.
Sepiolite	12.5	4.7	5.0	0.2	0.1	0.0	9.4	2.4	0.0	0.3	11.5	n.d.
Sulfur	n.d.	n.d.	n.d.	n.d.	19.1	0.1	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
	Fit of refinement											
Chi-square ²	4.9	3.86	4.76	2.85	4.75	6.88	4.06	4.81	4.44	2.85	4.53	3.00

¹Average errors are estimated standard deviations that were calculated by Siroquant based on square roots of diagonal elements of least-squares variance-covariance matrix.

²Chi-square is a computed statistical residual to measure the fit of refinement. Chi-square = 1 for perfect correspondence between least-squares model and observed data. Values below 6 are considered reasonable fits for these complex mine wastes due to systematic errors and imperfect physical corrections.

Table 5. Mineralogy of mine waste and grab samples from the Pike Hill mines study area.

Sample	Sample description	Phase
04Smith1-1	White salts coating sulfidic rock	Melanterite, gypsum
04Smith 1-2	Yellow soil	Jarosite, goethite, quartz, albite, muscovite
04PKHL2-1	Oxidized ore	Pyrrhotite, chalcopyrite, sulfur, goethite
04PKHL3-1	Rock with yellow-green coating	Jarosite, quartz, albite, muscovite
04PKHL4-A	Ochre floc	Ferrihydrite
04PKHL4-B	Ochre stalactite	Ferrihydrite
04PKHL4-C	Bright blue precipitate	Amorphous
04PKHL4-D	White precipitate	Amorphous
04PKHL4-E	Ochre floc	Ferrihydrite
04PKHL4-F	Host rock to white precipitate	Calcite, quartz, anorthite, muscovite, chlorite, kaolinite
04PKHL5-A	White foam	Amorphous
04PKHL5-B	Blue precipitate	Amorphous
04PKHL5-C	Blue precipitate	Glaucozerinite
04PKHL6	Starburst sprays of white crystals	Gypsum
04PKHL8	Bright blue and white salts	Gypsum, chalcantite
04PKHL9-C	Layer above black tailings	Jarosite, goethite, chalcopyrite, quartz, muscovite
04PKHL11-1	White salts sulfidic rock	Melanterite
04PKHL13-A	Thin yellow-green rock coating	Jarosite, gypsum, goethite, quartz, muscovite
04PKHL14	Jarosite-rich clot	Jarosite, quartz, albite, muscovite

Sulfates and Sulfides

Sulfide minerals were considered primary and sulfate minerals were considered secondary in the samples collected for this study. The sample that had the highest amount of sulfides, mostly chalcopyrite, was sample 04PKHL9-B from the gray tailings from the partially burnt area; it contained approximately 16 weight percent sulfides. This sample also contained 19 weight percent native sulfur and only traces (less than 1 weight percent) jarosite and gypsum. This sample was collected as a mineralogically unique subset sample to document variation within pile 04PKHL9, which contained the highest concentration of copper based on bulk chemistry (as discussed below). In contrast to the high amount of sulfides in sample 04PKHL9B, sample 04PKHL11A from dark gray tailings contained no detectable sulfides. Overall, composite mine-waste samples contained sulfides in concentrations ranging from less than 1 to approximately 4 weight percent (table 4). Sulfides present included chalcopyrite, pyrite, pyrrhotite, and sphalerite. A grab sample, 04PKHL2-1, of oxidized ore from a pile near the top of Pike Hill consisted of pyrrhotite, chalcopyrite, sulfur, and goethite (table 5). Composite sample 04PKHL10 of the quartz-rich flotation-mill tailings contained more sulfides (approximately 4 weight percent) and calcite (approximately 2 weight percent) when compared with the other composites (fig. 10). This sample also contained the highest concentrations of arsenic, cadmium, cobalt, and zinc. As the materials containing sulfides weather, they may generate acid and

leach metals of environmental concern. In addition, sulfide minerals define the acid-generating potential of the samples for acid-base accounting purposes. The background soils and downslope soil at the Smith mine did not contain detectable sulfides (approximately 1 weight percent) because these soils developed from unmineralized rock.

Jarosite was the dominant sulfate mineral in the mine-waste samples (table 5). Its concentration in composite mine-waste samples ranged from 7.5 weight percent in sample 04PKHL9, from the partially burnt tailings, to 18 weight percent in sample 04Smith2, from an upper waste pile at the Smith mine. The only composite mine-waste sample that did not fall within this range was sample 04PKHL10, from the quartz-rich tailings, and it contained no detectable jarosite (table 4; fig. 10). Clots and layers of jarosite also were found within the waste piles as indicated by grab samples 04Smith1-2, 04PKHL9-C (fig. 6D), and 04PKHL14 (table 5). Jarosite also occurred as thin yellowish-green coating on waste rock, from which samples 04PKHL3-1 and 04PKHL13-A; were collected (table 5; fig. 7D).

Other sulfate minerals identified at the site included glaucozerinite ($\text{Cu}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$), which was found in sample 04PKHL5-C from precipitate along an adit decline (fig. 5F). In addition, gypsum, an efflorescent sulfate salt, was present in many mine-waste samples in minor amounts of less than 4 weight percent. Gypsum also was found as white salts on the walls and ceilings of adits at Pike Hill, where samples 04PKHL6 and 04PKHL8 were collected (table 5; fig. 6B).

Other efflorescent sulfate salts were commonly present in amounts that were too small to detect with the use of XRD, although quantitative mineralogy suggests that as much as 4 weight percent salts were present in samples from the Pike Hill mines study area (table 4; fig. 10). These salts included copiapite and melanterite and lesser amounts of alunogen and rozenite. To verify the presence of these salts, three splits of mine waste were rinsed repeatedly with deionized water; the rinse pH was determined, and then the rinse water was evaporated to precipitate the salts. In addition, leachate water was filtered and evaporated. The pH of the rinse water as a function of the number of rinses is shown in figure 11. The pH values of less than 3.8 for the first few days (fig. 11) were less than the equilibrium pH for the stoichiometric dissolution of jarosite (Langmuir, 1997). This suggests that the dissolution of efflorescent sulfate salts was important at the beginning of the experiment. The evaporates produced by the rinse water and leachate solutions were calcium-sulfate and hydrated iron-sulfate salts, thus confirming the presence of these salts. Melanterite and chalcantite identified in grab samples 04PKHL11-1 and 04PKHL8, respectively, verified the presence of these salts at the site (table 5; fig. 6B). Efflorescent sulfate salts likely play a significant role in acid generation and metal sequestration. During rain events, these highly soluble salts may dissolve and contribute acid and metals to the receiving waters at mine sites.

Iron Oxides

The highest concentrations of iron were found in hardpan, as indicated by sample 04Smith4, and in ferricretes, as indicated by samples 04PKHL12 and 04PKHL13-B. The mineralogy of these samples was consistent with the chemistry

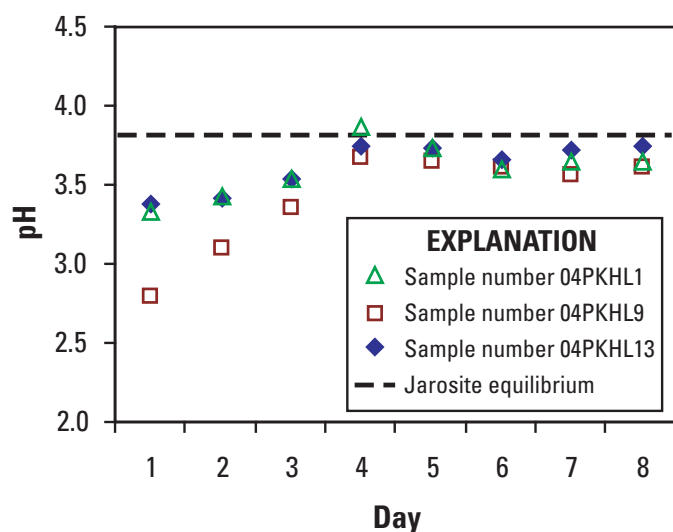


Figure 11. Effects on leachate pH of repeatedly washing with deionized water three mine-waste samples from the Pike Hill mines study area. [Black dashed line representing nominal pH of 3.8 for jarosite equilibrium from Langmuir (1997).]

in that they contained significant amounts of goethite. The ferricretes contained 34 to 61 weight percent goethite, whereas the hardpan contained 86 weight percent goethite (fig. 10). The red tailings from the partially burnt pile, where sample 04PKHL9-A was collected, contained the iron oxide hematite in a significant quantity of 72 weight percent. The only other samples that had detectable hematite were from the same pile. Composite sample 04PKHL9 contained approximately 7 weight percent hematite, and sample 04PKHL9-B, from the gray tailings, contained almost 2 weight percent hematite (table 4; fig. 10). Grab samples of ochre floc and stalactites were dominantly ferrihydrite, whereas amorphous precipitates included blue and white coatings and white foam near or in adits (table 5). The blue and white amorphous precipitates were likely copper- and aluminum-hydroxides. Aluminum-hydroxides are known to selectively sorb metals as a function of pH (Smith, 1999), which might exert a significant control on water chemistry.

Bulk Geochemistry

The concentrations of elements in the mine-waste piles were evaluated by examining the variations in concentrations among piles, by comparing the concentration values to USEPA Preliminary Remediation Goals (PRGs), and by comparing the values to concentrations of elements in mine waste from the Elizabeth and Ely mines. Grab samples of unique areas within the waste piles were collected in order to understand overall variability. The concentrations of all elements analyzed in mine waste are given in appendix 1; the concentrations of selected elements and PRGs for residential and industrial soils are given in table 6. The PRGs are guidelines, not legally enforceable standards, that are used for initial evaluations of potentially contaminated sites. In the text below, the concentrations of several elements are also compared to a range or average concentrations in eastern United States soils (Shacklette and Boerngen, 1984), which can be used to approximate a regional geochemical background level for a given element.

The concentrations of iron in almost all of the samples from the Pike Hill mines site exceeded the PRG for residential soils of 2.3 weight percent; the background soils contained 2.4 and 2.6 weight percent iron, and sample 04PKHL11-A, from the dark-gray tailings, contained 0.65 weight percent iron (table 6; fig. 12). The concentrations of iron in most of the samples exceeded the upper range of 10 weight percent for iron in soils in the eastern United States (Shacklette and Boerngen, 1984). Sample 04Smith4 from hardpan and samples 04PKHL12 and 04PKHL13-B from ferricrete contained concentrations of iron that exceeded the industrial PRG of 31 weight percent. The anomalous iron in these samples correlates with significant goethite of greater than 30 weight percent (fig. 10), based on quantitative mineralogy. The concentrations of iron calculated from quantitative mineralogy for the crystalline portion of the samples were generally less than those determined by ICP-AES. This underestimation of iron content based on mineralogy suggests that amorphous

Table 6. Concentrations of select elements in mine-waste and soil samples from the Pike Hill mines study area.

Element	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Tl	V	Zn
Units	mg/kg	wt. %	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	wt. %	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
PRG-residential¹	390	7.6	22	37	1,400	210	3,100	2.3	1,800	390	1,600	400	390	5.2	78	23,000
PRG-industrial¹	5,100	9.2	260	450	13,000	450	41,000	31	19,000	5,100	20,000	800	5,100	67	1,000	310,000
	Guidelines															
	Mine waste															
Sample	Sample type															
04Smth1	5.89	4.6	1	0.63	39.4	85.1	1,800	19	1,370	4.6	15	69.9	20.1	0.61	137	614
04Smth2	5.49	3.5	0.6	0.29	28.4	40.8	1,530	21	865	4	10	115	22.7	0.88	138	315
04Smth3	6.6	3.2	1	0.22	31.7	28.2	1,380	25	609	16.2	9.9	83.2	24.8	1.1	125	344
04Smth4	<3	0.16	0.6	0.1	1.3	23.1	1,120	47	39	0.2	1.4	22.2	2.1	0.2	32.9	55
04Smth5	<3	3	0.6	0.49	14	38.7	559	14	807	1.4	25.4	9.8	0.8	0.2	61.7	521
04Smth6	<3	4.7	0.5	0.13	10.7	52.8	19	2.6	1,120	0.36	27.3	14.1	0.3	0.3	63.5	66
04Smth7	<3	3.9	0.8	0.11	9.8	45.4	18	2.4	606	0.46	23	14.2	0.4	0.3	55.6	46
04PKHL1	10.3	3	6.3	0.59	35	24.9	4,410	20	166	37.4	7.2	89.2	48.9	1.3	83.8	246
04PKHL2	6.26	4.7	3.1	0.27	29.1	37	3,000	18	218	32.2	7	58.9	47	1.6	82.2	213
04PKHL3	11.9	4.1	3.3	0.35	47.9	41.2	3,240	19	238	18.5	7.9	85.7	47.6	1.6	89	354
04PKHL7	11.4	3.3	8.5	2.5	50.7	31.8	8,060	19	302	21.6	9.6	238	52	1.2	67	593
04PKHL9	27.8	2	9.7	2	103	20	9,200	27	223	44.5	13.6	182	124.2	0.83	47.6	640
04PKHL10	3	3.7	57	91.8	122	42.3	7,200	3.6	1,360	4.1	8.9	103	7.4	0.78	60.4	16,000
04PKHL11	7.63	2.8	3.2	0.64	36.2	24.3	6,400	19	159	19.4	7.1	78.3	60.7	1	63.1	233
05PKHL11-Dup	8.97	2.7	3	1.1	39.3	22.6	8,410	22	160	22.5	4.9	85.5	65.6	1.1	65.5	278
04PKHL11-A	<3	3.4	0.3	0.06	1.1	54.8	2,370	0.65	196	0.62	6.8	14	9.2	0.3	42.5	24
04PKHL12	<3	0.77	0.2	0.41	8	11.9	1,610	40	32	4.9	1.1	15.4	11.2	0.2	24.7	88
04PKHL13	12.9	3.7	6.6	0.29	34.4	32.1	3,670	20	234	34.5	7.4	102	53.9	2.3	72.5	218
04PKHL13-B	<3	0.27	0.5	0.1	3.6	17.8	874	46	22	1.9	<1	29.4	7.1	0.2	138	32

¹PRGs for residential and industrial soils are for noncancer-based chronic exposure with the exception of the PRG for chromium, which is for cancer-based chronic exposure.

Values from "PRG Intercal Tables: Soils" at <http://www.epa.gov/region09/waste/sfund/prg/files/04soils.pdf> (U.S. Environmental Protection Agency, 2004b) for all elements except lead, which is from "Region 9 PRG Table" at <http://www.epa.gov/region09/waste/sfund/prg/files/04prgtable.pdf> (U.S. Environmental Protection Agency, 2004c).

