



Assessment, Water-Quality Trends, and Options for Remediation of Acidic Drainage from Abandoned Coal Mines Near Huntsville, Missouri, 2003–2004



Scientific Investigations Report 2005–5202

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Cover photograph: Acidic mine drainage downstream from the Huntsville Gob reclamation project, 2004.

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By Eric D. Christensen

Prepared in cooperation with the Missouri Department of Natural Resources

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Conversion Factors and Datum

Multiply	Ву	To obtain
	Length	
centimeter (cm)	0 3037	inch (in)
millimeter (mm)	0.03937	inch (in)
micrometer (um)	0.0000394	inch (in)
meter (m)	3 281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square meter (m^2)	0.0001	hectare (ha)
hectare (ha)	2.4710	acre
square kilometer (km ²)	0.3861	square mile (mi ²)
	Volume	
liter (L)	0.2642	gallon (gal)
liter (L)	0.03531	cubic foot (ft ³)
	Flow rate	
liter per second (L/s)	15.85	gallon per minute (gal/min)
liter per second (L/s)	0.03531	cubic foot per second (ft^3/s)
liter per minute (L/min)	0.2642	gallon per minute (gal/min)
	Mass	
kilogram (kg)	2.205	pound avoirdupois (lb)
kilogram per day (kg/d)	0.001102	ton per day (ton/d)
metric ton	1.1023	ton, short (2,000 lb)
	Pressure	
kilopascal (kPa)	0.009869	atmosphere, standard (atm)

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

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μ S/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (μ g/L).

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Elevation, as used in this report, refers to distance above or below the vertical datum.

Assessment, Water-Quality Trends, and Options for Remediation of Acidic Drainage from Abandoned Coal Mines near Huntsville, Missouri, 2003–2004

By Eric D. Christensen

Abstract

Water from abandoned underground coal mines acidifies receiving streams in the Sugar Creek Basin and Mitchell Mine Basin near Huntsville, Missouri. A 4.35-kilometer (2.7-mile) reach of Sugar Creek has been classified as impaired based on Missouri's Water Quality Standards because of small pH values [< (less than) 6.5]. Samples collected from Sugar Creek from July 2003 to June 2004 did not have pH values outside of the specified range of 6.5 to 9.0. However, large concentrations of iron [416 to 2,320 mg/L (milligrams per liter)], manganese (8.36 to 33.5 mg/L), aluminum (0.870 to 428 mg/L), and sulfate (2,990 to 13,700 mg/L) in acidic mine drainage (AMD) from two mine springs as well as small and diffuse seeps were observed to have an effect on water quality in Sugar Creek. Metal and sulfate loads increased and pH decreased immediately downstream from Sugar Creek's confluence with the Calfee Slope and Huntsville Gob drainages that discharge AMD into Sugar Creek. Similar effects were observed in the Mitchell Mine drainage that receives AMD from a large mine spring. Comparisons of water-quality samples from this study and two previous studies by the U.S. Geological Survey in 1987-1988 and the Missouri Department of Natural Resources in 2000-2002 indicate that AMD generation in the Sugar Creek Basin and Mitchell Mine Basin is declining, but the data are insufficient to quantify any trends or time frame. AMD samples from the largest mine spring in the Calfee Slope subbasin indicated a modest but significant increase in median pH from 4.8 to 5.2 using the Wilcoxan rank-sum test (p < 0.05) and a decrease in median specific conductance from 5,000 to 3,540 µS/cm (microsiemens per centimeter at 25 degrees Celsius) during a 17-year period. AMD samples from the largest mine spring in the Mitchell Mine Basin indicated an increase in median pH values from 5.6 to 6.0 and a decrease in median specific conductance from 3,050 to 2,450 µS/cm during the same period.

Remediation of AMD at or near the sites of the three largest mine springs is geochemically feasible based on alkalinity addition rates and increased pH determined by cubitainer experiments and geochemical mixing experiments using the computer model PHREEQCI. Alkalinity values for seven cubitainer experiments conducted to simulate anoxic treatment options exceeded the targeted value for alkalinity [90 mg/L as calcium carbonate (CaCO₃)] specified in Missouri's Total Maximum Daily Load program by 18 percent or more, but maximum pH values were between 6.2 and 6.3, which is less than the targeted pH value of 6.5. Treatment of AMD by mixing with stream water or sewage effluent can further increase pH as indicated by geochemical modeling, but will not totally achieve water-quality goals because of limited discharges. A combination of treatments including settling ponds, oxic or anoxic limestone drains, and possibly successive alkalinity producing systems to remediate AMD will likely be required in the Sugar Creek Basin and Mitchell Mine Basin to consistently meet Missouri's Water Quality Standards.

Introduction

Sugar Creek originates north of the city of Moberly in Randolph County in north-central Missouri along a high ridge that divides water flowing to the Mississippi River from water flowing to the Missouri River. Sugar Creek originates at Sugar Creek Lake and flows west for 8.2 km (kilometers) to its mouth on the East Fork Little Chariton River and drains 58.2 km² (square kilometers). An unnamed tributary to the East Fork Little Chariton River with a drainage area of 3.2 km² originates in Huntsville, Missouri, and flows 4.5 km west to its mouth, 2.7 km downstream from Sugar Creek (fig. 1). For the purposes of this report this tributary and its associated drainage area is referred to as the Mitchell Mine Basin after the primary source of acidic mine drainage (AMD) in the basin. Associated drainage areas of three unnamed tributaries of Sugar Creek that are affected by AMD and water-quality sampling sites are similarly identified for the purpose of this report in figure 1 as the Huntsville Gob, Middle Creek, and Calfee Slope subbasins.

Upland areas in the vicinity of Huntsville (2000 population 1,553; Missouri Census Data Center, 2004) are underlain by bituminous coal deposits that were extensively mined underground from about 1865 to 1932 when large scale surface mining operations began (Gentile, 1967). Water from abandoned underground coal mines, reclaimed strip mines, and coal processing areas in and near Huntsville acidify receiving streams.

Historic water-quality data from Sugar Creek, Calfee Slope subbasin, and the Mitchell Mine Basin (Blevins and Ziegler, 1992; Missouri Department of Natural Resources, 2002) report pH values less than Missouri's Water Quality Standards range of 6.5 to 9.0 standard units. As a result, the Missouri Department of Natural Resources has classified a 4.35-km reach of Sugar Creek as impaired under Subsection 303(d) of the Clean Water Act, as amended, Title 33 United States Code, 1251 et seq., Total Maximum Daily Load (TMDL) program (Missouri Department of Natural Resources, 2002).

The U.S. Geological Survey, in cooperation with the Missouri Department of Natural Resources, Land Reclamation Program, conducted an investigation in 2003-2004 to assess the effects of AMD sources on segments of Sugar Creek and Mitchell Mine drainage, detect any water-quality trends, and to identify geochemically feasible remedial options. A review of available historic hydrologic and water-quality data for some mine springs and tributaries of Sugar Creek and other AMD sources in and around Huntsville from Blevins and Ziegler (1992), the Missouri Land Reclamation Commission (Dennis Stinson, Missouri Department of Natural Resources, written commun., 2002), and Missouri Department of Natural Resources (2002) indicate that three mine springs located in the Huntsville Gob and Calfee Slope subbasins, and Mitchell Mine Basin (HG-2M, CS-5M, and MM-3M, fig. 1), contribute the majority of AMD in the study area. However, large parts of the Sugar Creek Basin had not been previously assessed, sampled, or characterized.

Purpose and Scope

The purpose of this report is to assess the current (2003-2004) contaminant loads, effects of AMD on receiving streams, water-quality trends, and possible remedial options for AMD sources previously identified and those identified during the study. Historic data and the initial reconnaissance sampling were reviewed and subsequent sampling was conducted to identify, measure, and characterize the water quality and discharge of all visible sources of mine drainage in the Sugar Creek Basin and Mitchell Mine Basin. The effects of each identified AMD source on water quality in Sugar Creek and the effects of mine spring MM-3M on the Mitchell Mine drainage were determined; available historic data were used to identify any trends or changes in water quality that may have occurred during the last 2 to 15 years, where possible, and passive-treatment options were identified and evaluated that would be geochemically appropriate and physically possible to construct for mine drainage affecting Sugar Creek and the Mitchell Mine drainage in Huntsville. The potential to add alkalinity to water from mine springs and treatment with effluent from city sewage lagoons to increase pH values and counteract acidity, large iron (Fe²⁺, Fe^{3+}), and large sulfate concentrations also was addressed.

Description of Study Area

Large seasonal variation in temperature and precipitation in the study area result in large seasonal changes in the hydrology. At Moberly, Missouri, 6 km east of Huntsville (fig. 1), the average annual air temperature is 12.4 °C (degrees Celsius) with average monthly temperatures ranging from -2.5 °C in January to 25.4 °C in July for the 69-year period of record from 1936 through 2004. On average, the maximum temperature equals or exceeds 32.2 °C on 38.1 days and equals or falls below 0 °C on 111.7 days. Average monthly temperatures for the period of record and during the study are shown in figure 2. Average total annual precipitation at Moberly, Missouri, is 97.4 cm (centimeters). The average monthly precipitation for the period of record and during the study is shown in figure 3 (High Plains Regional Climate Center, 2004). Temperatures during the study were average to slightly cooler than average, while precipitation exceeded the annual average by 17.3 cm or 13.6 percent. Daily precipitation values during the study are presented in figure 4 (National Oceanic and Atmospheric Administration, 2003–2004). The large rainfall events in the fall of 2003 and the summer and fall of 2004 account for most of the increase in precipitation when compared to the period of record.

The Sugar Creek Basin and Mitchell Mine Basin lie in the Dissected Till Plains physiographic province (Fenneman and Johnson, 1946). The topography characteristically is gently rolling hills with some steep slopes along streams. Overall relief is approximately 55 m (meters) in the study area. Unconsolidated deposits of Pleistocene glacial drift and Quaternary alluvium of variable thickness overlie bedrock in the vicinity of Huntsville. The glacial drift formed a wide, southward sloping till plain that covered the preglacial topography and filled preglacial valleys (Work and others, 1982). The underlying Pennsylvanian age bedrock is exposed where streams have incised the preglacial uplands. Drainage divides in the study area characteristically are flat relative to the steeply incised slopes of the streams. Slopes tend to be forested because of their steepness. Soils belong to the Gosport-Gorin association on the uplands. These soils are moderately to somewhat poorly drained soils formed in weathered shale or in loess and thin alluvial deposits formed on erosion surfaces. Soils belonging to the Piopolis-Chequest association form in silty or clayey alluvium on flood plains. Some soils in reclaimed areas may be classified as belonging to the Bethesda-Schuline association; welldrained soils formed in material mixed by surface mining activities (Potter, 1989).