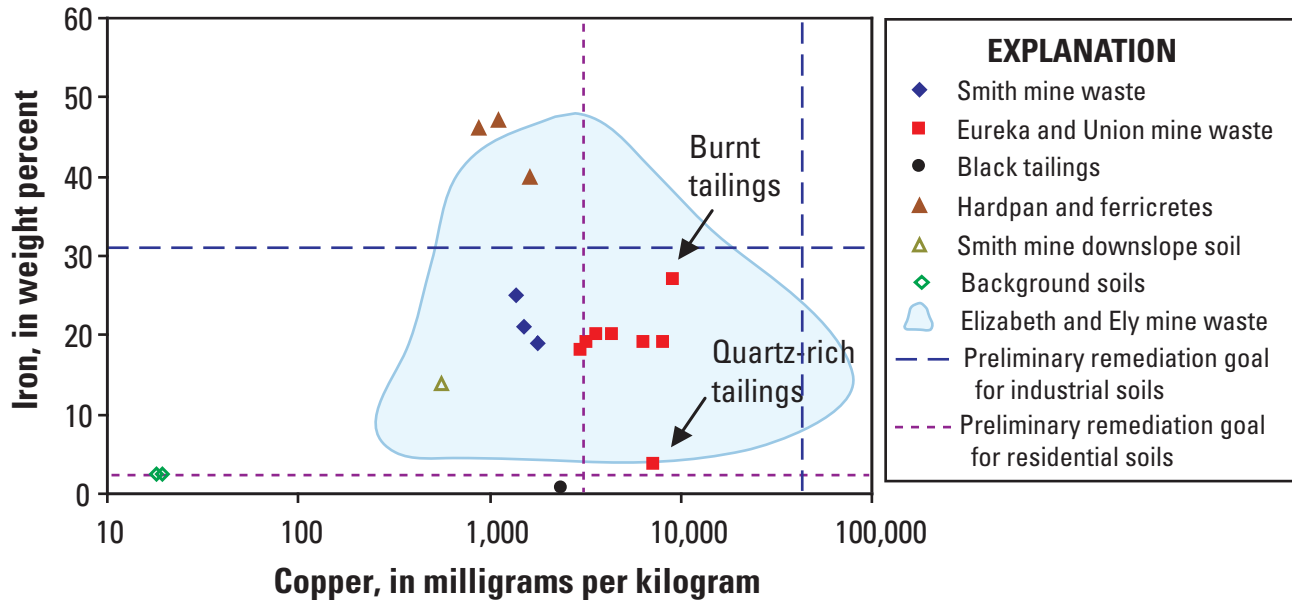


Figure 12. Concentrations of iron and copper in mine-waste and soil samples collected from the Pike Hill mines study area. [Data for the composition of mine waste, including waste rock and unoxidized tailings from the Elizabeth and Ely mines, from Hammarstrom and others (2001, 2003) and Piatak and others (2004). Preliminary remediation goals for residential and industrial soils are from U.S. Environmental Protection Agency (2004b)].

material, if present, may be iron rich. The concentrations of iron in the composite mine-waste samples ranged from 18 to 27 weight percent, except for a concentration of 3.6 weight percent from sample 04PKHL10 from the quartz-rich flotation-mill tailings. These concentrations were within the range found for mine-waste samples from the Elizabeth and Ely mines (fig. 12) (Hammarstrom and others, 2001, 2003; Piatak and others, 2004).

The highest concentrations of aluminum were 4.6 weight percent in sample 04PKHL2 from an upper waste-dump at the Eureka mine, and 4.7 weight percent in sample 04Smith6 from background soil. The hardpan and ferricrete contained the lowest concentrations of aluminum, which were 0.16 weight percent to 0.77 weight percent, respectively (table 6). The highest concentrations of manganese were in sample 04Smith1 from the uppermost mine dump at the Smith mine; sample 04Smith6 from background soil; and sample 04PKHL10 from the processed tailings. Because the background soil contained relatively high amounts of aluminum and manganese when it was compared to the mine-waste samples, these elements are not necessarily indicative of the mining-impacted soils. The concentrations of aluminum and manganese in all of the samples were less than the PRG for residential soils (table 6), and almost all of those concentrations were within the reported range of these elements in eastern United States soils (Shacklette and Boerngen, 1984).

Overall, copper was the most abundant trace metal in the mine-waste samples. The highest value of 9,200 mg/kg was found in sample 04PKHL9 from the partly burnt tailings. This burnt material also contained the highest concentrations of the

following elements: antimony, 5.7 mg/kg; bismuth, 9.35 mg/kg; molybdenum, 44.5 mg/kg; silver, 27.8 mg/kg; and tin, 36 mg/kg. The only samples that contained copper in concentrations within the reported range for eastern United States soils of less than 1 to 700 mg/kg (Shacklette and Boerngen, 1984) were the background samples 04Smith6 and 04Smith7 and sample 04Smith5 from the soil downslope from the Smith mine. Seven of the eight composite mine-waste samples collected from the Eureka and Union mines area contained concentrations of copper that were greater than the PRG for residential soils; the composite samples from the Smith mine did not exceed the PRG for residential soils (table 6; fig. 12). Generally, the samples that contained the highest concentrations of copper were those that had detectable chalcopyrite. The concentrations of copper in mine-waste samples from the Pike Hill mines site generally fall within the range of concentrations in mine waste from the Elizabeth and Ely mines (fig. 12).

Zinc was generally the next most abundant trace metal in these samples, although concentrations of zinc did not exceed the residential PRG of 23,000 mg/kg (table 6; fig. 13). The concentrations of zinc in most mine-waste composite samples were significantly greater than the reported mean concentration of 40 mg/kg for soils in the eastern United States (Shacklette and Boerngen, 1984). The highest concentration of zinc, 16,000 mg/kg, was found in sample 04PKHL10 from the processed flotation-mill tailings; that sample also contained approximately 1 weight percent sphalerite. This concentration of zinc was significantly higher than those in mine-waste samples collected from the Elizabeth and Ely mines as reported by

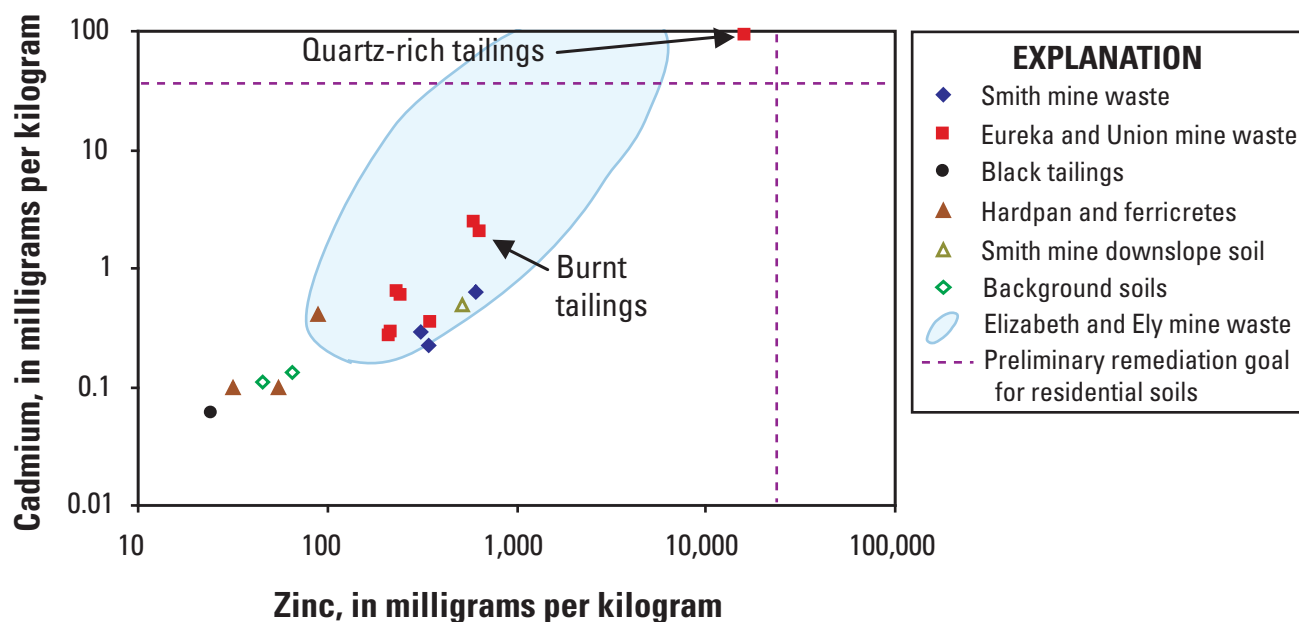


Figure 13. Concentrations of cadmium and zinc in mine-waste and soil samples collected from the Pike Hill mines study area. [Data for the composition of mine waste, including waste rock and unoxidized tailings from the Elizabeth and Ely mines, from Hammarstrom and others (2001, 2003) and Piatak and others (2004). Preliminary remediation goals for residential soils from U.S. Environmental Protection Agency (2004b)].

Piatak and others (2004) and Hammarstrom and others (2001, 2003) (fig. 13). Sample 04PKHL10 also contained the highest concentrations of arsenic, 57 mg/kg; calcium, 3.4 weight percent; cadmium, 91.8 mg/kg; and cobalt, 122 mg/kg. This concentration of cadmium exceeded the residential PRG of 37 mg/kg. The next highest concentrations of cadmium were 2.5 and 2 mg/kg in samples 04PKHL7 and 04PKHL9, respectively. Sample 04PKHL11-A from the dark gray tailings contained the lowest concentrations of cadmium and zinc, which were below the concentrations of these elements in the background soils (fig. 13). This material also contained concentrations of iron, molybdenum, and selenium that were less than or equivalent to background levels. In general, the concentrations of cadmium and zinc in composite mine-waste samples were within the range for these elements reported for the other mine sites in the Vermont copper belt (fig. 13). Note the positive correlation between zinc and cadmium (fig. 13); these elements are found together because cadmium substitutes for zinc in the structure of sphalerite, which is the dominant primary zinc-bearing mineral found at the site.

The concentrations of cobalt in both sample 04PKHL10 from the processed tailings and sample 04PKHL9 from the partly burnt waste material exceeded the reported upper range for cobalt in eastern United States soils (Shacklette and Boerngen, 1984). In addition, the concentrations of cobalt in all of the samples, except for sample 04Smith4 from the hardpan from the Smith mine, sample 04PKHL11-A from the dark gray tailings, and sample 04PKHL13-B from ferricrete, were greater than the mean value for cobalt in soil of the eastern

United States (Shacklette and Boerngen, 1984). One-half of the mine-waste samples contained chromium in concentrations greater than the mean for eastern United States soils; sample 04Smith1, from the uppermost mine dump at the Smith mine, contained the highest concentration of chromium, 85.1 mg/kg. Eight of the eleven composite mine-waste samples from the site contained molybdenum in concentrations greater than the range reported for eastern United States soils (Shacklette and Boerngen, 1984). The highest concentrations of nickel were found in the background-soil samples 04Smith6 and 04Smith7 and in sample 04Smith5, from soil downslope of the Smith mine; concentrations of nickel ranged from 23 to 27 mg/kg. The composite mine-waste samples contained concentrations of lead that ranged from 69.9 to 238 mg/kg, which were greater than the mean but within the reported range for lead in eastern United States soils (Shacklette and Boerngen, 1984). The other samples that were analyzed contained significantly less lead. Approximately one-half of the composite mine-waste samples and one sample of ferricrete contained concentrations of vanadium that were greater than the 78 mg/kg PRG for residential soils, but concentrations of vanadium in all of the samples were less than the reported upper range limit of 300 mg/kg for soils in the eastern United States (Shacklette and Boerngen, 1984).

The concentrations of selenium ranged from 0.3 and 0.4 mg/kg in the background-soil samples to 124.2 mg/kg in sample 04PKHL9 from the partially burnt flotation-mill tailings (table 6; fig. 14). The concentrations of selenium correlate with the concentrations of sulfur because of the substitution of

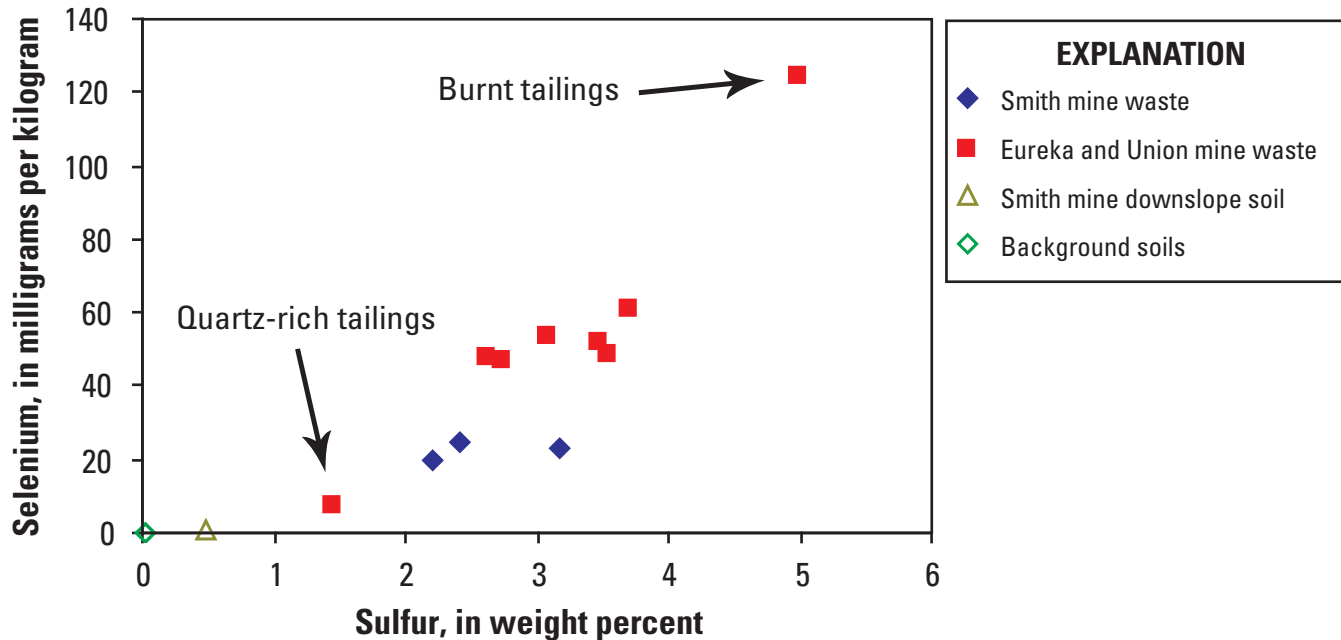


Figure 14. Concentrations of selenium and sulfur in mine-waste and soil samples collected from the Pike Hill mines study area. (Concentrations of selenium for the downslope Smith soil in sample 04Smith4, the dark gray tailings in sample 04PKHL11-A, and ferricretes in samples 04PKHL12 and 04PKHL13-B are not shown because the samples were not analyzed for sulfur.)

selenium for sulfur in sulfide and sulfate minerals (fig. 14). All of the samples except those from the background soils, sample 04Smith5 of the downslope soil at the Smith mine, and sample 04Smith4 from the hardpan contained elevated concentrations of selenium compared to the reported range of less than 0.1 to 3.9 mg/kg for soils in the eastern United States (Shacklette and Boerngen, 1984). Samples 04PKHL12 and 04PKHL13-B from the ferricretes, sample 04PKHL10 from the quartz-rich flotation-mill tailings, and sample 04PKHL11-A from the dark gray tailings contained concentrations of selenium that ranged from 7.1 to 11.2 weight percent, which was generally less than concentrations of selenium in the remaining composite mine-waste samples. Composite samples from the Smith mine averaged 22 mg/kg selenium whereas samples from the Eureka and Union mines ranged from 47 to 124.2 mg/kg selenium (fig. 14). The anomalous concentration of selenium in sample 04PKHL9 from the partially burnt flotation-mill tailings was consistent with anomalously high concentrations of selenium in samples from partially roasted waste rock at the Elizabeth Mine (Hammarstrom and others, 1999). This sample also contained the highest amount of sulfur.