Land use predominantly is agricultural, including pasture, on the flatter ridge tops. About 40 percent of the Sugar Creek Basin, including the subbasins (fig. 1), is forested, 32 percent pasture and grasslands, 22 percent row-crop and other agricultural use, 3.5 percent water and wetlands, and 2.5 percent urban. About 35 percent of the Mitchell Mine Basin is pasture and grassland, 25 percent urban, 25 percent forested, 8 percent rowcrop and other agricultural use, and 6 percent water and wet-



Figure 1. Location of Sugar Creek Basin, Huntsville Gob, Middle Creek, and Calfee Slope subbasins, Mitchell Mine Basin, and sampling sites in Randolph County, Missouri.







Figure 3. Average monthly precipitation measured and recorded at Moberly, Missouri, for July 2003 through September 2004 and for the 69-year period of record.



Figure 4. Daily precipitation measured and recorded at Moberly, Missouri, for July 2003 through September 2004.

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lands (U.S. Geological Survey, 2000). Less than 1 percent of the land in both basins, including surface-mined areas, is classified as barren. Areas affected by mining may be more extensive than those classified as barren as some unreclaimed spoil has undergone reforestation and, therefore, is classified as forested.

Bedrock near the surface within the study area is Pennsylvanian age from the Cherokee and Marmaton Groups^a. The Bevier, Wheeler, and Mulky coals and the formations just above and below them (fig. 5) were of particular economic importance. The Bevier coal was the largest coal bed mined in the Huntsville area. The thinner Wheeler coal that underlies the Bevier coal also was extracted. Although the two seams belong to different formations, they are separated only by a 2.5 to 5 cm thick layer of sandy clay or shale within the study area, were mined as a single unit, and averaged 1.22 m thick. For clarity, the two coal beds will be referred to as the Bevier-Wheeler coals. The Bevier-Wheeler coals lie above the level of the drainage network throughout most of the study area at an elevation of approximately 213 to 232 m above sea level (fig. 6).

Underground coal mining in the vicinity of Huntsville probably began soon after the founding of the city in 1831 (Gentile, 1967). Streams had eroded much of the coal seam that allowed easy access along outcrop lines. The coal seam is still visible at many locations within the Sugar Creek Basin. Not much is known about coal production during this early period until 1886, when the State and Federal governments began keeping records. In 1903, annual coal production peaked at 549,496 metric tons in Randolph County where the city of Huntsville is located (fig. 1). Coal production declined substantially in the early 1950's. The last underground mine in the Huntsville area produced 327 metric tons in 1965 (Gentile, 1967) and closed in 1966 (Blevins and Ziegler, 1992). Recoverable coal in the vicinity of Huntsville and east towards Moberly has been mostly, if not completely, removed (David C. Smith, Missouri Department of Natural Resources, written commun., 1986; Blevins and Ziegler, 1992).

The room and pillar method of underground mining was used in the removal of the Bevier-Wheeler coals (Hinds, 1912; David C. Smith, written commun., 1986). This method leaves approximately 50 percent of the coal as pillars to support the roof of the mine. The pillars and wooden roof props often were removed before a mine was abandoned allowing the roof to collapse (Weigel, 1921). After being abandoned, the underground mines can become partially or completely flooded (Blevins and Ziegler, 1992), although some remain dry.

Previous Studies

The geology and coal deposits of north-central Missouri, including the Huntsville area, have been described by Hinds (1912), Gentile (1967), Robertson (1973), Robertson and Smith

SYSTEM	SERIES	GROUP	SUBGROUP	FORMATION	LITHOLOGY				
				LENEPAH	Shales, red and green				
				NOWATA	Shales, red and green; shale, black, fissile near middle				
				ALTAMONT	Shales, limestone interbedded; unnamed coal				
			JOSE	BANDERA	Shales, brown and grey				
			APPANC	PAWNEE	Limestone, some shale				
				LABETTE	Lexington Coal, underclay				
LVANIAN	DINESIAN	MARMATON	FORT SCOTT	HIGGINSVILLE LITTLE OSAGE	Shale, grey; sandstone, fine- grained; limestone Summit Coal				
ENNS	DESM			BLACKJACK CREEK	Limestone, blocky				
				EXCELLO SHALE	Shale, grey and black, fissile				
				LAGONDA	Mulky Coal Shales, brown and grey, noncalcareous; sandstone				
				BEVIER	Bevier Coal, thin underclay				
		HEROKEE	SS SS	ARDMORE LIMESTONE MEMBER	Wheeler Coal, underclay				
		C	CABAI	VERDIGRIS	Shales, grey and green				
					Croweburg Coal, underclay				
				CROWEBURG	Shale, grey				
۰ <u>ـ</u> ــ				Usage follows non and Res	nenclature of the Missouri Geological Survey source Assessment Division (Thompson, 1995)				

NOTE: Dark bands represent coal horizons

Figure 5. Generalized stratigraphy in the Sugar Creek Basin and vicinity.

^aNomenclature follows the usage of the Missouri Geological Survey and Resource Assessment Division (Thompson, 1995).

(1979), Smith and Deason (1982), and Work and others (1982), and others. Studies containing information on hydrology and coal mining effects on water quality include Detroy and others (1983), Hall (1986), and Hall and Davis (1986). A preliminary study of abandoned underground mines in the Huntsville area conducted for Missouri's abandoned mine lands reclamation program (Wertis and Elifrits, 1984) outlined subsidence and water-quality issues. Blevins and Ziegler (1992) conducted a comprehensive study of underground coal mines at Huntsville in 1987–1988, including hydrogeology and water chemistry. This study builds on that early work.

Water Chemistry of Acidic Mine Drainage

AMD in which mineral acidity exceeds alkalinity can have small pH values and large dissolved sulfate (SO_4^{2-}) , iron (Fe^{2+}, Fe^{3+}) , manganese (Mn^{2+}) , and aluminum (Al^{3+}) concentrations, as well as other metals, resulting from the oxidation of iron sulfide minerals such as pyrite (FeS_2) and the dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water (Blowes and Ptacek, 1994; Cravotta, 1994; Rose and Cravotta, 1998). Pyrite is recognized as the major source of AMD in the eastern United States (Stumm and Morgan, 1996). The

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following five reaction equations show the generally accepted sequence of pyrite oxidation (Stumm and Morgan, 1996; Skousen and others, 1998; U.S. Department of the Interior, Office of Surface Mining, 2002; Cravotta and Kirby, 2003).

Oxidation of pyrite releases dissolved ferrous iron (Fe²⁺) and acidity (H⁺) into the water and takes place when the mineral is exposed to air and water:

$$\operatorname{FeS}_{2}(s) + 3.5O_{2} + H_{2}O \longrightarrow \operatorname{Fe}^{2+} + 2SO_{4}^{2-} + 2H^{+}$$
 (1)

Highly soluble Fe^{2+} can oxidize to relatively insoluble ferric iron (Fe^{3+}) in the presence of oxygen (O₂):

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O$$
 (2)

At pH values larger than about 3, Fe³⁺ hydrolyzes to form insoluble Fe^{III} oxy-hydroxides and related solids (Cravotta and Kirby, 2003) releasing additional acidity:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+$$
 (3)

or alternatively Fe³⁺ can be reduced by pyrite in the absence of oxygen and at pH values of about 4 (Nordstrom, 1982; Nordstrom and Alpers, 1999):

$$\text{FeS}_2(s) + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \implies 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$
 (4)

However, reaction 4 rapidly uses up all the available Fe^{3+} and the reaction may cease unless more Fe^{3+} is made available (Appelo and Postma, 1999). Additional Fe^{3+} can be generated by the reoxidation of Fe^{2+} (reaction 2) to sustain the pyrite oxidation cycle (Nordstrom and Alpers, 1999). The rate-determining step at relatively small pH values is the oxidation of Fe^{2+} to Fe^{3+} (reaction 2), usually catalyzed by autotrophic bacteria (bacteria that only require carbon dioxide or carbonates as a source of carbon) (Singer and Stumm, 1970; Nordstrom, 2000). The overall reaction often is given as (Blowes and Ptacek, 1994; Nordstrom and Alpers, 1999):

$$FeS_{2}(s) + 3.75O_{2} + 3.5H_{2}O \rightarrow Fe(OH)_{3}(s) + 2SO_{4}^{2-} + 4H^{+}$$
(5)

and is the result of summing reactions 1, 2, and 3.

In most samples of acidic underground coal-mine drainage, large concentrations of dissolved Fe^{2+} indicate that the reaction process is at an intermediate stage in the series of reactions that represent complete pyrite oxidation (reaction 5) (Stumm and Morgan, 1996; Rose and Cravotta, 1998). In wellestablished acid-generating environments, typical of abandoned underground coal mines, the sequence of reactions can be, reaction 4 to produce Fe^{2+} , which is then oxidized to Fe^{3+} aided by bacteria (reaction 2) (Singer and Stumm, 1970; Rose and Cravotta, 1998). The Fe^{3+} is then available for further pyrite oxidation. Although oxygen is not directly involved in the pyrite-oxidizing step, it is required for the regeneration of Fe^{3+} to maintain the pyrite-oxidation cycle (Rose and Cravotta, 1998).

Acidity (H^+) produced by pyrite oxidation (reaction 1) or hydrolysis (reactions 3 and 4) can be neutralized by reaction with calcareous minerals, typically calcite $(CaCO_3)$ (reaction 6) or dolomite $[CaMg(CO_3)_2]$ (reaction 7):

$$CaCO_3 + H^+ -> Ca^{2+} + HCO_3^-$$
 (6)

$$CaMg(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$$
 (7)

Alkalinity, as bicarbonate (HCO_3^{-}), and the presence of cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) in water, are common products of these and similar neutralization reactions (Cravotta and Kirby, 2003).

The acidity or net alkalinity of a solution, not pH, often is the best indicator of the presence and severity of AMD (Rose and Cravotta, 1998). AMD that initially has near-neutral pH values (pH of 6 to 7) at its point of emergence can have acidic pH [< (less than) 4.5] after complete oxidation and hydrolysis of dissolved iron and manganese (Cravotta and Kirby, 2003). Acidity, as described here, is the total base required to neutralize a solution including the hydrolysis of iron (reactions 2 and 3), manganese (reaction 8), and aluminum (reaction 9) (Hedin and others, 1994a).

$$Mn^{2+} + 0.5O_2 + H_2O \rightarrow MnO_2(s) + 2H^+$$
 (8)

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$$
 (9)

Acidity is measured by analytical methods (U.S. Environmental Protection Agency, 1979; Fishman and Friedman, 1989) that measure all acidity that must be neutralized to successfully treat AMD. Net-alkaline samples have alkalinity in excess of acidity and, conversely, net-acidic samples have acidity in excess of alkalinity. The characterization of AMD and selection of remediation options should, therefore, consider alkalinity and acidity as well as pH and the concentrations of dissolved metals. Acidity also may be calculated (Hedin and others, 1994a; Rose and Cravotta, 1998; Skousen and others, 1998).

Acidity_{calculated} [mg/L (milligrams per liter) as CaCO₃] =

$$50[10^{(3-pH)} + 2C_{Fe}/55.85 + 2C_{Mn}/55.94 + 3C_{A1}/26.98]$$
 (10)

where C_i is the concentration of metal i (Fe, Mn, or Al). Calculated acidity can be used to estimate net alkalinity:

Net alkalinity (mg/L as
$$CaCO_3$$
) =
Alkalinity – Acidity_{calculated} (11)

The estimated net alkalinity should have similar values to the measured analytical acidity (Cravotta and Kirby, 2003).

Mine Drainage and Stream Remediation

Sugar Creek is listed by the Missouri Department of Natural Resources (2000) as a Class P (perennial prairie type) stream and is classified as a "limited" warm-water fishery. Sugar Creek is subject to antidegradation policies for existing beneficial uses, including livestock and wildlife watering, protection of warm-water aquatic life, and the protection of human health associated with fish consumption. A 4.35-km segment of Sugar Creek is listed as impaired as a result of AMD under the Clean Water Act TMDL program (Missouri Department of Natural Resources, 2002) (fig.1). Data collected by Missouri Department of Natural Resources (2002) during 2000-2002 reported pH values in Sugar Creek less than the allowable range of 6.5 to 9.0 on several occasions. Implementation under the TMDL program would require pH values to be 6.5 to 9.0 and alkalinity to be at least 90 mg/L (milligrams per liter) as calcium carbonate (CaCO₃). The intent of the TMDL program is to determine the amount of a contaminant that a stream can assimilate without exceeding water-quality standards. In the case of Sugar Creek, small pH is episodic. During periods of low discharge, when pH values may be small, large metal concentrations (mainly iron, but also aluminum and manganese) in the AMD are not being diluted sufficiently by stream water in Sugar Creek, which characteristically has larger pH values and alkalinity than the AMD. The target value of 90 mg/L as CaCO₃ for alkalinity, established by the Missouri Department of Natural Resources, is intended to provide adequate buffering capacity to ensure pH remains larger than 6.5. To meet the target value for alkalinity and eliminate small pH episodes in Sugar Creek, the effect of individual AMD sources on water quality was assessed quantitatively to help determine appropriate remedial options.

Under Missouri's Water Quality Standards General Criteria (Missouri Department of Natural Resources, 2000) that are "...applicable to all waters of the state at all times...":

"...Waters shall be free from substances in sufficient amounts to cause the formation of putrescent, unsightly or harmful bottom deposits or prevent full maintenance of beneficial uses;"

"...Waters shall be free from substances in sufficient amounts to cause unsightly color or turbidity, offensive odor or prevent full maintenance of beneficial uses;"

"...Waters shall be free from physical, chemical or hydrologic changes that would impair the natural biological community...".

Reaches of the tributary streams downstream from the mine springs in the Huntsville Gob and Calfee Slope subbasins and Mitchell Mine Basin (fig. 1) may require remediation based on these criteria and large iron and aluminum, and possibly nickel and zinc concentrations in excess of Missouri's Water Quality Standards for protection of aquatic life (Missouri Department of Natural Resources, 2000).

Restoration of water quality in mining effected areas involves both land reclamation and treatment of AMD. In the past, numerous occurrences of ground subsidence and red, acidic water have been reported in Huntsville and the surrounding area by local residents. An open limestone channel (OLC) in the Huntsville Gob drainage and the typical red staining associated with AMD are shown in figure 7. Site HG-6S (fig. 1) shows iron and possibly aluminum flocculants and precipitates that clog stream beds, which are detrimental to aquatic life, and may be considered the "unsightly" effects of AMD (fig. 8).

Acidic surface runoff to streams from mine spoil was aggravated by AMD emerging from underground coal mines. Other reported problems included steep and unstable banks of coal waste and burning coal and coal wastes. The Missouri Department of Natural Resources conducted reclamation projects on abandoned mine land totaling 44.1 ha (hectares) in the Huntsville area from 1983 to 1994. During the same period, several mine shafts were plugged and entrances to abandoned mines were closed or otherwise remediated. Acidity problems in Sugar Creek are now less serious than before reclamation largely because of the removal of coal wastes and decreased potential for acid generation during run-off events at the Huntsville Gob (Missouri Department of Natural Resources, 2002). However, the potential for acidity problems still exists for the 4.35 km of Sugar Creek downstream from its confluence with the Huntsville Gob drainage (fig. 1) because of AMD from ground-water seeps in the reclaimed areas and continued contributions of AMD from flooded underground mines discharging to tributary streams. Sugar Creek usually dilutes the AMD, maintaining a pH value larger than 6.5 in the creek, except during periods of extreme low discharge when water quality in the creek declines.

Conventional or "active" treatment of AMD involves aeration of the affected water and the addition of alkalinity using strong chemicals such as soda ash (NaHCO₃) or caustic soda (NaOH) (Skousen and others, 1998). These treatment approaches often are cost prohibitive because of expensive chemicals and ongoing labor and maintenance outlays. Alternatively, "passive" treatment options for AMD can be used that include wetlands or settling ponds and some form of limestonebased alkalinity generating system (Turner and McCoy, 1990; Hedin and others, 1994a; Hedin and others, 1994b; Ziemkiewicz and others, 1997; Skousen and others, 1998; Cravotta and Trahan, 1999; Watzlaf and others, 2000). The addition of limestone to mine drainage can be effective for the neutralization of AMD and attenuation of metal transport. As pH increases with increased alkalinity to near-neutral values, concentrations of some soluble metals, including Fe³⁺ and Al³⁺ decrease; however, concentrations of sulfate, Fe²⁺, and Mn²⁺ may not be affected (Blowes and Ptacek, 1994; Cravotta and Trahan, 1999). Generally, for AMD as documented in the Sugar Creek Basin (Wertis and Elifrits, 1984; Blevins and Ziegler, 1992; Missouri Department of Natural Resources, 2002), alkalinity generating systems such as anoxic limestone drains (ALDs), successive alkalinity producing systems (SAPS), or OLCs, can be appropriate to treat AMD. Mine drainage that is net-alkaline may require the use of aerobic wetlands or other means of oxygen introduction into the system to precipitate metals (Skousen and others, 1998). The treatment or combination of treatments determined as appropriate for a particular source of AMD largely is dependent on the initial net alkalinity (equation 11), dissolved oxygen, and metal concentrations of the water to be treated. "Passive" treatment systems generally

10 Assessment, Water Quality, and Options for Remediation of Acidic Drainage from Abandoned Coal Mines near Huntsville, MO



Figure 7. Acidic mine drainage in an open limestone channel downstream from the Huntsville Gob reclamation project looking north from sampling site HG-7S.



Figure 8. Iron and possibly aluminum flocculants and precipitates that clog stream beds on the east side of the Huntsville Gob reclamation project. These are detrimental to aquatic life, and may be considered the "unsightly" effects of acidic mine drainage.

have slower rates of AMD neutralization and contaminant removal than "active" treatment systems, but can have lower maintenance costs (Skousen and others, 1998).

An assessment of the hydrologic and chemical characteristics of the AMD sources and receiving streams in the Sugar Creek Basin was undertaken in this study to determine the relative effects on water quality and to compare the geochemical merits of different "passive" treatment options. A flowchart of passive-treatment options (Hedin and others, 1994a; Skousen and others, 1998; Pennsylvania Department of Environmental Protection, 1999; Cravotta and Kirby, 2003) based on the previously discussed principles can help direct the decision making process for choosing an appropriate treatment is shown in figure 9.



Figure 9. Options for the passive treatment of acidic mine drainage.

Acknowledgments

The author thanks Paul Behum, U.S. Department of the Interior, Office of Surface Mining, for assistance with defining and assessing remedial priorities and options and sharing his experience with the treatment of AMD in Missouri.

Methods

Water-Quality Site Selection, Sampling, and Analysis

Based on historic data and initial field reconnaissance (July 8 to 9 and 22 to 24, 2003), and water-quality sampling completed in September 2003, a sampling schedule and plan were established. Sampling sites, schedules, and analytes are presented in table 1. Locations of AMD sources, previouslysampled stream sites, and when possible, historic-data sites, were located and documented using hand-held global positioning system (GPS) equipment and a digital camera. Field measured pH, specific conductance, and water temperature had been recorded during the two preliminary site visits in July 2003 to assist in the identification of AMD sources. Sampling sites have been designated by two letters followed by a number and a letter (table 1, column 1). The first two letters indicate the basin or subbasin; SC, Sugar Creek; HG, Huntsville Gob subbasin; MC, Middle Creek subbasin; CS, Calfee Slope subbasin; MM, Mitchell Mine Basin; or MW, monitoring well. The assigned numbers following the two letters increase downstream within each basin or subbasin. The last letter indicates the water source; M for mine spring or S for stream site. Sampling site numbers are assigned for identification purposes only and are unique to this study. A station identification number also was assigned to each of the sampled sites in the U.S. Geological Survey National Water Information System (NWIS) database (table 1, column 2).