Acid-Base Accounting

Paste pH and acid-base accounting results (table 7; fig. 15) indicate that the soils in only a few samples are not net acid generating. The paste pH and NNP of the background soils in samples 04Smith6 and 04Smith7 were above 4 and positive, respectively; these samples fall within the non-acid

generating field (fig. 15). The only other sample in this category was sample 04PKHL10 from the processed flotation-mill tailings; it had a neutral paste pH and NNP of 47.5 kilograms CaCO_3 per ton ($\text{kg CaCO}_3/\text{t}$). That sample contained the highest concentrations of several metals, including cadmium and zinc, which likely were from sphalerite, but it also contained significant carbonate, which was estimated to be 2.4 weight percent calcite. For that sample only, the acid-neutralizing capacity from calcite was greater than the acid-generating potential from sulfides and sulfates.

Other mine-waste samples had paste-pH values of less than 4 and negative NNP, which suggests that they would produce acid upon weathering. The composite mine-waste samples from the Smith mine had a paste pH of approximately 3 and NNP values ranging from -21.7 to $-33.6 \text{ kg CaCO}_3/\text{t}$ (fig. 15; table 7). Sample 04Smith5 from the downslope soil at this mine had a paste pH of 2.8 and slightly negative NNP of $-2.6 \text{ kg CaCO}_3/\text{t}$. The lowest paste pH of 2.3 and most negative NNP of $-112.8 \text{ kg CaCO}_3/\text{t}$ in figure 15 were from soils from the partially burnt flotation-mill tailings. The remaining composite samples from the Eureka and Union mines were potentially acid generating and had paste-pH values of less than 4 and NNP that ranged from -33.3 to $-57.1 \text{ kg CaCO}_3/\text{t}$. The paste pH of ferricrete samples 04PKHL12 and 04PKHL13-B, which were not analyzed by ABA, was less than 4; this suggests that the ferricretes may be acid generating (table 7).

The range in paste pH and NNP values may result from the complex mixture of minerals in the mine-waste samples.

Table 7. Paste pH and acid-base accounting results for mine-waste and soil samples from the Pike Hill mines study area.[wt. %, weight percent; kg CaCO₃/t, kilograms CaCO₃ per ton; n.a., not analyzed; <, less than; italic numbers in parentheses are replicates]

Sample	Paste pH (USGS) ¹	Paste pH (Vizon) ¹	Total sulfur (wt.%)	Sulfate sulfur (wt.%)	Sulfide sulfur (wt.%)	Maximum Potential Acidity (AP) (kg CaCO ₃ /t)	Neutralization Potential (NP) (kg CaCO ₃ /t)	Net-Neutralization Potential (NNP) ² (kg CaCO ₃ /t)	Fizz
04Smith1	3.1	3.1	2.20	1.65	0.55	17.2	-4.5	-21.7	None
04Smith2	2.8	3.1	3.17	2.31	0.86	26.9	-6.7 (-7.0)	-33.6	None
04Smith3	2.7	2.7	2.41	1.87	0.54	16.9	-9.0	-25.9	None
04Smith 5	2.8	3.1	0.48	0.42	0.06	1.9	-0.7	-2.6	None
04Smith6	5.7	6.1	0.02	0.02	<0.01	<0.3	7.2	7.2	None
04Smith7	5.4	5.7	0.03 (0.03)	0.02 (0.02)	0.01	0.3	-0.2	-0.5	None
04PKHL1	2.7	2.6	3.55	2.4 (2.10)	1.15	35.9	-7.5	-43.4	None
04PKHL2	2.7	2.9	2.74	1.93	0.81	25.3	-8.0	-33.3	None
04PKHL3	2.8	2.9	2.63	1.82	0.81	25.3	-8.7	-34.0	None
04PKHL7	3.1	4.1	3.48	1.77	1.71	53.4	-3.7	-57.1	None
04PKHL9	2.3	2.3	4.99	1.70	3.29	102.8	-10.0	-112.8	None
04PKHL10	7.0	7.5	1.44	0.09	1.35	42.2	90 (88.8)	47.5	Moderate
04PKHL11	2.5	2.4	3.70	2.42	1.28	40.0	-5.0	-45.0	None
04PKHL12	2.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
04PKHL13	2.7	2.7	3.07 (3.10)	2.01	1.06	33.1	-5.5	-38.6	None
04PKHL13-B	2.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

¹Paste pH determined by the U.S. Geological Survey and Vizon SciTec, Inc.²The net-neutralization potential is equal to the value of the neutralization potential minus the value of the maximum potential acidity.

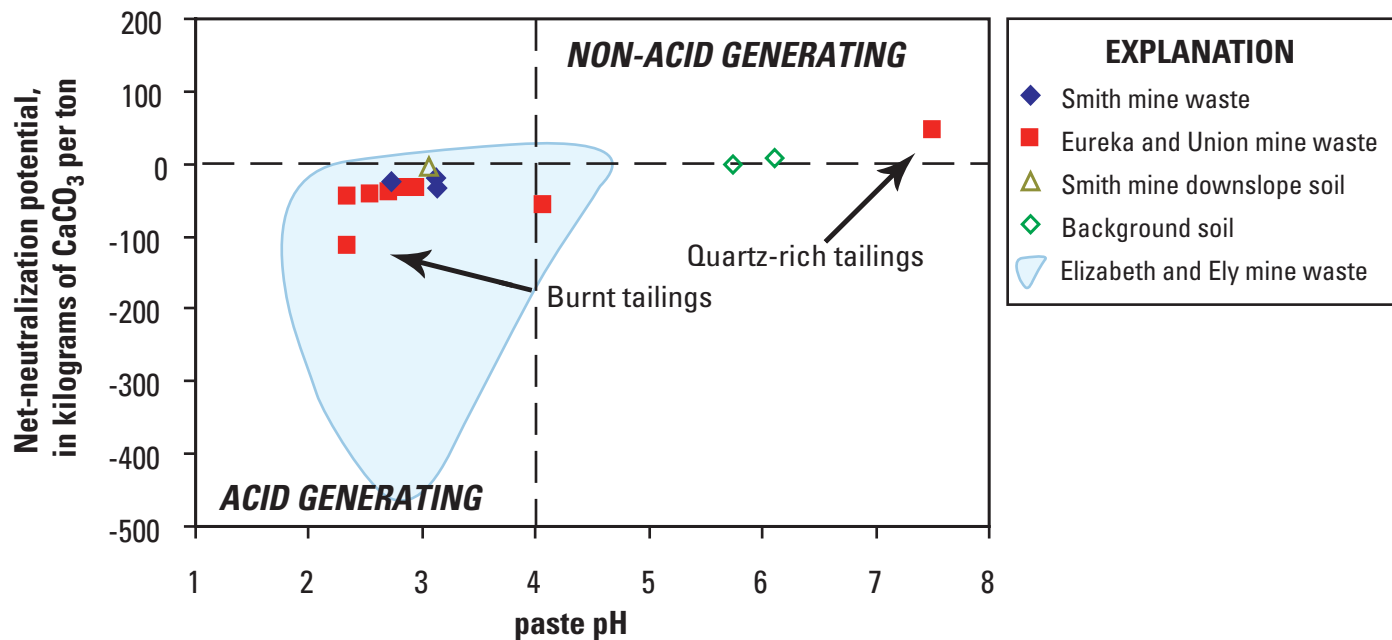


Figure 15. Acid-base accounting results for mine-waste and soil samples from the Pike Hill mines study area compared with samples from the historic mine-waste piles at the Elizabeth mine and mine waste from the Ely mine. [Data for the Elizabeth and Ely mines are from Hammarstrom and others (2003) and Piatak and others (2004). Mine-waste samples from the Elizabeth Mine do not include samples containing the underlying carbonate-rich till unit, which would increase net neutralizing potential and paste pH.]

Sulfur-bearing minerals were the dominant acid generators, and carbonate and silicate minerals were the dominant acid neutralizers in these samples. In most of the samples from the Pike Hill mines site, sulfur had been oxidized to sulfate, and, thus, sulfate sulfur was significantly greater than sulfide sulfur (table 7); samples 04PKHL7, 04PKHL9, and 04PKHL10 were the exceptions.

The values for paste pH and NNP for most mine-waste samples from the Pike Hill mines fall within the range for paste pH and NNP for mine waste from the Elizabeth and Ely mines (fig. 15). Subeconomic mineralized and waste rocks at the Elizabeth Mine overlie a carbonate-rich till, which increases the paste pH and NNP for samples that contained this material. Samples of this till or waste rock mixed with till were not included in figure 15. The lowest NNP of approximately -420 kg CaCO₃/t for samples from these mines was for unoxidized pyrrhotite-rich black tailings from the Ely Copper Mine (Piatak and others, 2004). Acid generation in samples from the Pike Hill area did not reach this extreme.

Leachate Chemistry

The results of the tests for the chemistry of leachates from the samples were compared with water-quality guidelines for the protection of aquatic life (U.S. Environmental Protection Agency, 2006) and drinking-water and groundwater standards (U.S. Environmental Protection Agency, 2003; Vermont Department of Environmental Conservation, 2005). The concentrations of elements or compounds that exceeded

water-quality guidelines are shown in bold type in table 8. The concentrations of all of the elements that were analyzed are shown in appendix 2, and reference waters that were analyzed with the leachates are shown in appendix 3. Water-quality guidelines for cadmium, copper, nickel, lead, and zinc are hardness dependent and were calculated based on a hardness of 100 mg/L as CaCO₃. This was a realistic approximation because the hardness of waters receiving drainage from the mines ranged from 85 to 110 mg/L as CaCO₃.

The major anion in all of the samples was SO₄, whereas Al, Ca, Cu, Fe, K, Mg, and Si dominated the cations; some samples contained significant quantities of Mn and Zn. The elements and compounds that exceeded various water-quality guidelines were Al, Cd, Cu, Fe, Mn, Se, SO₄, and Zn (table 8). Copper was generally the most abundant trace metal in the leachates. The only samples that had concentrations of leached copper that were less than the acute toxicity standard of 13 µg/L were from the background soils and sample 04PKHL10 from the quartz-rich flotation-mill tailings; the concentrations of all of the other leachates exceeded this criterion (fig. 16). The concentration of copper in composite sample 04PKHL10 was the third highest based on bulk chemistry (table 6), but leachate testing suggests that copper is not readily leached. In contrast, the highest concentration of copper in the leachates, 17,000 µg/L, was from sample 04PKHL9 from the partially burnt flotation tailings, and that sample also contained the highest concentration of copper of 9,200 mg/kg that was reported for the solid samples. The amount of copper in a sample did not consistently correlate with the amount

Table 8. Select analytical results of leachate tests on mine-waste and soil samples from the Pike Hill mines study area.

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligrams per liter; mV , millivolts; $\mu\text{g}/\text{L}$, micrograms per liter; n.d., not determined; <, less than; values in bold exceed water-quality guidelines]

Characteristic/ element	pH	Specific conductance $\mu\text{S}/\text{cm}$	Dissolved oxygen mg/L	Oxidation- reduction potential mV	Fe ²⁺ /Fe _{total}		Al	Cd	Co	Cu	Fe	Mn	Ni	Pb	Se	SO ₄	V	Zn				
					Hach	AES													$\mu\text{g}/\text{L}$	AES	$\mu\text{g}/\text{L}$	MS
Aquatic toxicity ²	-	-	-	-	-	-	750	2.0	-	13	1,000	-	470	65	4.6	-	-	120				
Drinking water ³	-	-	-	-	-	-	50-200	5	-	1,300	300	840	100	15	50	250	-	5,000				
							Guidelines															
							Mine waste leachate															
04Smith1	3.6	225	8	509	0.8	2,010	3.44	41.9	754	467	900	10.2	0.1	<1	110	<0.5	710					
04Smith2	3.4	244	8	497	0.7	126	2.03	64.2	698	207	221	15.2	<0.05	<1	117	<0.5	205					
04Smith3	3.2	304	7	444	0.3	79.9	0.39	4.64	534	98.7	66.4	1.5	0.4	<1	167	<0.5	77.9					
04Smith5	3.3	295	8	411	n.d.	577	1.19	20.2	479	75	898	9.3	0.5	<1	142	<0.5	380					
04Smith6	5.9	17.6	8	283	n.d.	<50	<0.02	0.07	<0.5	<20	42.5	<0.4	<0.05	<1	4	<0.5	0.6					
04Smith7	5.9	13.3	8	277	n.d.	<50	<0.02	0.09	<0.5	<20	28.6	<0.4	<0.05	<1	3.5	<0.5	0.7					
04PKHL1	3.1	577	8	390	0.7	630	1.23	7.89	1,280	252	66.1	0.8	1	2.6	350	<0.5	146					
04PKHL2	3.2	314	8	373	0.8	92.4	0.66	11.1	695	128	33	1.4	<0.05	1.5	175	<0.5	82.6					
04PKHL3	3.2	315	8	581	0.8	62.8	0.66	3.53	844	76.8	24.8	0.7	0.2	1	160	<0.5	86.5					
04PKHL7	3.7	260	8	571	0.7	125	22.1	81	2,270	63	1,020	23.9	2.2	2	142	<0.5	3,340					
04PKHL9	2.9	967	8	564	0.1	8,090	10.2	1,020	17,000	3,130	251	44	0.72	9.1	690	<0.5	955					
04PKHL10	7.1	206	6	374	n.d.	<50	23	1.06	6.2	<20	38.5	<0.4	<0.05	<1	91	<0.5	700					
04PKHL11	3.1	934	8	470	0.5	1,520	3.5	53.7	2,240	308	95.7	3.6	1.2	5.8	718	<0.5	318					
04PKHL12	2.9	583	8	537	0.4	339	0.6	30.8	53.3	3,090	42.2	5.8	1.8	<1	261	<0.5	79.9					
04PKHL13	3.3	525	8	567	0.6	497	2.41	6.45	999	83.2	52.6	0.5	0.87	2.2	329	<0.5	110					
04PKHL13-B	2.8	737	8	537	0.3	461	2.53	46.9	262	5,020	56.5	7.5	0.76	<1	312	<0.5	263					

¹Hach, colorimetric method using Hach spectrophotometer; MS, inductively coupled plasma-mass spectrometry; AES, inductively coupled plasma-atomic emission spectrometry; IC, ion chromatography.