Water-quality samples, discharge, and field measurements of physical properties were collected synoptically at all AMD sites with measurable discharge and selected stream sites during a period of stable high baseflow and no precipitation (September 4 to 11, 2003). Although a total of approximately 14 cm of rain was recorded at Moberly, Missouri, between August 29 and September 1, 2003 (fig. 4), measured discharges for Sugar Creek and its tributary streams were stable during the synoptic sampling. Of the 54 mine springs and surface-water sites sampled during reconnaissance and the initial sampling in September 2003, 41 sites were selected for additional sampling in January, March, and June 2004 to characterize seasonal or temporal variation in discharge and water quality. Additional samples for geochemical modeling were collected at selected sites in December 2003 (table 1). Discharge and water-quality data were collected at AMD sites with measurable discharge and selected surface-water sites during the synoptic sampling in September 2003.

Four monitoring wells (MW 04-01, 04-02, 04-03, and 04-04, fig. 1 and table 1) were installed and developed in June and July 2004 to sample underground mine water. Monitoring wells 04-01, 04-02, and 04-03 located in the Huntsville Gob subbasin were drilled to the top of the Ardmore Limestone (fig. 5) from 14.7 to 21.9 m below land surface and cores were collected to verify the stratigraphy. These three wells encountered voids at depths corresponding to the Bevier-Wheeler coals. The screened interval (1.5 to 4.5 m in length) for the wells was set to intercept underground mine water at the level of the voids, and the pipe annulus above the screen was sealed with cementbentonite grout to 1 m below land surface. Site MW 04-04 was drilled in the Calfee Slope subbasin, upgradient from mine spring site CS-5M (fig. 1) to 3.7 m below land surface at the top of the Ardmore Limestone. No voids were encountered. Screen was installed in the lower 1.5 m and the well was completed as described above. All wells were developed and initially sampled upon completion for dissolved oxygen, pH, oxidationreduction potential (Eh), specific conductance, water temperature, alkalinity, sulfate, aluminum, dissolved iron, and manganese. Samples were collected using a stainless steel submersible pump, Teflon^{®b} tubing, and cartridge filters. Monitoring wells 04-01, 04-02, and 04-03 were resampled in August 2004 for data used in geochemical modeling and analyzed for the constituents shown in table 1.

Field measurements of discharge, dissolved oxygen, pH, Eh, specific conductance, and water temperature were made in accordance with the U.S. Geological Survey's standard methods using field calibrated instruments (Rantz and others, 1982; U.S. Geological Survey, 1997, 2004a). Grab samples were collected as close as possible to AMD sources and for stream samples where flow was well mixed. The samples were then transported immediately to a mobile laboratory at a central location where alkalinity and bicarbonate concentrations were determined by digital incremental titration with sulfuric acid (0.16 or 1.6N H₂SO₄). Samples for analyses not requiring filtration [alkalinity, acidity, and total organic carbon (TOC)] were collected in sample-rinsed polyethylene bottles. Total recoverable metal samples were collected in acid-rinsed polyethylene bottles and preserved with nitric acid (HNO₃). Samples for major anions were filtered directly from the AMD source or stream using a syringe, filter holder, and a 47-mm (millimeter) diameter mixed cellulose ester filter with a 0.45-µm (micrometer) pore size and immediately transferred to a sample-rinsed polyethylene bottle. Samples for dissolved metals were filtered in the same manner and transferred to acid-rinsed polyethylene bottles and preserved with nitric acid. Alternatively, when possible or when large sediment and algal concentrations made the syringe filter method impractical, samples were filtered using a peristaltic pump and 0.45-µm Geotech®c cartridge filter directly from the source or from samples collected in 1-L (liter) polyeth-

^bRegistered trademark of EI du Pont de Nemours & Co.

^c Registered trademark of Geotech Environmental Equipment, Inc., Denver, Colorado.

Table 1. Location of surface water, mine springs, and underground mine sample sites near Huntsville, Missouri, sampling schedule, and constituents analyzed during 2003–2004.

[NWIS, National Water Information System; UTM, Universal Transverse Mercator; L, lake; F, field measurements of physical properties; --, no data; S, stream; MI, major ions; G, geochemical modeling; M, mine spring; E, sewage effluent; W, monitoring well]

Site	NWIS	Loca in UTM co	tion, oordinates		Sample/field measurements ^b							
(fig. 1)	station number	Northing	Easting	Туре	Jul-03	Sep-03	Dec-03	Jan-04	Mar-04	Jun-04	Jul/Aug-04	
SC-1S	392827092284601	4369519	544772	L	F							
SC-1.1S	392817092290201	4369229	544390	S	F							
SC-2S	392811092291201	4369030	544143	S	F	F,MI	F	F	F	F		
SC-3S	392716092312301	4367327	541044	S	F	F,MI		F	F	F		
SC-4S	392713092281101	4367250	545623	S		F						
SC-4.7S	392703092292701	4366932	543808	S		F						
SC-4.8S	392701092300501	4366865	542901	S		F						
SC-4.9S	392704092303501	4366953	542183	S		F						
SC-5S	392716092312201	4367317	541070	S		F,MI		F	F	F		
SC-6S	392716092312401	4367318	541018	S			F,MI,G	F,MI	F,MI	F,MI		
HG-2M	392634092310101	4366010	541576	М	F	F,MI,G	F,MI,G	F,MI	F,MI	F,MI,G	F,MI,G	
HG-3S	392637092310501	4366133	541492	S		F,MI		F,MI	F	F		
HG-4M	392637092310401	4366139	541497	М	F	F,MI,G	F,MI,G	F,MI	F,MI	F,MI		
HG-5S	392636092310301	4366087	541519	S		F						
HG5.5S	392634092310201	4366010	541538	S		F						
HG-6S	392638092305701	4366149	541662	S		F			F			
HG-6.9S	392638092310401	4366151	541490	S		F,MI	F	F	F	F		
HG-7S	392638092310501	4366163	541466	S		F.MI	F.MI,G	F.MI	F,MI	F.MI.G	F,MI	
HG-8S	392648092312201	4366469	541057	S				F	F	F		
HG-10S	392648092312301	4366467	541042	S				F	F	F		
HG-11S	392707092312201	4367040	541062	S		F.MI		F.MI	F.MI	F.MI		
HG-12S	392719092313301	4367408	540802	S				F	F	F		
SC-7S	392723092313801	4367531	540670	S		F.MI	F.MI	F.MI	F.MI	F.MI		
MC-2S ^c	392655092320301	4366665	540081	S	F							
MC-3M ^c	392658092320001	4366758	540153	М	F							
MC-3.3S	392659092320001	4366789	540153	S	F	F						
MC-4S ^c	392702092315901	4366881	540176	S	F							
MC-4 9S	392703092320101	4366912	540128	S	F	F						
MC-5S ^c	392704092320001	4366943	540152	S	F	F						
SC-8S ^c	392736092323801	4367915	539246	S	F	FMI		F	F	F		
CS-2S ^c	392635092322401	4366033	539578	S		FMI		F	F	F		
CS-2 5M	392636092322401	4366076	539535	M		F					_	
CS-2.6M	392636092322701	4366076	539511	M		F						

Table 1. Location of surface water, mine springs, and underground mine sample sites near Huntsville, Missouri, sampling schedule, and constituents analyzed during 2003-2004.-Continued

[NWIS, National Water Information System; UTM, Universal Transverse Mercator; L, lake; F, field measurements of physical properties; --, no data; S, stream; MI, major ions; G, geochemical modeling; M, mine spring; E, sewage effluent; W, monitoring well]

Site number ^a	NWIS	Location, in UTM coordinates			Sample/field measurements ^b							
(fig. 1)	station number	Northing	Easting	Туре	Jul-03	Sep-03	Dec-03	Jan-04	Mar-04	Jun-04	Jul/Aug-04	
	202(20002222201	10//151	5202(0	G	F	E 1 <i>G</i>						
CS-3S°	392639092323301	4366171	539360	S	F	F,MI		F	F	F		
CS3.1M	392637092323401	4366106	539343	М		F						
CS3.2M	392640092323401	4366199	539343	S		F						
CS-3.9M	392645092323801	4366352	539247	М		F						
CS-4S ^c	392647092323801	4366414	539253	S		F,MI		F	F	F		
CS-4.9M ^c	392648092324101	4366444	539175	Μ		F						
CS-5M ^c	392647092323701	4366426	539260	М	F	F,MI,G	F,MI	F,MI	F,MI	F,MI		
CS-6S ^c	392648092323701	4366451	539270	S		F,MI		F	F	F		
CS-7S ^c	392710092323901	4367129	539223	S		F,MI		F	F	F		
CS-8S ^c	392712092323901	4367200	539221	Е	F	F,MI,G		F,MI	F,MI	F,MI		
CS-9S ^c	392729092323801	4367712	539240	S	F	F,MI		F,MI	F,MI	F,MI		
SC-9S ^c	392732092324901	4367815	538969	S		F,MI,G		F,MI	F,MI	F,MI		
SC-10S	392745092332401	4368186	538129	S	F							
MM-2S ^c	392608092323801	4365215	539250	S		F.MI	F	F	F	F		
MM-3M ^c	392609092323701	4365249	539281	М	F	F.MI.G	F.MI	F.MI	F.MI	F.MI		
MM-4S ^c	392610092323801	4365267	539245	S		F.MI	F	F	F	F		
MM-4.1M ^c	392609092323801	4365247	539242	ŝ			F					
MM-4.4S ^c	392614092324701	4365408	539027	S	F							
MM-5S ^c	392627092333401	4365803	537906	S		FMI	F	F	F	F		
MM-6S ^c	392627092333301	4365797	537930	F	F	FMIG	FMI	FMI	FMI	FMI		
MM-7S ^c	392627092333501	4365788	537906	S		FMI	F	F	F	F		
WINI-75	572027072555501	+303700	557700	5		1,1111	1	1	1	1		
MW 04-01	392616092304201	4365473	542018	W						F	F,MI,G	
MW 04-02	392629092310101	4365874	541566	W							F,MI,G	
MW 04-03	392626092310101	4365767	541576	W							F,MI,G	
MW 04-04	392646092323601	4366397	539298	W							F,MI	

^aThe first two letters represent the basin; SC, Sugar Creek; HG, Huntsville Gob; MC, Middle Creek; CS, Calfee Slope; and MM, Mitchell Mine; and MW, monitoring well; the final letter represents the type of sampling site; S, stream; and M, mine spring.