²Toxicity standards are for freshwater Criteria Maximum Concentrations (acute), except iron and selenium for Criterion Continuous Concentration (chronic exposure). Values from U.S. Environmental Protection Agency (2006). Calculated for a hardness of 100 mg/L for hardness-dependent criteria. Standard for aluminum based on total metals, not dissolved and for pH 6.5 to 9.0 only.

³National Primary Drinking Water Standards are given for cadmium, copper, lead, and selenium, whereas National Secondary Drinking Water Standards are given for aluminum, iron, sulfate, and zinc (U.S. Environmental Protection Agency, 2003). Vermont Primary Groundwater Quality Standards are given for manganese and nickel (Vermont Department of Environmental Conservation, 2005).

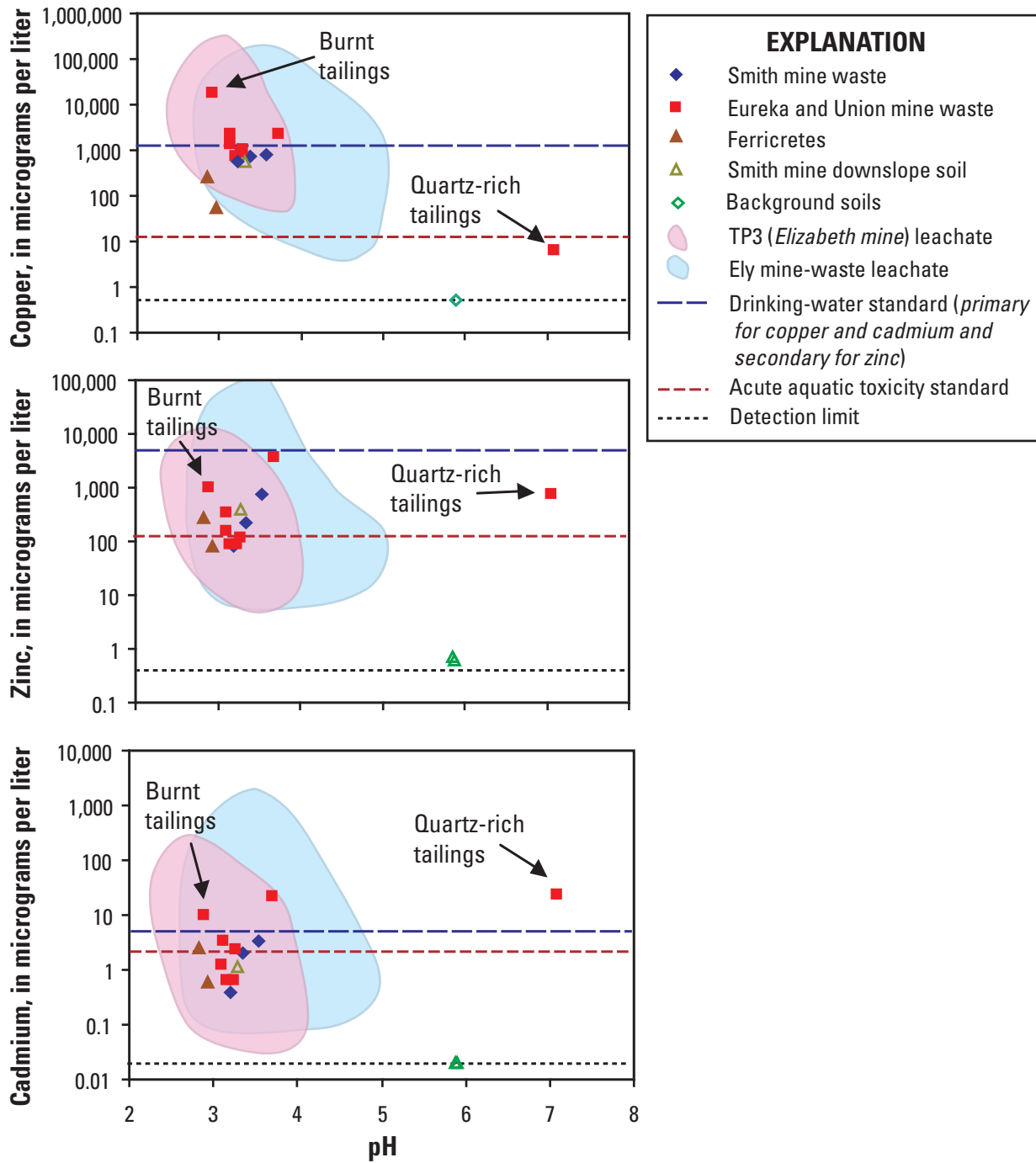


Figure 16. Concentrations of dissolved metal in leachate as a function of pH for samples from the Pike Hill mines study area compared with leachate from the historic mine-waste piles at the Elizabeth mine and mine waste from the Ely mine. [Drinking-water standards are from U.S. Environmental Protection Agency (2003). Aquatic toxicity values are based on a hardness of 100 mg/L as calcium carbonate (U.S. Environmental Protection Agency, 2006). Data for the Elizabeth and Ely mines are from Hammarstrom and others (2003) and Piatak and others (2004).]

of copper leached from the sample; this was likely due to mineralogical variations among samples. Leachates from sample 04PKHL9 as well as 2,270 $\mu\text{g/L}$ copper from sample 04PKHL7 and 2,240 $\mu\text{g/L}$ copper from sample 04PKHL11 exceeded the drinking-water standard of 1,300 $\mu\text{g/L}$ copper; leachates from the samples of ferricrete contained less copper than that of composite mine-waste samples (fig. 16).

The next most abundant trace element in the leachates was zinc. The concentrations of zinc in leachates from the background soils were significantly less than those from mine waste (fig. 16). The concentrations of zinc in leachate from four composite mine-waste samples and one sample from ferricrete did not exceed the acute aquatic toxicity standard (fig. 16). These samples did not necessarily have the lowest concentrations of zinc based on the bulk chemistry. For example, sample 04Smith3 contained 344 mg/kg zinc (table 6); however, the concentration of zinc in leachate of 77.9 $\mu\text{g/L}$ was well below the acute aquatic toxicity standard. In contrast, sample 04Smith2 contained comparable zinc of 315 mg/kg, but the leachate contained 205 $\mu\text{g/L}$ zinc and exceeded the standard. In addition, sample 04PKHL10 from the quartz-rich flotation-mill tailings contained anomalous zinc of 16,000 mg/kg, and the leachate contained only 700 $\mu\text{g/L}$ zinc. The lack of consistent correlations between bulk and leachate chemistry suggests that other factors, such as mineralogy, affected the leachability of metals in the samples from the Pike Hill mines site. For example, zinc in sphalerite was less likely to leach than zinc in highly soluble efflorescent sulfate salts.

Other constituents of concern in the leachates included aluminum, cadmium, iron, manganese, and sulfate. The concentrations of cadmium in leachates from seven composite mine-waste samples and one ferricrete sample exceeded the acute toxicity standard for aquatic life (fig. 16). The three highest concentrations also exceeded the drinking-water standard. The concentration of iron in the leachates reached 5,020 $\mu\text{g/L}$, and the highest values were from samples that were collected from the ferricretes and the partially burnt tailings. For those samples, the concentrations of iron in the leachate exceeded the chronic toxicity standard for aquatic life. The concentrations of manganese in the leachates from a few mine-waste samples exceeded the Vermont Groundwater Quality Standard of 840 $\mu\text{g/L}$. For selenium, the two waste piles that contained the highest concentrations based on bulk chemistry (table 6) also had concentrations in leachate that exceeded the acute toxicity standard. Four waste pile samples and two ferricrete samples from the Eureka and Union mines area had concentrations of leached sulfate that exceeded the secondary drinking-water standard of 250 mg/L.

The pH of leachate from all of the mine-waste samples except for the quartz-rich processed flotation-mill tailings, which contained calcite, was less than 4.2, which was the pH of the ESP solution. This decrease in leachate pH indicates that precipitation interacting with most of the mine waste at the site will produce acidic runoff.

The same leachate-testing procedures that were used for this study were performed on samples of mine waste from the

Elizabeth Mine and the Ely Copper Mine that were collected during similar studies (Hammarstrom and others, 2003; Piatak and others, 2004). Concentrations of cadmium, copper, and zinc in leachate from most of the samples from the Pike Hill study area were within the compositional range of leachate from the Elizabeth and Ely mines (fig. 16). The pH of the leachate from sample 04PKHL10 from the quartz-rich flotation-mill tailings was higher than that of leachates from the other mines sites; the concentration of copper was low; the concentrations of zinc and cadmium were within the ranges of the other leachates (fig. 16). In general, runoff from the Pike Hill mines site is expected to be similar in composition to that from the historic waste piles at the Elizabeth and Ely mines based on the results of leaching experiments. The pH of the runoff at the Pike Hill mines site may be higher because of the higher percentage of carbonate in the host rock compared to that of the Elizabeth and Ely mines.

Mine Drainage and Regional Surface Waters

Surface-mine drainage, mine pools, seeps, downstream waters, and background samples indicate that water quality varies throughout the study area. Reference waters, blanks, and replicates were used for quality assurance and quality control purposes (appendix 3). For the following section, plots show samples categorized according to water type, general location (table 3), and collection date (appendix 4). Kiah and others (2007) reported that the August 2005 samples were collected during low flow conditions relative to annual variations. A summary of the dissolved concentrations of selected elements in the water samples is given in table 9. Dissolved and total concentrations for the full set of elements analyzed and water-quality characteristics are given in appendix 4.

Background Waters

The geochemistry of the background samples collected from river and stream sites CKBK-3, PKHL-11, PKHL-15, and PKHL-17 near the Pike Hill mines is probably a result of the geochemistry of the rocks that underlie the watershed. Pike Hill Brook and the unnamed tributary to Cookville Brook drain the mines site and flow into the Waits River (fig. 2). Both brooks originate in the calcareous Waits River Formation, and the Waits River predominately flows over this unit. Because of this, the pH, alkalinity, and hardness of the background water samples were high. The pH ranged from 6.8 to 8.6, alkalinity ranged from 85 to 138 mg/L as CaCO_3 , and hardness ranged from 96 to 161 mg/L as CaCO_3 (appendix 4). Characteristics such as alkalinity and hardness affect the response of water bodies to the deleterious effects of mine drainage and the toxicity of metals to aquatic organisms. In general, hardness and alkalinity mitigate metal toxicity to aquatic life. In addition, the concentrations of dissolved Al, Fe, and SO_4 of less than 50 $\mu\text{g/L}$ and total base metals (Cu + Zn + Cd + Ni + Co + Pb) of less than 5 $\mu\text{g/L}$ were low in background waters (figs. 17, 18, and 19).

Table 9. Dissolved concentrations of select elements in water samples from the Pike Hill mines study area. [mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; D, field replicate sample; FA, filtered acidified split; FA, inductively coupled plasma-mass spectrometry; AES, inductively coupled plasma-atomic emission spectrometry; concentrations in bold exceed water-quality guidelines]

Characteristic/Element	pH	Al µg/L AES	Cd µg/L MS	Co µg/L MS	Cu µg/L MS	Fe µg/L AES	Mn µg/L MS	Ni µg/L MS	Pb µg/L MS	Se µg/L MS	SO ₄ mg/L IC	Zn µg/L MS
Aquatic toxicity ¹		750	2.0	-	13	1,000	-	470	65	4.6	-	120
Drinking water ²		50-200	5	-	1,300	300	840	100	15	50	250	5,000
Guidelines												
Water samples—October 2004												
Sample number	Site number											
CKBK-1-2 FA	CKBK-1	12	0.11	0.21	5.2	<20	12.5	0.8	<0.05	2.2	14.7	16
CKBK-2-2 FA	CKBK-2	18,200	16.2	186	5,030	<20	1,870	61.8	0.1	<1	260	3,030
CKBK-3-2 FA	CKBK-3	<10	<0.02	0.03	<0.5	<20	4.3	<0.4	<0.05	<1	11.7	1.3
CKBK-4-2 FA	CKBK-4	75	<0.02	0.64	3	13,200	871	0.5	<0.05	2.4	1.7	3.5
CKBK-5-2 FA	CKBK-5	5,700	4.36	97.3	992	6,390	1,320	25.9	0.67	1.2	233	1,550
PKHL-1-2 FA	PKHL-1	39,700	10.5	218	1,980	99,300	6,980	38.3	3.4	2	1,200	6,240
PKHL-2-2 FA	PKHL-2	11,400	11.7	226	2,910	23,200	1,400	31.1	2.2	<1	394	2,890
PKHL-4-2 FA	PKHL-4	1,170	6.95	95.2	4,950	20	629	22.6	0.1	<1	231	684
PKHL-5-2 FA	PKHL-5	18	4.15	55.9	1,800	<20	383	15.9	<0.05	1.2	190	418
PKHL-6-2 FA	PKHL-6	11	0.8	1.22	44.1	<20	42.4	2	<0.05	2.9	100	81.6
PKHL-7-2 FA	PKHL-7	8,060	3.08	135	107	53,800	1,080	16.8	0.4	<1	396	2,080
PKHL-8-2 FA	PKHL-8	10,600	5.73	181	205	38,500	1,170	23.2	0.82	<1	407	2,530
PKHL-9-2 FA	PKHL-9	11,100	22.2	190	6,470	1,480	1,360	35	1.5	1.3	333	3,080
PKHL-10-2 FA	PKHL-10	8,420	9.61	170	2,400	9,590	958	23	1.9	<1	298	2,100
PKHL-10-2 D FA	PKHL-10	8,310	9.48	172	2,250	9,270	953	22.9	1.9	<1	295	2,060
PKHL-11-2 FA	PKHL-11	43	<0.02	0.07	1	43	21.6	0.4	0.06	<1	8.7	<0.5
PKHL-12-2 FA	PKHL-12	<10	0.76	10.6	13.7	31	118	2.5	<0.05	1.4	50.7	128
PKHL-13-2 FA	PKHL-13	<10	0.14	1.08	9.7	233	67.6	0.6	<0.05	2.8	16.8	19.4
PKHL-14-2 FA	PKHL-14	<10	0.11	1.04	7	311	120	0.5	<0.05	2.1	15	13.4
PKHL-15-2 FA	PKHL-15	<10	<0.02	0.03	<0.5	28	4.8	<0.4	<0.05	2	7.5	<0.5

Table 9. Dissolved concentrations of select elements in water samples from the Pike Hill mines study area.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; D, field replicate sample; FA, filtered acidified split; MS, inductively coupled plasma-mass spectrometry; AES, inductively coupled plasma-atomic emission spectrometry; concentrations in bold exceed water-quality guidelines]

Characteristic/Element	pH	Al	Cd	Co	Cu	Fe	Mn	Ni	Pb	Se	SO ₄	Zn
Units												
Methods		AES	MS	MS	MS	AES	MS	MS	MS	MS	IC	MS
Water samples—August 2005												
Sample number	Site number											
01139940Aug FA	01139940	11	0.1	0.12	3.6	<20	20.6	1.4	<0.05	<1	11.6	13.2
CKBK-2-3 FA	CKBK-2	<10	3.61	39	608	<20	411	17.8	<0.05	<1	88	772
CKBK-3-3 FA	CKBK-3	<10	<0.02	0.06	<0.5	26	20	0.8	<0.05	<1	7.5	1
CKBK-4-3 FA	CKBK-4	37	<0.02	4.93	1.2	8,970	699	1.7	0.08	<1	3.8	6.1
CKBK-5-3 FA	CKBK-5	2,330	2.25	49	597	750	849	15.4	0.3	1.1	180	945
PKHL-1-3 FA	PKHL-1	36,100	12	240	2,310	68,200	6,350	43.3	4.2	2.7	1,142	7,360
PKHL-2-3 FA	PKHL-2	9,200	9.3	233	1,980	23,300	1,230	30.5	2.8	1.9	418	2,940
PKHL-4-3 FA	PKHL-4	670	6.51	88.2	4,870	34	616	24.3	0.2	<1	200	712
PKHL-5-3 FA	PKHL-5	<10	2.93	39.3	1,120	<20	273	12.7	<0.05	1.2	128	314
PKHL-6-3 FA	PKHL-6	<10	0.95	0.48	64.2	<20	28.9	3	<0.05	1.2	90	96.1
PKHL-7-3 FA	PKHL-7	6,250	3.3	191	2.9	32,400	977	23.2	0.3	<1	598	2,030
PKHL-9-3 FA	PKHL-9	6,920	22.9	188	6,790	717	1,320	34.3	1.7	1.6	373	3,570
01139830Aug FA	PKHL-10	6,620	8.11	186	1,940	10,600	888	24.4	2.7	2	342	2,230
01139830Aug D FA	PKHL-10	6,340	8.01	187	1,990	10,200	903	25	2.7	1.4	351	2,290
011398302Aug FA	PKHL-11	<10	<0.02	0.03	1.5	<20	3.1	0.9	<0.05	<1	8.3	1.8
01139832Aug FA	01139832	<10	1.61	21.6	26	<20	233	5.2	<0.05	<1	95	247
01139833Aug FA	PKHL-12	<10	0.83	5.26	15.5	59	94	2.8	<0.05	<1	50	99.9
01139838Aug FA	PKHL-13	<10	0.13	0.89	8.2	130	98.2	1.2	<0.05	<1	8	8.8
01139839Aug FA	PKHL-14	<10	0.14	0.94	7.2	163	240	1.2	<0.05	<1	5.7	10.1
01139826Aug FA	PKHL-15	<10	<0.02	0.03	0.5	<20	4	0.8	<0.05	<1	6.7	3
01139840Aug FA	01139840	<10	0.04	0.05	5.8	52	0.7	1.1	<0.05	<1	6.7	4.6
01139841Aug FA	01139841	<10	<0.02	0.03	0.97	<20	7.1	0.9	<0.05	<1	7	1
PKHL-16-3 FA	PKHL-16	<10	2.6	44.8	43.9	<20	410	8.3	<0.05	<1	125	451
PKHL-17-3 FA	PKHL-17	<10	<0.02	0.03	<0.5	<20	16	1.3	<0.05	<1	11	1.9

¹Toxicity standards are for freshwater Criteria Maximum Concentrations (acute), except iron and selenium for Criterion Continuous Concentration (chronic exposure). Values from U.S. Environmental Protection Agency (2006). Calculated on a hardness of 100 mg/L for hardness-dependent criteria. Standard for aluminum based on total metals, not dissolved and for pH 6.5 to 9.0 only.

²National Primary Drinking Water Standards are given for cadmium, copper, lead, and selenium, whereas National Secondary Drinking Water Standards are given for aluminum, iron, sulfate, and zinc (U.S. Environmental Protection Agency, 2003). Vermont Primary Groundwater Quality Standards are given for manganese and nickel (Vermont Department of Environmental Conservation, 2005).

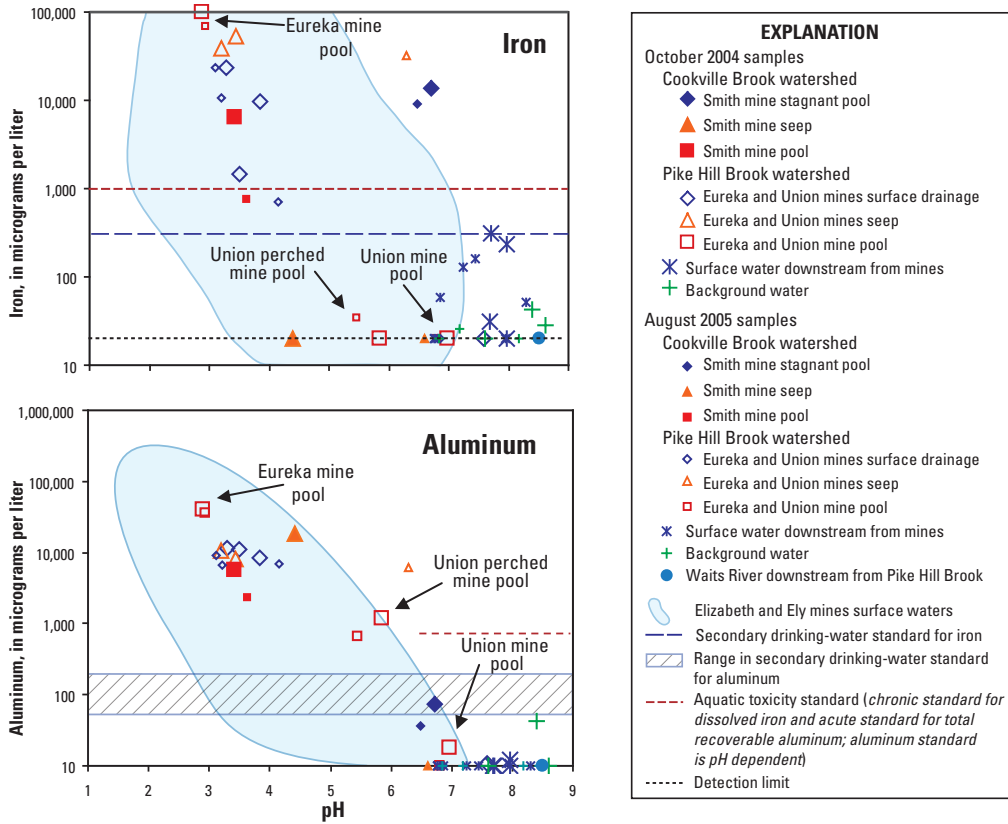


Figure 17. Dissolved concentrations of iron and aluminum and pH for waters from the Pike Hill mines study area compared with surface waters from the Elizabeth and Ely mines. [Surface-water-composition data for the Elizabeth and Ely mines are from Seal and others (2001).]

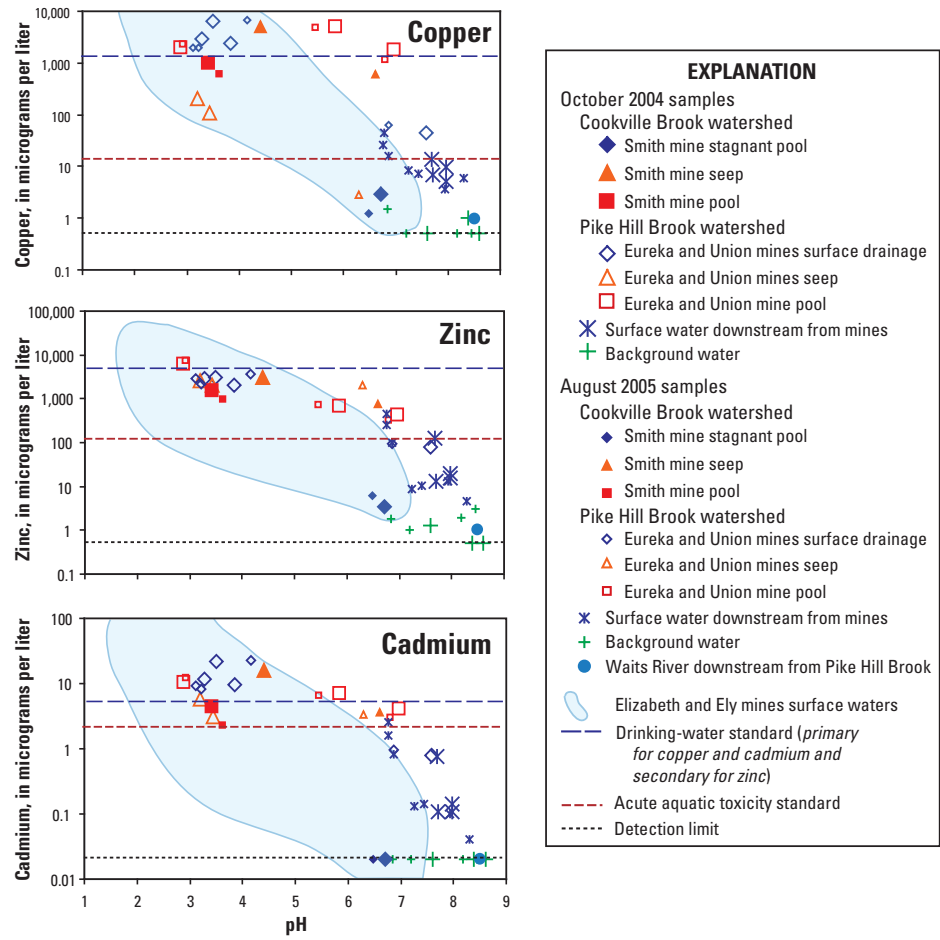


Figure 18. Dissolved concentrations of copper, zinc, and cadmium and pH for waters from the Pike Hill mines study area compared with surface waters from the Elizabeth and Ely mines. [Surface-water-composition data for the Elizabeth and Ely mines are from Seal and others (2001).]

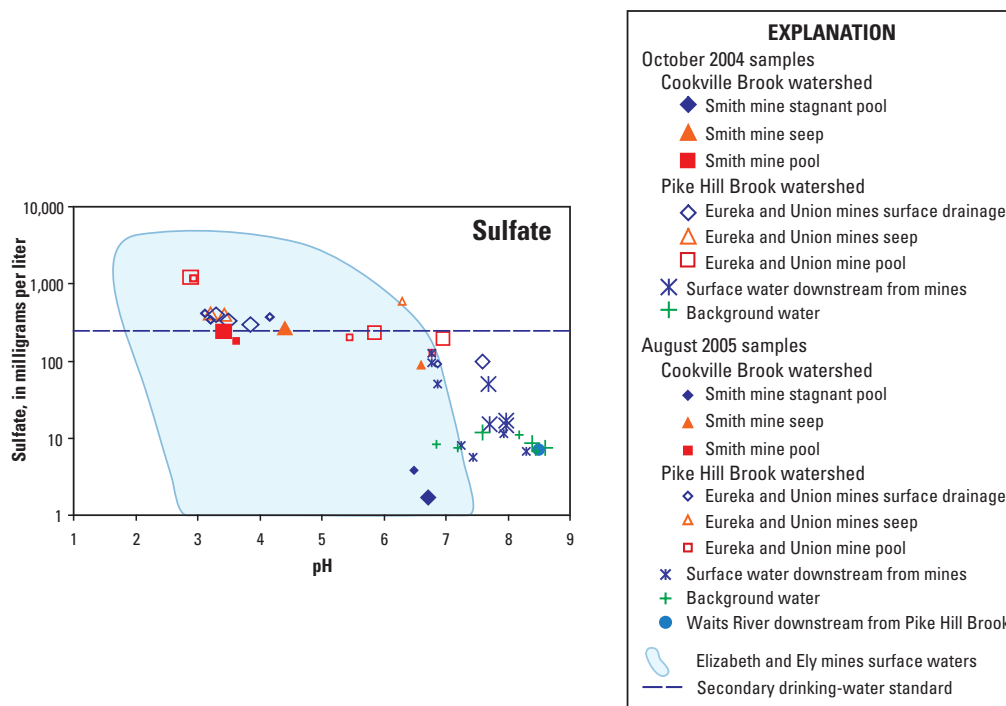


Figure 19. Dissolved concentrations of sulfate and pH for waters from the Pike Hill mines study area compared with surface waters from the Elizabeth and Ely mines. [Surface water composition data for the Elizabeth and Ely mines are from Seal and others (2001).]