^bF (field measurements); pH, specific conductance, oxidation-reduction potential (Eh), dissolved oxygen, and temperature; MI (major ions); constituents for F plus dissolved iron (Fe), manganese (Mn), aluminum (Al), sulfate (SO₄), alkalinity and/or acidity; G (geochemical modeling samples); constituents for F and MI plus hardness, calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), chlorine (Cl), silica (SiO₂), ammonia as nitrogen (NH₃), nitrite plus nitrate as nitrogen (NO₂+NO₃), orthophosphorus as phosphorus (PO₄), total Al, barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), total Fe, lead (Pb), lithium (Li), total Mn, molybdenum (Mo), nickel (Ni), silver (Ag), strontium (Sr), vanadium (V), and zinc (Zn).

^cData-collection site for the Blevins and Ziegler (1992; fig. 4) study.

ylene bottles. Ferrous iron samples were filtered with a syringe and 0.1-µm mixed cellulose ester filter and preserved with hydrochloric acid (HCl). Nutrient samples were filtered with a 47-mm mixed cellulose ester filter or cartridge filter with a 0.45-um pore size and immediately transferred to opaque polyethylene bottles. All samples were stored at 4 °C or less and shipped within 48 hours for laboratory analysis. Major ions, metals, and nutrients were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado, by inductively-coupled plasma (ICP), ion chromatography (IC), colorimetry, and electrometric titration following methods of Fishman and Friedman (1989) and Fishman (1993). Acidity was determined by electrometric titration and samples were analyzed at the Ocala Water Quality and Research Laboratory in Ocala, Florida, following methods of Fishman and Friedman (1989) and starting in July 2004 by Severn Trent Laboratories in Arvada, Colorado, following methods of the U.S. Environmental Protection Agency (1979). Dissolved total iron and ferrous iron concentrations were determined by colorimetric analysis following methods adapted from Ball and others (1999) at the U.S. Geological Survey laboratory in Lee's Summit, Missouri. Dissolved total iron also was determined by ICP at the National Water Quality Laboratory. Ball and Nordstrom (1994) determined that colorimetric determination of dissolved total iron using FerroZine^{®d} was more accurate, precise, and sensitive than ICP methods. Comparison of ICP and colorimetrically determined total dissolved iron concentrations from this study indicated general agreement with a coefficient of determination (r^2) of 0.98 and slope of 1.07 (fig. 10).

Ferric iron concentrations were calculated by the difference in values of ferrous iron concentrations and total dissolved iron concentrations determined by colorimetry, and used in the computation of Eh for comparison with Eh values measured by platinum electrode in the field in accordance with U.S. Geological Survey standard methods (U.S. Geological Survey, 1997). Dissolved iron concentrations from the National Water Quality Laboratory were used in all other computations.

Approximately 10 percent of all samples collected were quality control and assurance samples (data not presented). Concentrations for replicate samples indicated precision within 5 percent for all analyzed constituents. However, reanalysis of five samples with total iron concentrations smaller than dissolved iron concentrations and large ionic strengths indicated a 10 to 15 percent variation in total iron concentrations for three samples from the original reported values. Differences in analysis methods for total and dissolved iron and potential errors from sample dilution before analysis because of large ionic strength were likely sources of the error (L.K. Kenagy, U.S. Geological Survey, National Water Quality Laboratory, written commun., 2004). Total iron was not analyzed in the majority of samples (table 1), so dissolved iron concentrations could not be compared with the total concentrations in most samples; therefore, large dissolved metal concentrations, particularly iron and manganese should be considered approximate.

Charge-balance errors as large as 33 percent occurred in some large ionic-strength samples. Adjustments in sulfate concentration have been used to correct for potential errors, for example dilution errors, associated with an analytical method (Cravotta, 1994). If the initial charge balance computed was larger than plus or minus (\pm)5 percent, sulfate concentrations were adjusted to achieve a charge balance within \pm 1 percent for geochemical modeling.

For each sampling event, highly purified water (either deionized water or certified inorganic free blank water) was used for field blanks that were collected, processed, preserved, transported, and handled by identical methods to those used for environmental samples. The blank samples had concentrations less than detection limits for most analytes. Two of the four field blank samples from the synoptic sampling events, however, indicated detectable concentrations of some analytes (including sulfate, aluminum, iron, and manganese) that were either near the reporting limits for the analyte or small relative to the concentrations in the environmental samples being collected during the concurrent sampling event. Measurable concentrations in blank water can result from trace amounts of constituents in the blank water or residual contamination of the sampling or analytical equipment. The blank sample data support the conclusion that sample collection and processing procedures are an inconsequential source of bias to the sample data.

Cubitainer Experiments, Geochemical Modeling, and Calculation of Loads

In addition to the evaluation of field data, 17 cubitainer experiments using water from mine spring sites CS-5M and HG-2M, downstream surface-water site HG-7S, and three monitoring wells, MW 04-01, 04-02, and 04-03 (fig. 1), were used to study the qualitative and quantitative effects of limestone dissolution on alkalinity addition to environmental samples. In accordance with methods of Watzlaf and Hedin (1993) and Cravotta (2003), collapsible 3.78-L polyethylene cubitainers were filled to approximately two-thirds capacity with 4 kg (kilograms) of 2.5-cm screened and sorted limestone fragments obtained from a local quarry (fig. 11). The limestone fragments were thoroughly rinsed with tap water and air dried before being loaded into the cubitainers. At the start of the experiments, 2.5 L of sample water was added to near capacity of the cubitainers with limestone and any trapped air expelled. The porosity created by the limestone fragments was determined to be 45 percent by measuring the volume of water displaced in an 18.9-L bucket packed with the limestone fragments. The cubitainers were then sealed with a rubber stopper to minimize gas exchange.

Field samples of water (influent) were collected into empty cubitainers leaving no headspace and immediately transported to a mobile laboratory at a centralized location. Within 1 hour, these samples were used to fill the experimental cubitain-

^dRegistered trademark of the Hach Company, Loveland, Colorado.



Figure 10. Relation of dissolved total iron concentrations determined by inductively coupled plasma methods and by colorimetric methods.

ers. Experiments were conducted under circulated and uncirculated conditions for comparison of alkalinity addition rates. Circulation was maintained by peristaltic pump (fig. 11) at a nominal rate of 0.1 to 0.5 L/min (liter per minute). During each experimental round, one or more unsealed cubitainers were used to simulate OLCs, and were compared with sealed cubitainers to simulate enclosed ALDs. Samples were maintained at room temperature (20 to 25 °C). At the completion of the exper-



Modified from Cravotta (2003)

Figure 11. Cubitainer setup used for experiments to evaluate alkalinity addition rates.

iments, samples were withdrawn from each cubitainer for laboratory analysis of dissolved iron, manganese, aluminum, and sulfate.

Experiments consisted of five to seven cubitainers during each of three experimental rounds. One duplicate cubitainer containing a replicate water sample with limestone fragments and one control cubitainer without limestone fragments were included in each experimental round. For the duration of the individual experiments (48 to 72 hours), samples were withdrawn through a valve by syringe from the bottom of the cubitainers and immediately analyzed for pH and alkalinity. At the beginning of the experiment, samples were withdrawn and analyzed for alkalinity every 1 to 1.5 hours for the first 4 hours. Because the alkalinity changed little with prolonged contact time after this initial period, the sample interval was expanded to approximately 4 hours for the remainder of the first 24 hours and 8 to 12 hours thereafter.

The computer program PHREEQC (Parkhurst and Appelo, 1999) [PHREEQC is public domain software. PHREEQCI, version 2.10 (the version used in this study), is documented and available online from the U.S. Geological Survey (2004b)] was used with thermodynamic data from the database WATEQ4F (Ball and Nordstrom, 1991) to compute aqueous speciation and mineral saturation indices from water-quality data, and to calculate the composition of the final mixture after mixing AMD with stream water or sewage effluent. Field data used in the computation of saturation indices are presented in table 2. The chemical composition, temperature, calculated oxidation-

Site number (fig. 1)	Date	Discharge, instanta- neous (L/s)	Discharge, instanta- neous (ft ³ /s)	Dissolved oxygen (mg/L)	pH (SU)	Eh (volts)	pe ^a	Specific conductance (µS/cm)	Temperature (°C)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Alkalinity, as calcium carbonate (mg/L)
SC-6S	12/29/2003	394	13.9	14.9	78	0.37	63	508	3.0	65.6	16.3	4 36	93	118
HG-2M	09/11/2003	28	01	10	4.6	44	0.5 7 4	3 350	15.5	445	171	13.4	72.9	
110 2101	12/29/2003	.20	.01	1.0	4.6	42	7.4	3 490	11.0	410	140	12.4	63.8	21
	06/08/2004	.12	.01	1.9	4.5	.12	8.6	2,970	13.5	431	147	E12.0	66.4	25
	08/30/2004	.32	.01	.0	4.5	.39	6.6	3,470	15.2	445	139	E5.30	62.0	17
HG-4M	09/11/2003	.11	.004	13.2	2.7	.60	10.1	6.320	19.8	285	126	<.480	16.0	
110 111	12/30/2003	.08	.003	3.3	2.9	.59	10.0	7,180	9.9	420	182	<32.0	24.3	
HG-7S	12/30/2003	E>1.5	E>.05	7.6	4.4	.52	8.8	3.300	1.3	314	112	E6.78	38.6	11
	06/08/2004	.73	.03	5.1	3.0	.61	10.3	4.550	22.7	482	189	E10.8	63.5	
CS-5M	09/09/2003	1.2	.04	6.8	5.2	.33	5.6	3,540	13.8	448	279	31.8	207	34
CS-8S	09/08/2003	.71	.03	>20.0	10.7	.29	4.9	752	27.0	69.6	17.1	11.1	38.9	139
SC-9S	09/08/2003	15	.54	6.4	7.5	.35	5.9	605	19.8	73.7	19.2	6.10	13.6	95
MM-3M	09/05/2003	E2.6	E.09	<.1	5.9	.21	3.5	2,580		323	156	23.6	87.4	160
MM-6S	09/04/2003	E23	E.81	6.6	8.8	.40	6.8	706	23.9	63.9	15.8	12.6	47.4	142
MW 04-01	08/31/2004			.1	6.2	.27	4.5	4,600	14.7	543	377	23.1	237	508
MW 04-02	08/31/2004			.0	4.2	.43	7.3	7,520	14.5	434	294	17.6	81.6	
MW 04-03	08/31/2004			.0	4.8	.40	6.7	4,670	14.0	454	268	12.5	71.0	