Seeps and Mine Pools

Water in the seeps and mine pools found at the site varied from low pH to high pH; from oxic to anoxic, based on dissolved oxygen; from oxidizing to reducing, based on iron speciation; and generally contained concentrations of metals that exceeded water-quality guidelines (figs. 17, 18, 19, and 20). The Pike Hill seeps PKHL-7 and PKHL-8 were anoxic, reducing environments that had low pH during October 2004 and near neutral pH during August 2005 (fig. 20). The concentrations of Al, Cd, Cu, Fe, SO_4 , and Zn in water from seeps and mine pools exceeded aquatic toxicity standards or drinking-water standards, or both (figs. 17, 18, and 19). The exception was the concentration of copper in sample PKHL-7-3 that was below these standards. The pH and the concentration of sulfate were higher, whereas the concentrations of aluminum, copper, and iron were lower in the water collected from this seep during the drier August 2005 sampling compared with the October 2004 sampling. The pH was also higher in the Smith mine seep water from site CKBK-2 that was sampled during August 2005 compared to sample from October 2004. The concentrations of Al, Cd, Cu, Mn, SO_4 , and Zn decreased dramatically in the August 2005 sample compared to October 2004 sample from this site; concentrations of iron were below the detection limit of 20 $\mu\text{g}/\text{L}$ in samples from both collecting events. The increase in pH and the decrease in metals may indicate the mixing of the seep water with the near neutral, low metal water of the unnamed tributary that flows into

Cookville Brook. The concentrations of cadmium, copper, and zinc still exceeded the water-quality guidelines even in this relatively dilute sample.

The Smith and Eureka mine pools were generally oxidized waters with low pH, whereas the perched and unperched Union mine pools had near neutral pH and varied from reducing to oxidizing (fig. 20). The acidic Eureka mine pool, which is sampling site PKHL-1 in figure 5C, contained the highest concentrations of Al, Fe, Mn, SO_4 , and Zn and had high concentrations of Cd and Cu, whereas the acidic Smith mine pool, which was sampling site CKBK-5, contained intermediate concentrations of Al, Cd, Cu, Fe, Mn, SO_4 , and Zn when compared to other samples from the site. The concentrations of all of these elements in samples from both sites, except sulfate in samples from site CKBK-5, exceeded some water-quality guidelines (figs. 17, 18, and 19). The concentrations decreased and pH increased slightly in the samples that were collected during August 2005 compared with the samples that were collected during October 2004. In contrast to the acidic Smith and Eureka mine pools, the Union mine pools had near neutral pH; the perched Union mine pool, which was site PKHL-4, had a slightly lower pH of 5.5–5.9 than the unperched pool, which was site PKHL-5 and had pH of 6.8–7.0. The higher pH mine pools of the Union mine had lower concentrations of aluminum and iron compared with the lower pH mine pools of the Smith and Eureka mines. Despite this, the concentrations of metals such as cadmium, copper, and zinc exceeded some water-quality guidelines.

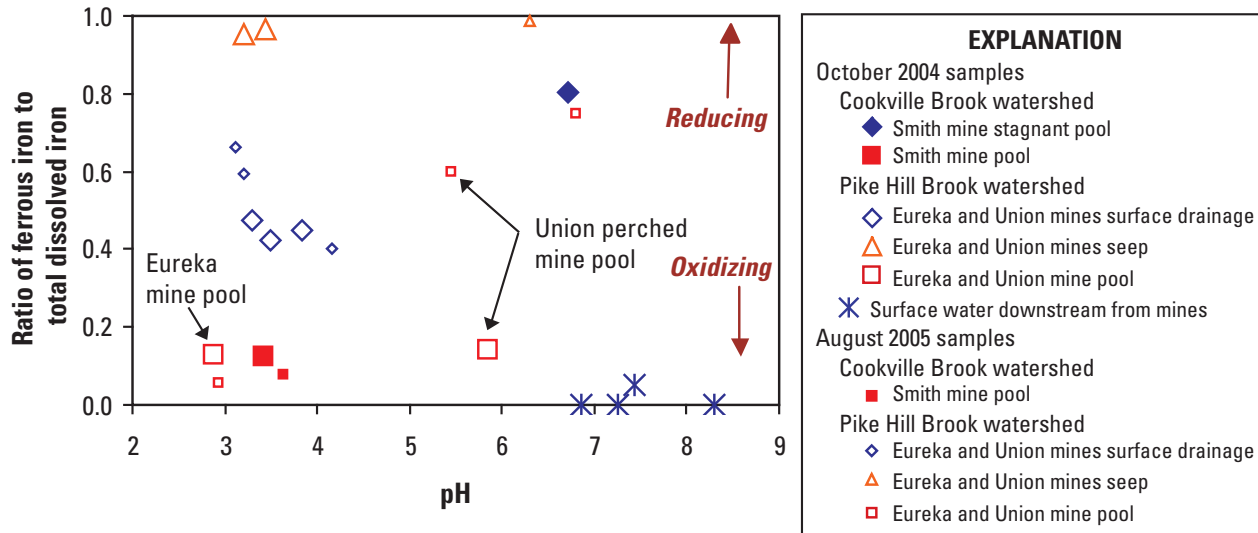


Figure 20. Ratio of ferrous to total dissolved iron and pH in water samples from the Pike Hill mines study area.

Surface-Mine Drainage

Samples of stagnant, ponded surface water were collected from sampling site CKBK-4 at the Smith mine (fig. 4A). These samples were the only ones from the surface-mine-drainage-sample set that were proximal to mine workings. This small pond was reducing, as indicated by Fe^{2+}/Fe_{total} equal to 0.8 (fig. 20), near neutral, and contained low-to-nondetectable concentrations of Al, Cd, Cu, SO_4 , and Zn that were less than water-quality guidelines. The pH and the low metals content suggest that this water was minimally influenced by the mine workings or waste at the Smith mine. These waters contained concentrations of iron and manganese that exceeded water-quality guidelines. Water from site PKHL-6, a small stream that drains the Union mine haulageway before it infiltrates waste pile 04PKHL11, was similar in composition to that of the ponded water from the Smith mine in that it was oxidized, had a neutral pH, and contained concentrations of most metals that were less than water-quality guidelines (figs. 17, 18, and 19). This water contained concentrations of copper as much as five times greater than the acute aquatic toxicity standard. Unlike the water from Smith pond, the concentrations of aluminum and iron in water from this stream were at or below the detection limits.

Three water sampling sites directly downstream of the Union and Eureka mines and near the headwaters of Pike Hill Brook were formed by the increased channelization of flow from the Pike Hill mine site; from upstream to downstream, those sites are PKHL-9, PKHL-2, and PKHL-10. Site PKHL-9 included water that discharges from the Eureka mine workings and from upper waste piles. Site PKHL-2 included discharge from site PKHL-9 and discharge from the Union mine workings that had filtered through some of the lower waste piles. Site PKHL-10 was the stream into which all of the water from this area of the site drained before it was diluted downstream

by a small unimpacted tributary. Water from these three sites (fig. 20) had subequal proportions of dissolved ferric and ferrous iron, or Fe^{2+}/Fe_{total} , of 0.40 to 0.66 and pH that ranged from 3.1 to 4.2. This surface-mine drainage contained dissolved concentrations of aluminum that ranged from 6,620 to 11,400 $\mu\text{g/L}$ and concentrations of iron that ranged from 717 to 23,300 $\mu\text{g/L}$ (fig. 17). These mine-drainage samples contained concentrations of sulfate as much as 418 mg/L, copper as much as 6,790 $\mu\text{g/L}$, zinc as much as 3,570 $\mu\text{g/L}$, manganese as much as 1,400 $\mu\text{g/L}$, and cadmium as much as 22.9 $\mu\text{g/L}$. The concentrations of Al, Cd, Cu, Fe, Mn, SO_4 , and Zn exceeded the water-quality guidelines. For samples from site PKHL-10, the values found during this study for all of the water-quality characteristics were within the ranges found during the 14-month study of Kiah and others (2007), which overlapped the duration of this study.

Downstream Waters and Mine-Drainage Effects

The downstream surface waters were generally oxygenated and had neutral pH (fig. 20; table 9). Sampling sites that directly drained the mines were seeps, mine pools, and surface-mine drainage, whereas sites located farther downstream were mine drainage that was diluted by unimpacted downstream waters (fig. 2; table 3). A more detailed description of the regional water quality and streamflow from October 2004 to December 2005 was reported in Kiah and others (2007).

The pH of the waters downstream of the mines ranged from 6.8 to 8.3 and reached 8.5 in the Waits River downstream of Pike Hill Brook. The pH generally increases with increasing distance downstream of the site (fig. 21). The concentrations of aluminum and sulfate decreased downstream in Pike Hill Brook, as indicated by the results of analysis of the October 2004 and August 2005 samples (fig. 21). This was likely because of the dilution of impacted waters by unimpacted

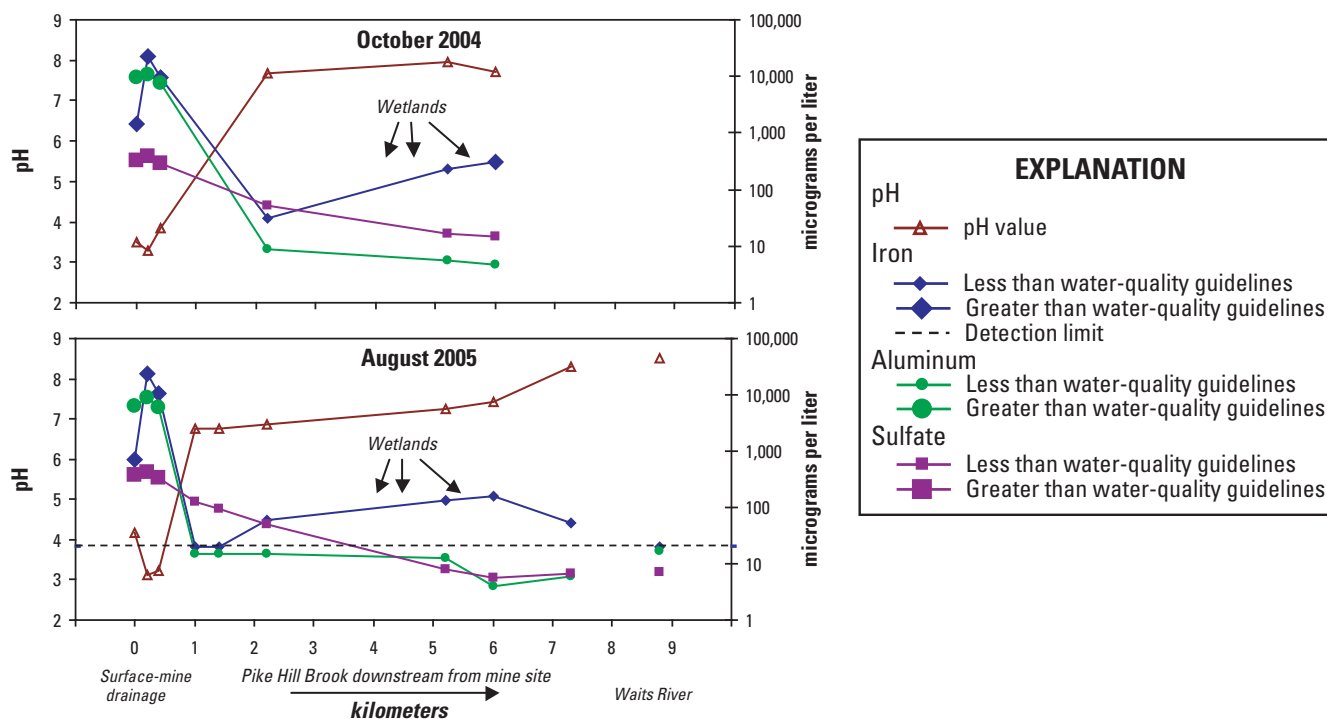


Figure 21. Downstream variations in the concentrations of aluminum, iron, sulfate, and pH in Pike Hill Brook and the Waits River, October 2004 and August 2005. ICP-MS data are used for aluminum because concentrations of aluminum determined by ICP-AES for these samples were generally less than the detection limit.

waters and by the precipitation of aluminum-hydroxysulfate phases as pH increased. Concentrations of iron showed a different trend than those for aluminum and sulfate. Initially in Pike Hill Brook, concentrations of iron decreased as pH increased. Farther downstream, however, the concentrations of iron increased after the water had flowed through three sets of wetlands that are approximately 3.7, 4.5, and 5.2 km downstream from the mine (fig. 20). This may be an indication of the dissolution of ferric hydroxides particulates in anaerobic parts of the wetlands [see Kiah and others (2007) for a detailed discussion]. As with the concentrations of iron, the concentrations of manganese increased after water had flowed through a wetland approximately 5 km downstream of the mine. The concentrations of aluminum, iron, and sulfate decreased to less than the water-quality guidelines in water samples that were collected from Pike Hill Brook downstream from the confluence with the first unimpacted tributary and approximately 0.5 km downstream from the mine site (fig. 21).

The concentrations of cadmium, copper, and zinc decreased downstream from the mine site (fig. 22). Concentrations that exceeded water-quality guidelines were found as much as 2.2 km downstream for copper and zinc and as much as 1.0 km downstream for cadmium. No substantial increases in the concentrations of cadmium, copper, and zinc were found downstream from the wetlands.

In this study, the waters at the mouth of Pike Hill Brook did not contain concentrations of metals that exceeded water-quality guidelines, presumably because of processes such as

dilution, precipitation, and sorption. However, Kiah and others (2007) reported that concentrations of cadmium and copper in samples collected between October 2004 and December 2005 exceeded water-quality guidelines. Water-quality guidelines for concentrations of metals were not exceeded in samples from the Waits River downstream of the confluence of Pike Hill Brook that were collected during this study or during the study by Kiah and others (2007).

The concentrations of lead in the water samples ranged from less than the detection limit of 0.05 to 4.2 µg/L. These concentrations did not exceed the aquatic toxicity standard of 65 µg/L lead or the drinking-water standard of 15 µg/L lead. As with concentrations of lead, the concentrations of selenium, which ranged from less than 1 to 2.9 µg/L, did not exceed the aquatic toxicity standard of 4.6 µg/L or the drinking-water standard of 50 µg/L.