Table 2.	Values for selected physical	I properties and dissolved constit	uent concentrations used in the com	putation of saturation indices and (geochemical mixing calculations.
					J

[L/s, liters per second; ft³/s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; --, no data; E, estimated; <, less than; >, greater than]

Site number (fig. 1)	Date	Chloride (mg/L)	Silica (mg/L)	Sulfate (mg/L)	Sulfate (adjusted) ^b (mg/L)	Sulfate (adjusted) ^c (percent)	Ammonia, as nitrogen (mg/L)	Nitrite plus nitrate, as nitrogen (mg/L)	Phosphate, as phosphorus (mg/L)	Aluminum (mg/L)	Barium (mg/L)	Beryllium (mg/L)	Cadmium (mg/L)	Chromium (mg/L)
SC-6S	12/29/2003	8.10	4.55	112			0.016	0.379	0.016	0.056	0.052	< 0.0004	< 0.003	0.005
HG-2M	09/11/2003	16.3	24.1	3,850	2,940	-24	3.48	<.022	.016	E43.8	<.080	<.016	<.080	<.200
	12/29/2003	14.5	24.0	3,550	2,700	-24	2.69	<.016		42.2	<.100	<.020	<.160	<.210
	06/08/2004	14.2	24.5	3,920	2,640	-33	2.70	.019		E31.3	<.200	<.040	<.320	<.420
	08/30/2004	10.1	29.2	2,590			2.68	.180	<.09	29.6	<.100	<.020	<.160	<.210
HG-4M	09/11/2003	21.1	77.5	10,300	7,250	-30	5.90	<.022	.750	E488	.037	.032	<.006	E.007
	12/30/2003	13.8	101	9,040	6,990	-23	5.09	<.016	.438	378	<.400	<.080	<.640	<.840
HG-7S	12/30/2003	9.62	24.1	2,860	2,480	-13	1.95	.048	.020	64.2	<.100	<.020	<.160	<.210
	06/08/2004	12.9	41.4	7,310	4,490	-39	4.04	.041		E130	<.200	<.040	<.320	<.420
CS-5M	09/09/2003	16.6	47.7	4,130	3,530	-15	3.32	<.022		E.727	.013	<.001	<.006	<.015
CS-8S	09/08/2003	51.7	13.9	154			2.20	.292	.044	E.028	.022	<.0004	<.002	E.003
SC-9S	09/08/2003	8.42	7.80	199			.222	.154	<.007	.065	.051	<.0004	<.002	E.003
MM-3M	09/05/2003	21.5	25.2	1,920	1,750	-9	1.53	<.022	<.007	E.050	<.050	<.010	<.050	<.125
MM-6S	09/04/2003	65.6	12.8	114			2.50	.050	.990	E.018	.013	<.0004	<.002	<.005
MW 04-01	08/31/2004	16.8	12.5	2,620	2,910	11	3.15	<.016	<.090	.011	<.050	<.010	<.080	<.105
MW 04-02	08/31/2004	10.1	26.6	6,030			5.04	<.016	.235	151	E.044	E.011	<.080	<.105
MW 04-03	08/31/2004	6.37	15.4	3,240			1.97	<.016	<.090	9.75	E.018	<.010	<.032	<.042

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Table 2. Values for selected physical properties and dissolved constituent concentrations used in the computation of saturation indices and geochemical mixing calculations.—Continued

Π_{s} , liters per second: ft ³ /s, cubic feet per second: mg/	L. milligrams per liter: SU, standard units:	18/cm, microsiemens per centimeter at 25 de	egrees Celsius: °C, degrees Celsius:	no data: E. estimated: <. less than: >. greater than]
[Ers, news per second, it 75, easie reet per second, ing)	E, minigrans per mer, 50, standard ants,	as/em, merosiemens per centimeter at 25 ac	egrees censius, e, degrees censius,	no data, E, estimated, <, less than, >, greater than]

Site number (fig. 1)	Date	Cobalt (mg/L)	Copper (mg/L)	lron (mg/L)	Lead (mg/L)	Lithium (mg/L)	Manganese (mg/L)	Molybdenum (mg/L)	Nickel (mg/L)	Silver (mg/L)	Strontium (mg/L)	Vanadium (mg/L)	Zinc (mg/L)
SC-6S	12/29/2003	E0.001	< 0.005	0.049	< 0.0001	0.005	0.284	0.007	0.009	< 0.003	0.198	< 0.005	0.005
HG-2M	09/11/2003	<.120	<.280	461	.0004	.196	10.3	<.160	.280	<.200	1.40	<.240	.616
	12/29/2003	<.130	<.003	463	.0003	.175	9.35	<.200	.302	<.140	1.23	<.230	.544
	06/08/2004	<.260	<.500	422	.0003	E.174	9.17	<.400	E.143	<.280	1.36	<.460	.482
	08/30/2004	<.130	<.250	416	.0003	.179	8.36	<.200	.144	<.140	1.32	<.230	<.150
HG-4M	09/11/2003	.433	<.021	1,780	<.0004	.671	28.9	<.012	1.59	<.015	.170	<.018	4.40
	12/30/2003	E.377	<1.00	1,720	E.0002	.727	27.7	<.800	2.24	<.560	.371	<.920	5.72
HG-7S	12/30/2003	E.084	<.250	494	<.0002	.190	9.88	<.200	.438	<.140	.609	<.230	1.01
	06/08/2004	E.500	<.500	894	.0003	.380	20.3	<.400	.720	<.280	.986	<.460	1.97
CS-5M	09/09/2003	<.009	<.021	525	<.0002	.388	11.1	<.300	E.018	<.015	.762	<.018	.062
CS-8S	09/08/2003	<.003	<.007	E.005	<.0001	.010	.003	<.004	E.006	<.005	.230	<.006	<.003
SC-9S	09/08/2003	<.003	<.007	.026	<.0001	.017	.881	<.004	.008	<.005	.221	<.006	<.003
MM-3M	09/05/2003	<.009	<.175	179	<.0002	.198	3.47	<.100	E.012	<.125	1.36	<.150	E.048
MM-6S	09/04/2003	<.003	<.007	.023	<.0001	.009	.269	<.004	<.007	<.005	.193	<.006	<.003
MW 04-01	08/31/2004	<.065	<.125	50	<.0002	.223	1.74	<.100	<.050	<.070	6.19	<.115	<.075
MW 04-02	08/31/2004	E.125	<.125	1,560	<.0002	.373	23.5	<.100	.639	<.070	1.82	<.230	1.30
MW 04-03	08/31/2004	E.042	.050	483	<.0002	.187	7.46	<.040	.251	<.028	2.04	<.115	.468

^ape computed from field measurements of Eh (table 5). pe = Eh*16.9.

^bSulfate concentration adjusted to achieve charge balance within plus or minus (±)1 percent. If the initial charge balance was within ±5 percent the sulfate concentration was not adjusted.

^cAdjusted percent = [(adjusted concentration - initial concentration)/initial concentration]*100.

reduction potential (pe = Eh*16.9), and pH for a sample (table 2) were entered into PHREEQCI to obtain a solution composition and compute saturation indices. Alkalinity concentrations were not analyzed for samples with a pH of less than approximately 4.5. Because some carbon concentration was required for the computation of saturation indices of carbonate minerals, a partial pressure for carbon dioxide (PCO_2) of 10.1 kPa (kilopascals) was assumed.

Charge-balance errors were as large as 33 percent for some samples. As a result sulfate concentrations were adjusted to achieve charge balance for geochemical modeling (table 2). Adjustments ranged from a 9 to 39 percent decrease in sulfate concentrations in 9 samples and an 11 percent increase in one sample. Generally, a 5 percent uncertainty in concentration is approximately 0.02 units in saturation indices. For some minerals, such as gypsum [CaSO₄:2H₂O], which has a saturation index near equilibrium, this may shift the saturation index from indicating slightly supersaturated conditions to indicating slightly undersaturated conditions with respect to the solid phase. For example, the saturation index for gypsum (SI_{gyp}) is calculated from the dissolution reaction:

$$CaSO_{4}:2H_{2}O \rightarrow Ca^{2+} + SO_{4}^{2-} + 2H_{2}O$$

$$SI_{gyp} = \log [\{Ca^{2+}\}\{SO_{4}^{2-}\}/K_{gyp}] = \log \{Ca^{2+}\} + \log \{SO_{4}^{2-}\} - \log K_{gyp}$$
(12)

where brackets {} represent the activity of the indicated species and K_{gyp} is the equilibrium constant for gypsum. Assuming a maximum 40 percent error in sulfate concentration:

 $SI_{gyp} = \log \{Ca^{2+}\} + [\log \{SO_4^{2-}\} + \log (0.60)] - \log K_{gyp}$ or = log {Ca²⁺} + [log {SO₄²⁻} + log (1.40)] - log K_{gyp} where log (0.60) = -0.222 and log (1.40) = 0.146,

so that $SI_{gyp} = -0.2$ to 0.2 should be interpreted as a saturation index near zero. Similar calculations with a 10 percent uncertainty in sulfate concentrations yield values of ± 0.046 for the saturation index.

The saturation index indicates the thermodynamic potential for dissolution or precipitation of a solid phase by water. If the saturation index is a negative number, the water is undersaturated with respect to the solid phase and potentially can dissolve it. If the saturation index is a positive number, the water is supersaturated with respect to the solid phase and potentially can precipitate it.

Computed values of saturation indices for selected solid phases are presented in table 3. Saturation indices for muscovite (K-mica) and other silicate minerals are presented because of the potential for dissolution under surface conditions. However, for some solid phases even though the saturation index is positive, precipitation may not be likely under normal surface temperatures and pressures because of kinetic factors.