Comparison with Elizabeth and Ely Surface Waters

The concentrations of iron and aluminum and the pH of water in most of the samples collected from the Pike Hill mine site are similar to those found in water samples from the Elizabeth and Ely mine sites (figs. 17, 18, and 19). Background waters for the Elizabeth and Ely mines are not shown in those figures, but the background waters at those sites also contained low amounts of metals (Seal and others, 2001). In addition, the pH of background waters for the Elizabeth and Ely mines

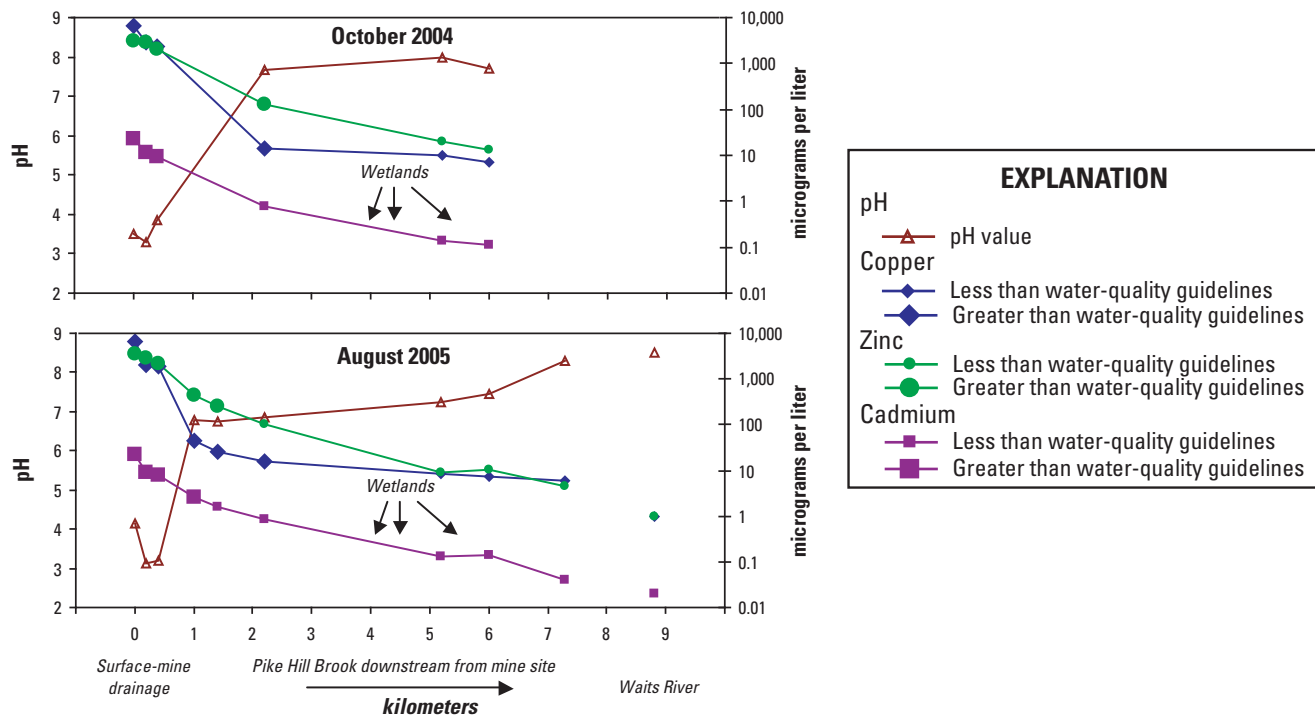


Figure 22. Downstream variations in the concentrations of copper, zinc, cadmium, and pH in Pike Hill Brook and the Waits River, October 2004 and August 2005.

was equal to or less than that found in the Pike Hill background samples, as a result of the more calcareous host rock. The concentrations of cadmium, copper, sulfate, and zinc in most of the samples from the Pike Hill mines area are within the ranges found in surface waters from the Elizabeth and Ely mines (figs. 18 and 19). The concentrations of these metals in surface mine-drainage samples and mine-pool samples from the Pike Hill mine fall within the range of higher concentration values for samples from the Elizabeth and Ely mines.

Stream Sediments

Mineralogy

The mineralogy of the stream sediments largely reflects the silicate mineralogy of the host rocks. Estimates of the amounts of minerals in stream sediments were based on quantitative X-ray diffraction analysis and are given in table 10 and illustrated in figure 23. Most of the stream-sediment samples consisted of quartz, plagioclase feldspars, micas (that is, muscovite) or altered micas (for example, vermiculite), and hornblende (fig. 23). Other silicates present in lesser amounts included kaolinite and chlorite. The only other minerals identified by XRD in stream-sediment samples were goethite, jarosite, chalcocopyrite, calcite, and dolomite, and those minerals are discussed below.

Two of the samples of sediments upstream from mine-impacted waters are those that were collected at site 011398302-SD, from the clean tributary to Pike Hill Brook, and at site 01139826-SD, from the upstream Waits River

sample. In both of those samples, only silicate phases were greater than the reliable detection limit of a few weight percent. Stream-sediment samples that were collected from Pike Hill Brook downstream of the mine site contained significant goethite of approximately 20 weight percent, a few weight percent jarosite, and traces of chalcocopyrite (fig. 23). These were either primary or secondary minerals associated with the mine site. Brown secondary precipitates coated the streambed in this area. Downstream trends suggest that goethite content decreased and that jarosite and chalcocopyrite were undetectable, which reflects a decrease in minerals associated with the mine site downstream. The stream-sediment sample collected from the unnamed tributary to Cookville Brook at site 01139940-SD, which was downstream from the Smith mine, contained trace to nondetectable amounts of primary minerals, that is chalcocopyrite, and secondary minerals, that is goethite and jarosite, that are associated with the sulfide deposit. The only other minerals of note in the stream-sediment samples were calcite and dolomite; these carbonates are acid neutralizers found in the host rock of the mineral deposit. The sample from site 01139840-SD at the mouth of Pike Hill Brook and from site 01139841-SD at the Waits River at East Corinth Road contained up to 6 weight percent carbonates (fig. 23).

Minerals associated with the mine may weather and produce acid and runoff containing trace elements that may have a detrimental effect on the aquatic ecosystem; these minerals decreased rapidly downstream. In addition, acid-neutralizing carbonates that could be of benefit to the aquatic ecosystem were found in stream sediments upstream from the confluence of Pike Hill Brook with the Waits River and in the Waits River downstream of the site.

Table 10. Estimates of the amounts of minerals in stream-sediment samples from the Pike Hill mines study area.

[n.d., not determined; ideal formulas for minerals are given in table 4, except dolomite ($\text{CaMg}(\text{CO}_3)_2$), hornblende ($(\text{Ca},\text{Na})_{2-3}(\text{Mg},\text{Fe},\text{Al})_5\text{Si}_6(\text{Si},\text{Al})_2\text{O}_{22}(\text{OH})_2$), and vermiculite ($\text{Mg}_x(\text{Mg},\text{Fe},\text{Al})_3(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$)]

Mineral	Sediment-sample number												
	011398302- SD	01139830- SD	01139830- SD-BC	01139832- SD	01139833- SD	01139833- SD-D'	01139833- SD	01139838- SD	01139839- SD	01139840- SD	01139841- SD	01139940- SD	01139826- SD
Minerals (weight percent)													
Albite	7.2	4.4	4	7.3	6.7	8.4	12.1	11.9	13	8.3	6.9	13.4	
Anorthite	10.4	7.7	7.2	13	22.6	11.9	14	17.1	11.9	10	10	7.9	
Calcite	0	0	0	0	0	0	0	0	4.4	0	0	0	
Chalcopyrite	0	1.6	1.2	0.5	0.3	0.2	0.2	0.2	0	0.2	0.2	0	
Chlorite	0.7	0	0	0	1.3	1.5	0	0	0.9	0	0.4	0.2	
Dolomite	n.d.	n.d.	n.d.	n.d.	0	0.6	0	n.d.	n.d.	6.2	n.d.	n.d.	
Goethite	0.1	19.7	18.9	2.8	1.1	1.3	0	0	0	0	0	0	
Hornblende	11.5	1.1	3.8	4.4	4.8	6	1.7	3.8	3.2	2.9	4.1	2.8	
Jarosite	0	2.6	2.3	0.3	0.2	0.2	0	0	0	0	0.1	0.3	
Kaolinite	1.9	1.8	2.2	2.4	1.8	1.4	1.5	0.1	0.9	1.6	1.8	1.1	
Muscovite	5.9	7.9	8.5	4.3	5.7	7.1	7.8	5.7	4	5	5.7	6	
Quartz	58.1	49.7	47.2	56.2	52.4	59.6	60.5	57.7	60.4	65.1	68.9	65.9	
Vermiculite	4.2	3.5	4.7	8.7	3.1	1.8	2.3	3.3	1.4	0.8	1.9	2.4	
Fit of refinement													
Chi-square ²	5.27	4.15	4.3	5.71	6.77	5.03	5.72	5.93	6.36	6.89	4.51	4.91	

¹01139833-SD-D is a replicate sample of 01139833-SD.

²Chi-square is a computed statistical residual to measure the fit of refinement. Chi-square = 1 for perfect correspondence between least-squares model and observed data. Values below 6 are considered reasonable fits for these complex mixtures due to systematic errors and imperfect physical corrections.

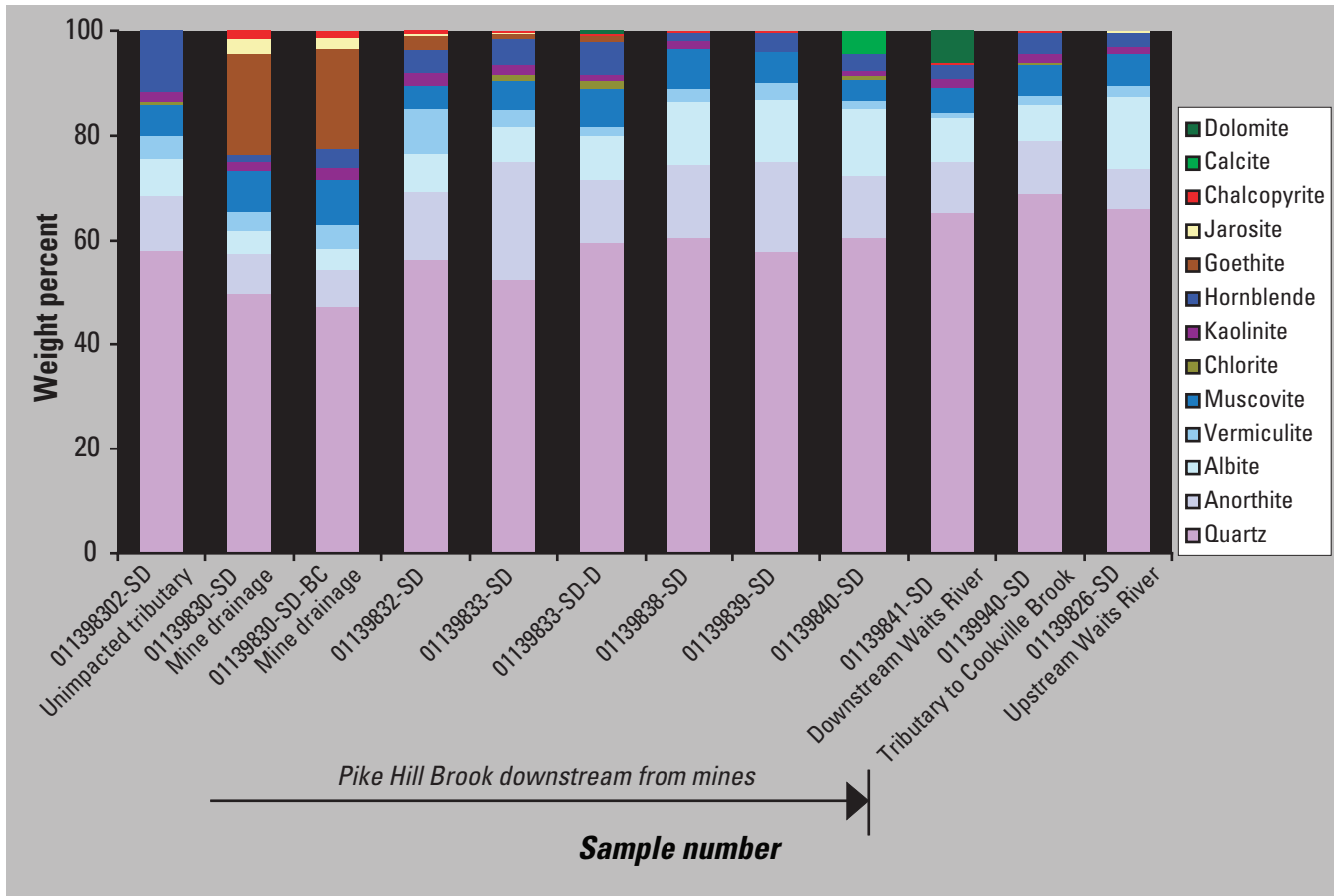


Figure 23. Relative weight percentages of minerals in stream sediments from the Pike Hill mines study area.

Bulk Geochemistry

The concentrations of elements in stream sediments from Pike Hill Brook, from a tributary to Cookville Brook, and from the Waits River are given in table 11 and appendix 5. The concentrations of Ag, Bi, Cd, Cu, Fe, Mo, Pb, S, Sb, Se, Sn, and Zn, which are likely associated with the mineral deposits, were highest in stream-sediment samples collected from sites 01139830-SD and 01139830-SD-BC directly downstream of the Eureka and Union mines. In contrast, the concentrations of these elements in the stream-sediment sample collected at site 01139940-SD downstream of the Smith mine were significantly lower. The concentrations of most of these elements in this sample were similar to those in stream sediment collected in unimpacted waters at sites 01139826-SD and 011398302-SD. The stream sediment downstream from the Smith mine did contain elevated concentrations of cadmium, copper, and zinc compared to background levels.

Probable effect concentrations (PEC) are concentrations of contaminants above which harmful effects on sediment-dwelling organisms are expected to occur frequently. The PECs for As, Cd, Cr, Cu, Ni, Pb, and Zn are given in table 11 and are based on MacDonald and others (2000). These

consensus-based criteria were calculated by determining the geometric mean of several published PEC-type sediment-quality standards (MacDonald and others, 2000). To evaluate the biological significance of contaminant mixtures, mean PEC quotients were calculated for the stream-sediment samples (table 11). Mean PEC quotients were determined by dividing the concentrations of an element by its consensus-based PEC, summing the values, and normalizing to the number of PECs for each sediment sample (MacDonald and others, 2000). Concentrations that were below the detection limit were not included in the calculations. For this study, sediment samples were predicted to be toxic when the mean PEC quotients were greater than 0.5. The concentrations of cadmium, copper, and zinc in many samples were greater than the individual PECs (table 11; fig. 24). Mean PEC quotients greater than 0.5 are shown in bold type in table 11 and included stream sediments from sites directly downstream from the Union and Eureka mines, where samples 01139830-SD and 01139830-SD-BC were collected, and directly downstream from the Smith mine, where sample 01139940-SD was collected. In Pike Hill Brook, mean PEC quotients exceeded 0.5 as far downstream as approximately 5.2 km from the mine, where sample 01139838-SD was collected.