One of the proposed methods for treating AMD near Huntsville was to mix AMD discharges with alkaline or nearneutral (pH 6 to 7) stream water or effluent from sewage treatment lagoons located adjacent to the Calfee Slope drainage and the Mitchell Mine drainage (fig. 1). For a mixture of two solutions the concentration of a conservative constituent can be described as:

$$C_{i,3} = [C_{i,1}P_1 + C_{i,2}P_2]/[P_1 + P_2]$$
(13)

where $C_{i,n}$ is the concentration of constituent i in solution n and P_n is the proportion or volume of solution n used in the mixture. A mixing model (Parkhurst and Appello, 1999) with PHREEQCI was used to compute the composition of the resultant solutions based on equation 13. Two solutions were mixed and the proportions adjusted until, through an iterative process, the targeted pH of 6.5 was reached. Because the neutralization of AMD usually does not affect concentrations of sulfate (Rose and Cravotta, 1998), sulfate can be considered relatively conservative in the context of AMD treatment.

Additional mixtures were modeled to simulate the behavior of less conservative and non-conservative constituents during AMD treatment. Mixed solutions were modeled to react with calcite and atmospheric carbon dioxide and oxygen and precipitate mineral phases to simulate settling ponds, OLCs, and oxic limestone drains (OLDs). Atmospheric pressures for PCO_2 of 0.032 kPa and PO_2 of 20.3 kPa were assumed. Mineral phases that may react to equilibrium fairly quickly, such as gypsum, siderite [FeCO₃], amorphous ferrihydrite [Fe(OH)₃ (a)], goethite [FeCOH], amorphous aluminum hydroxide [Al(OH)₃ (a)], gibbsite [Al(OH)₃], birnessite [MnO₂], and manganite [MnOOH], were allowed to precipitate. These simulated results were then compared to the mixtures computed from mass balance equation 13.

Dissolved metal loads are calculated from the sum of sampled iron, manganese, and aluminum concentrations multiplied by the instantaneous discharge:

$$Load_{metal} = [(C_{Fe} + C_{Mn} + C_{Al}) Q]F$$
(14)

where $\text{Load}_{\text{metal}}$ is the dissolved metal load expressed in kilograms per day, C_i is the concentration of metal i (Fe, Mn, or Al) in milligrams per liter, Q is discharge in liters per second, and F equals 0.0864, the conversion factor to kilograms per day. Sulfate loads are calculated in the same manner:

$$Load_{sulfate} = [C_{sulfate}Q]F$$
 (15)

where $\text{Load}_{\text{sulfate}}$ is the sulfate load expressed in kilograms per day and C_{sulfate} is the sulfate concentration in milligrams per liter. However, uncertainties in sulfate concentration can affect the calculation of loads. At constant discharge a given percentage adjustment in sulfate concentration will result in an equal percentage change in the calculated loads. Computed adjustments to sulfate concentrations to achieve sample charge balance were from -39 to 11 percent for 10 samples (table 2).

The loads calculated using equations 14 and 15 are instantaneous loads. The unit kilograms per day was chosen for convenience and because discharge from the mine springs in the Sugar Creek Basin can be stable during limited time periods as

Table 3. Values for selected physical properties and saturation indices^a computed by the program PHREEQCI for selected minerals dissolved in mine springs and ground water.

[Values are unitless; --, insufficient data; (am) or (a), amorphous]

Site number and date sample collected															
		-			HG-2M				HG-4M		CS-5M	MM-3M	MW 04-01	MW 04-02	MW 04-03
Mineral	Chemical formula	-	09/11/2003	12/29/2003	06/08/2004	08/30/2004	Mean ^b	09/11/2003	12/30/2003	Mean ^b	- 09/09/2003	09/05/2003	08/31/2004	08/31/2004	08/31/2004
		pН	4.6	4.6	4.5	4.5	^c 4.5	2.7	2.9	^c 2.8	5.2	5.9	6.2	4.2	4.8
		ped	7.5	7.0	8.6	6.5	^c 6.9	10.1	9.9	^c 10	5.6	3.5	4.6	7.3	6.7
Calcite	CaCO ₃		-3.9	-3.6	-3.5	-3.6	-3.6	-7.9	-7.6	-7.7	-2.8	-1.4	-0.4	-4.8	-3.6
Dolomite	CaMg(CO ₃) ₂		-8.0	-7.4	-7.2	-7.5	-7.5	-15.9	-15.3	-15.6	-5.5	-2.8	7	-9.6	-7.1
Gypsum	CaSO ₄ :2H ₂ O		1	1	1	1	1	2	.0	1	0	2	0	.0	0
Nesquehonite	MgCO ₃ :3H ₂ O		-7.1	-6.8	-6.7	-6.8	-6.8	-11.0	-10.7	-10.8	-5.7	-4.4	-3.3	-7.7	-6.5
Rhodochrosite	MnCO ₃		-3.0	-2.7	-2.6	-2.8	-2.8	-6.4	-6.2	-6.3	-1.8	8	4	-3.6	-2.8
Manganite	MnOOH		-8.3	-8.9	-7.6	-9.7	-8.6	-11.1	-10.7	-10.9	-8.4	-8.9	-7.3	-9.5	-8.7
Birnessite	MnO ₂		-14.5	-15.5	-12.7	-17.0	-14.9	-16.6	-16.2	-16.4	-15.9	-17.7	-14.7	-16.2	-15.4
Siderite	FeCO ₃		-1.6	-1.2	-1.2	-1.4	-1.4	-4.8	-4.7	-4.8	4	.6	.8	-2.0	-1.3
Ferrihydrite	Fe(OH) ₃ (a)		.5	1	1.2	8	.2	-2.0	-1.9	-1.9	.4	0	1.3	5	.3
Goethite	FeOOH		6.1	5.3	6.7	4.7	5.7	3.7	3.5	3.6	5.9	5.5	6.9	5.0	5.8
Melanterite	FeSO ₄ :7H ₂ O		-2.4	-2.3	-2.4	-2.5	-2.4	-1.9	-1.7	-1.8	-2.3	-2.9	-3.5	-1.8	-2.4
Jarosite-H	$(\mathrm{H_{3}O})\mathrm{Fe_{3}(SO_{4})_{2}(OH)_{6}}$		-2.3	-4.8	1	-6.0	-3.3	-1.4	-3.1	-2.3	-5.2	-9.7	-6.4	-3.5	-4.0
Jarosite-Na	NaFe ₃ (SO ₄) ₂ (OH) ₆		.0	-2.3	2.2	-3.9	-1.0	-1.9	-2.7	-2.3	-1.7	-5.8	-2.0	-1.5	-1.4
Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆		3.1	.9	5.3	-1.1	2.0				1.3	-2.6	.9	1.7	1.7
Alunite	$KAl_3(SO_4)_2(OH)_6$		6.8	6.2	5.5	5.3	5.9				5.0	5.3	4.2	5.6	5.7
Alum-K	KAl(SO ₄) ₂ :12H ₂ O		-6.9	-6.8	-7.0	-7.5	-7.0				.7	-9.8	-10.8	-6.1	-7.5
Jurbanite	AlOHSO ₄		1.3	1.3	1.1	1.1	1.2	.4	.5	.5	.1	5	-1.2	1.4	.9
Basaluminite	$Al_4(OH)_{10}SO_4$		3.5	3.6	2.1	2.0	2.8	-12.0	-10.4	-11.2	2.1	4.5	3.2	1.0	2.8
Strontianite	SrCO ₃		-5.9	-5.5	-5.5	-5.6	-5.6	-10.6	-10.1	-10.4	-5.0	-3.2	-1.8	-6.7	-5.4
Barite	BaSO ₄							.6		.6				.8	.4
Unnamed mineral	ZnCO ₃ :H ₂ O		-5.2	-4.9	-4.9		-5.0	-8.2	-7.9	-8.1	-5.1	-3.7		-5.9	-5.0
Unnamed mineral	ZnSO ₄ :H ₂ O		-7.5	-7.6	-7.6		-7.6	-6.5	-6.6	-6.5	-8.5	-8.7		-7.1	-7.6
Adularia	KAlSi ₃ O ₈		-2.1	-2.3	-2.7	-2.8	-2.5				4	.3	4	-3.2	-2.7
Albite	NaAlSi ₃ O ₈		-3.9	-4.1	-4.5	-4.2	-4.2	-9.6	-8.8	-9.2	-2.1	-1.6	-1.9	-5.0	-4.4
K-mica	KAl ₃ Si ₃ O ₁₀ (OH) ₂		4.9	4.2	3.2	3.3	3.9				6.3	8.9	8.0	1.9	4.0
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$		9	-1.4	-2.2	-2.0	-1.7				.7	2.6	1.7	-3.3	-1.8

Table 3. Values for selected physical properties and saturation indices^a computed by the program PHREEQCI for selected minerals dissolved in mine springs and ground water.—Continued

[Values are unitless; --, insufficient data; (am) or (a), amorphous]

								Site number ar	ıd date sampl	e collected					
					HG-2M				HG-4M		CS-5M	MM-3M	MW 04-01	MW 04-02	MW 04-03
Mineral	Chemical formula		09/11/2003	12/29/2003	06/08/2004	08/30/2004	Mean ^b	09/11/2003	12/30/2003	Mean ^b	09/09/2003	09/05/2003	08/31/2004	08/31/2004	08/31/2004
		pН	4.6	4.6	4.5	4.5	^c 4.5	2.7	2.9	^c 2.8	5.2	5.9	6.2	4.2	4.8
		ped	7.5	7.0	8.6	6.5	^c 6.9	10.1	9.9	^c 10	5.6	3.5	4.6	7.3	6.7
Chlorite 14Å	$Mg_5Al_2Si_3O_{10}(OH)_8$		-31.0	-33.1	-33.8	-33.1	-32.8	-57.9	-57.4	-57.6	-24.0	-16.8	-12.9	-36.4	-29.5
Kaolinite	$Al_2Si_2O_5(OH)_4$		3.7	3.3	2.7	3.0	3.2	-4.6	-4.3	-4.5	4.0	5.4	4.6	2.0	3.0
Gibbsite	Al(OH) ₃		.7	.5	.2	.3	.4	-3.9	-4.0	-4.0	.6	1.5	1.4	2	.5
Al-hydroxide (am)	$Al(OH)_3(a)$		-2.1	-2.3	-2.6	-2.5	-2.4	-6.7	-6.8	-6.7	-2.2	-1.3	-1.4	-3.0	-2.3
Chalcedony	SiO ₂		.3	.3	.3	.4	.3	.7	1.0	.9	.6	.3	.0	.3	.1
Silica (am)	SiO2 (a)		6	6	6	5	6	1	.1	0	3	6	9	5	8

^aSaturation index (SI), SI = log(IAP/Ksp). Computations performed using PHREEQCI (Parkhurst and Appelo, 1999), version 2.10, with thermodynamic data for IAP (ion activity product) and Ksp (species equilibrium constant) from the database WATEQ4F (Ball and Nordstrom, 1991). Saturation indices are unitless.