Table 11. Concentration of select elements in stream-sediment samples from the Pike Hill mines study area.

[Selenium determined by hydride-generation atomic absorption spectrometry; others elements by a combination of inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry, except replicate 01139830-SD-R was analyzed by inductively coupled plasma-mass spectrometry; mg/L, milligrams per liter; µg/L, micrograms per liter; PEC, probable effect concentration; <, less than; concentrations in bold exceed criteria]

Element	Al	As	Cd	Co	Cu	Cr	Fe	Mn	Mo	Ni	Pb	S	Sb	Se	Sn	Zn	PEC quotient ¹
Units	percent	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	percent	mg/kg	mg/kg	mg/kg	mg/kg	percent	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
PEC or hazard rating ¹	33	4.98	111	149	48.6	128	4										0.5
Guidelines																	
Stream-sediment samples																	
Sample number																	
01139826-SD	3.8	<1	0.1	4.4	40	7.7	2.04	920	0.21	13.5	16.5	0.01	0.08	<0.2	2.5	44	0.2
011398302-SD	5.76	2	0.5	19	75	262	3.36	2,530	0.86	32.3	25.6	0.06	0.13	0.5	4.5	134	0.5
01139830-SD	3.03	8	5.8	43.2	31	8,070	21.5	686	22.7	7.9	59	2.12	1.28	49.8	8.2	1,070	8.4
01139830-SD-R ²	2.67	23	5	51.1	28.8	6,200	20	613	11.6	9.8	61	-	1.3	52.1	-	981	6.6
01139830-SD-BC	3.51	9	5.4	46.6	36	6,550	20.8	574	13.8	9.7	61.9	1.61	1.34	52	10.4	1,010	6.9
01139832-SD	5.08	7	3.2	74.4	48	3,530	7.64	1,100	4.71	20.5	31.1	0.41	0.39	8.7	4.2	675	3.9
01139833-SD	4.96	22	4.8	147	51	3,540	6.67	1,830	2.43	24.1	25.5	0.41	0.35	6.8	2.9	834	4.1
01139833-SD Dup ³	4.93	3	5.6	138	50	3,490	6.73	1,750	3.18	23.9	25.5	0.46	0.28	6	3.3	907	4.0
01139838-SD	5.36	<1	1.6	49.5	49	298	2.72	1,540	0.5	19.5	21.3	0.04	0.07	0.3	2.6	283	0.7
01139839-SD	4.62	<1	0.9	23.3	34	119	1.84	1,300	0.22	13.8	18.9	0.02	0.05	<0.2	1.6	191	0.4
01139840-SD	4.29	<1	1.4	22.1	27	98.1	1.4	1,380	0.19	12.2	21.8	0.02	0.06	<0.2	2.9	224	0.3
01139841-SD	4.06	1	0.1	4.6	32	8	1.35	667	0.16	11.2	18.2	0.01	0.07	0.2	2.4	43	0.1
01139940-SD	4.74	<1	1.5	35.5	53	539	2.43	1,650	0.45	31.4	13.1	0.04	0.06	<0.2	2.1	685	1.1

¹Guidelines for all elements except selenium are Probable Effect Concentrations calculated from the geometric mean of several sediment-quality guidelines (MacDonald and others, 2000). PECs are intended to indicate concentrations above which harmful effects on sediment-dwelling organisms are expected to occur. Selenium guideline is a hazard rating above which sediment may be hazardous in terms of food-chain bioaccumulation and reproductive impairment in fish and aquatic birds (Lemly, 1995).

²Replicate split of sample sent for chemistry analysis.

³Field replicate ("Dup").

⁴Mean PEC quotient is calculated from element concentrations and PECs and is an indication of the biological significance of contaminant mixtures (MacDonald and others, 2000). In this evaluation, samples are considered toxic if mean PEC quotients are greater than 0.5.

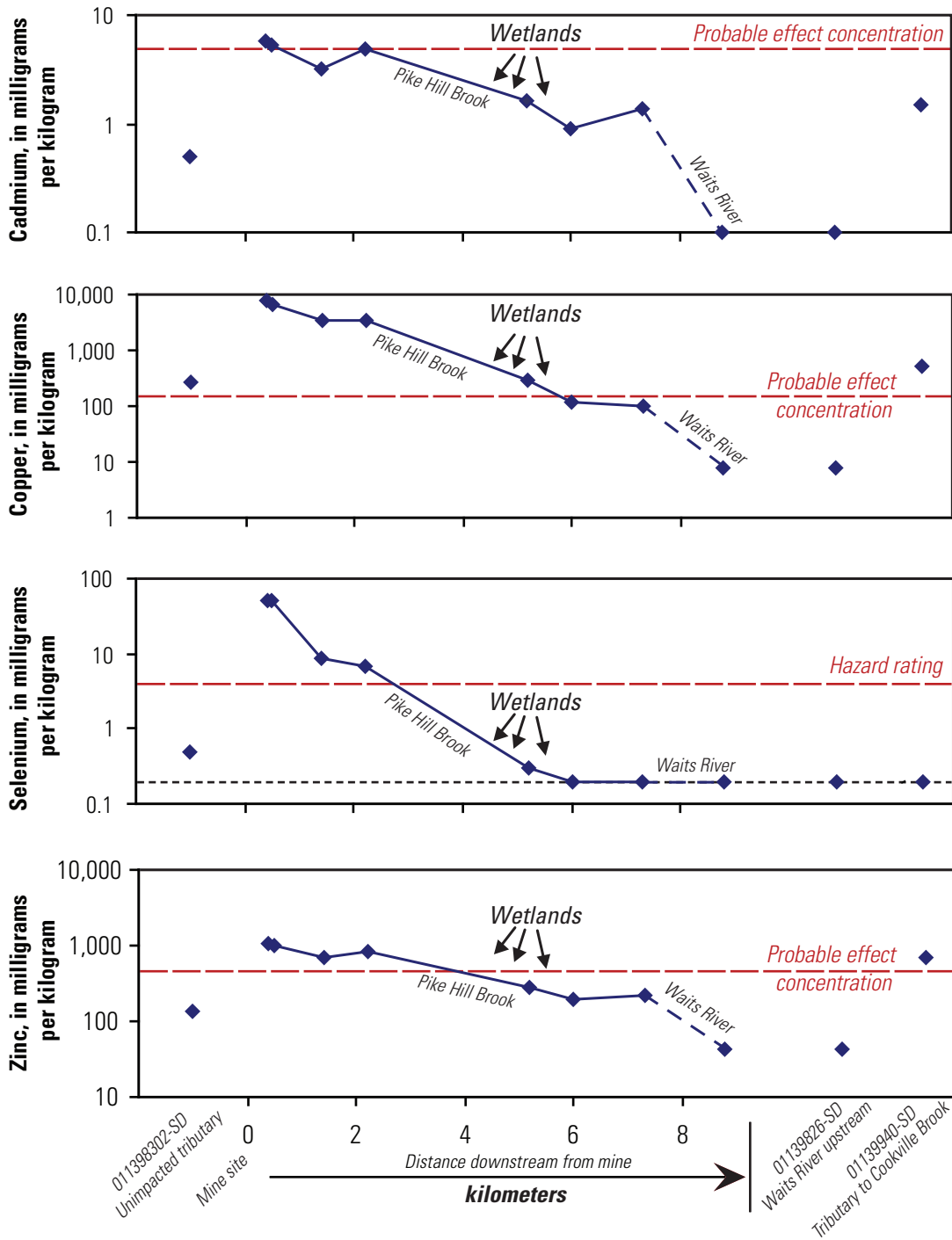


Figure 24. Concentrations of cadmium, copper, selenium, and zinc in stream sediments collected from the Pike Hill mines study area. [Probable effect concentrations are from MacDonal and others (2000). Selenium hazard rating from Lemly (1995).]

Based on comparison to PECs and mean PEC quotients for these selected elements, stream sediments downstream from the Pike Hill mines site in both Pike Hill Brook and the tributary to Cookville Brook contained concentrations of elements that may be harmful to sediment-dwelling organisms. However, the speciation of these elements and partitioning among various organic and inorganic solid phases affect their bioavailability, rather than their total concentration. Therefore, in this comparison of total concentration to PECs, the threat to aquatic organisms from the sediment may be overstated.

The concentrations of selenium in the stream sediments were compared to a hazard rating developed by Lemly (1995). Selenium in sediments can be absorbed or ingested by aquatic organisms and bioaccumulate throughout the food chain (Lemly, 1997). A protocol for conducting a hazard assessment of selenium to assess food-chain bioaccumulation and reproductive impairment in fish and aquatic birds was developed by Lemly (1995) and is based on five ecosystem components: water, sediments, benthic macroinvertebrates, fish eggs, and aquatic bird eggs. Each of the components is assigned a hazard rating, and the hazard assessment is a sum of the hazard ratings of all five components. In this study, only the hazard rating for the sediment component was examined. Concentrations of selenium less than the no-hazard rating of less than 1 mg/kg were seen in the samples collected from areas unimpacted by mine drainage, downstream from the wetlands in Pike Hill Brook, and downstream from the Smith mine; however, concentrations of selenium were in the high hazard level of greater than 4 mg/kg in samples that were collected as much as approximately 2 km downstream from the Eureka and Union mines (table 11; fig. 24). As mentioned previously, the actual toxicity of an element such as selenium is related to its bioavailability rather than to its total concentration, and thus the actual toxicity may be overestimated here. The results of sequential partial dissolutions used to characterize the distribution of selenium in a stream-sediment sample from Pike Hill Brook suggest selenium was not dominantly present in the bioavailable fraction (Piatak and others, 2006b).

The downstream variations in the concentrations of cadmium, copper, selenium, and zinc in stream sediments are shown in figure 24. The concentrations of these elements in sediment collected from areas unimpacted by the mines were low. The concentrations of these and other trace elements associated with the mineral deposits near the mines generally decreased with increasing distance from the mines; below the wetlands, concentrations of these elements in sediments did not exceed these standards (fig. 24).

The concentrations of most elements in the Pike Hill mine sediments were similar to those in stream sediment from the Elizabeth Mine that were reported by Hammarstrom and others (1999). For example, the concentrations of aluminum and iron in Elizabeth Mine sediments ranged from 1.3 to 6.2 percent and from 2.2 to 34 percent, respectively (Hammarstrom and others, 1999). In Pike Hill mines sediments,

aluminum ranged from 3.8 to 5.76 percent and iron from 1.35 to 21.5 percent (table 11). The maximum concentrations of 8,070 mg/kg of copper and 1,070 mg/kg of zinc in stream sediment from the Pike Hill mines were greater than the maximum values of 3,930 mg/kg of copper and 836 mg/kg of zinc reported in stream sediment from the Elizabeth Mine (Hammarstrom and others, 1999). Concentrations of cadmium were comparable with a maximum value of 5.8 mg/kg for Pike Hill mines sediments compared to a maximum value of 7 mg/kg for the Elizabeth Mine sediments. As with Pike Hill stream sediments, the concentrations of trace elements in stream sediments from the Elizabeth mine study area decreased with increasing distance from the mine.

Conclusions

Mine waste, mine drainage, and stream sediments at the Pike Hill Copper Mine Superfund site were sampled and analyzed to provide a relative ranking of their potential environmental impact and for comparison with the results of similar studies of the nearby Elizabeth and Ely mines Superfund sites. The results indicated that background soils, waters, and stream sediments contained low concentrations of most metals. The background soils were categorized as non-acid generating based on acid-base accounting, and background waters had near neutral pH values and were alkaline and hard. These features are reflections of the calcareous host rocks in the Pike Hill study area.

Most mine-waste samples from the Eureka and Union mines area contained concentrations of copper and iron that exceeded USEPA PRGs and concentrations of selenium and zinc that were significantly higher than the reported mean concentrations of those elements in soils in the eastern United States. The low paste-pH values and negative net-neutralization potentials indicated that most material around the Eureka and Union mines was potentially acid generating. Leachate tests on mine waste indicated that Al, Cd, Co, Cu, Fe, Mn, Se, SO₄, and Zn were leached in concentrations that were higher than water-quality guidelines. Mine waters around and directly downstream from the Eureka and Union mines contained high concentrations of some elements including as much as 39,700 µg/L Al, 22.9 µg/L Cd, 6,790 µg/L Cu, 99,300 µg/L Fe, 6,980 µg/L Mn, and 7,360 µg/L Zn, which validates the conclusions of the leachate test. Concentrations of these elements in many water samples exceeded water-quality guidelines. Generally in surface waters, the pH increased and the concentrations of these elements decreased downstream from the Eureka and Union mines in Pike Hill Brook. Stream sediments also contained concentrations of cadmium, copper, selenium, and zinc that exceeded toxicity standards for aquatic life; the concentrations of those elements also decreased with increasing distance from the mines.

The environmental impact of the Smith mine area is potentially less than that of the Eureka and Union mines. Mine waste at the Smith mine contained concentrations of iron that exceeded the USEPA PRG. It was also acid generating, although generally slightly less acid generating than material from the Eureka and Union area. Although the concentrations of metals in leachate from Smith mine waste did not reach maximum concentrations, Smith mine waste contained comparable concentrations of metals relative to leachate from Eureka and Union mines waste; concentrations of cadmium, copper, and zinc in Smith mine leachates did exceed the acute aquatic toxicity standards. The concentrations of metals in mine waters at the Smith mine generally did not reach the maximum values found at the Eureka and Union mines, although concentrations of some metals exceeded acute toxicity standard, drinking-water standards, or both. Stream sediment downstream from the Smith mine contained intermediate concentrations of trace elements when compared with sediments from Pike Hill Brook downstream from the Eureka and Union mines.

These preliminary results suggest that the environmental impact from the Pike Hill mines site is comparable to that from the Elizabeth and Ely mines based on mine-waste chemistry and potential acid-generation and on mine-drainage and stream-sediment chemistry. At the Pike Hill mines site, USEPA PRGs for several elements were exceeded in mine-waste samples. In addition, the aquatic ecosystem in waters draining the Pike Hill Superfund site is potentially threatened, based on leachate tests and water and stream-sediment metal content.

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