^bMean is calculated for sites with two or more sampling events.

^cMeans for pH and pe are calculated from the computed concentrations of H+ and the theoretical value for e- (electron concentration), respectively.

^dpe is calculated from field measurements of Eh (table 5), pe = Eh*16.9.

recorded by Blevins and Ziegler (1992) and observed during this study. Inferences about the size of loads from mine springs during a day or several days may be reasonable, but should not be confused with the average daily loads that commonly are reported.

Assessment of Acidic Mine Drainage and Effects on Receiving Streams

Data from AMD, surface-water, and sewage-effluent sites for which instantaneous discharge, field measurements of physical properties (dissolved oxygen, pH, Eh, specific conductance, and temperature), acidity, alkalinity, sulfate, and major metals concentrations were collected and total metal (aluminum, iron, and manganese) and sulfate loads were calculated are presented in table 4. All sampled sites and data on physical properties and additional constituents are presented in table 5, at the back of this report.

The two primary contributors of AMD to Sugar Creek are from mine springs located in the Huntsville Gob and Calfee Slope subbasins. The Huntsville Gob subbasin drains 2.17 km² and the Calfee Slope subbasin drains 2.28 km². The Middle Creek subbasin drains 1.37 km² (fig. 1). Water from Middle Creek drainage was not observed discharging to Sugar Creek during the September 2003 sampling event, even though mine springs within the subbasin had measurable discharge at that time. The Middle Creek drainage may contribute stored acidity to Sugar Creek during run-off events, but this was not observed during the course of this study. Although AMD degraded water quality in Sugar Creek during July 2003 through June 2004, the pH in Sugar Creek remained within the Missouri Water Quality Standards range of 6.5 to 9.0. Field measurements during the period of study detected one instance of alkalinity less than the targeted alkalinity level of 90 mg/L within the TMDL listed reach of Sugar Creek (fig. 1).

The majority of AMD in the Mitchell Mine Basin can be attributed to a single source; mine spring site MM-3M, near the headwaters of the drainage (fig. 1). Immediately downstream from the mine spring at surface-water site MM-4S the pH was less than 6.5 for three of five samples collected from September 2003 through June 2004, and alkalinity was less than 90 mg/L in September 2003 (table 5).

A graph comparing pH and net alkalinity for all sites sampled from Sugar Creek during the study (fig. 12) shows that the water in Sugar Creek had pH values larger than the targeted TMDL of 6.5 and was net alkaline, whereas the water from AMD sources and their receiving streams mostly had pH values less than 6.5 and was net acidic. Stream water with pH values larger than 6.5 and that was net alkaline was affected by discharges of sewage effluent that typically had alkaline pH values ranging from 7.6 to 10.7.

Huntsville Gob Subbasin

Mine spring sites HG-2M and HG-4M discharge AMD to the Huntsville Gob drainage (fig. 1). Both springs had continuous discharge during the study. Local landowners have observed perennial discharge from site HG-2M from the time a drain and pipe were installed as part of an abandoned mine land remediation project in the early 1990's. Site HG-2M likely discharges AMD from flooded underground mines as well as water from around the drain. Site HG-4M (fig. 1) is located at the base of a large sloping field that has been regraded and capped with topsoil as part of the reclamation project (fig. 6) and likely discharges AMD resulting from water flowing through buried residual coal and other pyritic waste material. The OLCs collect runoff and AMD from diffuse seeps on the perimeter of the reclaimed area. Discharge from individual seeps along the OLCs and seeps to the west of the reclaimed area (fig. 1, HG-5.5S) were not measured because of low discharge volumes. Stream sampling site HG-7S (fig. 1) was located to capture AMD from the majority of the diffuse seeps as well as the combined discharge from the other sampling sites upstream. The upper part of the Huntsville Gob drainage is an OLC that has been reoriented and lined with landscape fabric and limestone rip-rap (boulders) (fig. 1). Surface-water site HG-11S (fig. 1) is located downgradient from all identified AMD sources in the upper 750 m of the Huntsville Gob subbasin and the OLC.

The reclaimed upland areas in the southeast part of the Huntsville Gob subbasin are extensively undermined by two abandoned mine operations that had shafts located nearby (Hinds, 1912; David C. Smith, written commun., 1986). The probability of extensive underground mines in this area is supported by the voids encountered while installing monitoring wells for this study. Iron staining of OLCs at the elevation of the Mulky and Bevier-Wheeler coals may represent seepage from mine voids located below the regraded and remediated land surface. The inferred outcrop line for the Mulky Coal in the reclaimed area of the Huntsville Gob subbasin would be approximately 7 m upslope from the inferred outcrop line for the Bevier-Wheeler Coal as shown in figure 6. The underground mines likely are a substantial source of AMD discharging from sites HG-2M and HG-4M, as well as other smaller seeps.

Mine spring site HG-2M accounted for 31 to 62.5 percent of the combined AMD discharge at downstream site HG-7S for four synoptic sampling events and ranged from 0.28 to 0.42 L/s (liter per second). Median pH at site HG-2M was 4.6, average dissolved oxygen 0.6 mg/L, and the water was net acidic for all measurements (table 4). Mine spring site HG-4M accounted for 6.6 to 25 percent of discharge at site HG-7S for the same four synoptic events with an average discharge of 0.085 L/s. Median pH was 2.7, average dissolved oxygen was 4.4 mg/L, and the discharge was net acidic for all measurements.

Changes in field measurements of physical properties and dissolved metal and sulfate concentrations with distance downstream for the Huntsville Gob drainage for all four synoptic

Site number ^a (fig. 1)	Date	Discharge, instanta- neous (L/s)	Discharge, ^b instanta- neous (ft ³ /s)	Dissolved oxygen (mg/L)	pH (SU)	Eh (volts)	Specific conduct- ance (µS/cm)	Temper- ature (°C)	Acidity, ^c as calcium carbonate (computed) (mg/L)	Alkalinity, as calcium carbonate (mg/L)	Net Alkalinity, ^d as calcium carbonate (mg/L)	Sulfate (mg/L)	Aluminum (mg/L)	Iron (mg/L)	Manganese (mg/L)	Sulfate Load ^e (kg/d)	Metal Load ^f (kg/d)
								;	Stream wate	r							
SC-2S	09/10/2003	17	0.60	7.0	7.8	0.40	268	24.1	0	107	107	16.6	0.007	0.017	0.066	24	0.13
SC-3S	09/10/2003	16	.57	4.9	7.5	.46	357	20.2	1	63	62	50.6	.007	.041	.405	70	.63
SC-5S	09/10/2003	.09	.003	4.7	7.3	.43	669	19.8	0	124	124	215	.004	.023	.201	1.7	.002
SC-6S	12/29/2003	394	13.9	14.9	7.8	.37	508	3.0	1	118	117	112	.056	.049	.284	3,810	13.2
	01/13/2004	63	2.23	13.5	7.6	.33	936	1.2	2	153	151	320	.020	.068	.749	1,740	4.56
	03/10/2004	187	6.60	12.1	8.1	.22	747	8.7	1	133	132	212	.024	.031	.383	3,430	7.07
	06/07/2004	26	.93	4.6	7.5	.34	615	24.3	3	154	151	166	.101	.241	1.00	370	3.0
HG-3S	09/11/2003	.40	.01	3.0	3.0	.62	4,890	21.5	2,440		-2,440	5,250	144	862	21.3	180	36
HG-6.9S	09/11/2003	.06	.002	8.4	6.8	.15	3,390	21.1	48	152	104	2,570	<.150	20.5	5.99	13	<.14
HG-7S	09/11/2003	.45	.02	4.8	3.0	.62	4,540	20.6	3,270		-3,270	5,890	207	1,130	24.8	230	53
	12/30/2003	E>1.5	E>.05	7.6	4.4	.52	3,300	1.3	1,260	11	-1,250	2,860	64.2	494	9.88	E>370	E>74
	01/14/2004	1.3	.05	9.2	3.7	.55	4,650	.2	2,050		-2,050	5,010	109	783	17.3	560	100
	03/11/2004	1.7	.06	16.8	3.7	.58	3,940	4.3	1,470		-1,470	3,880	81.1	552	12.1	570	95
	06/08/2004	.73	.03	5.1	3.0	.61	4,550	22.7	2,400		-2,400	7,310	E130	894	20.3	460	E66
	08/30/2004	E>1.2	E>.04	5.8	3.5	.59	3,200	25.2	1,140		-1,140	2,650	67.0	406	10.1	E>270	E>50
HG-8S	01/13/2004	1.9	.07	9.9	3.9	.60	3,980	.2									
	03/10/2004			8.8	3.5	.59	2,660	11.8									
	06/07/2004			2.7	2.6	.70	4,310	31.2									
HG-11S	09/10/2003	.65	.02	7.1	2.8	.78	3,410	18.5	740		-740	3,070	85.7	86.4	13.3	170	10
	01/13/2004	>2.6	>.09	11.3	4.7	.42	2,660	2.3	652		-652	2,260	39.5	233	7.75	>510	>63
	03/10/2004	6.2	.22	8.4	5.0	.45	1,680	11.2	315	3	-312	1,350	16.4	120	4.42	720	75
	06/07/2004	E.28	E.01	5.3	2.9	.74	2,760	29.3	407		-407	3,220	45.6	40.7	11.4	E64	E1.9
SC-7S	09/10/2003	E17	E.60	5.8	7.2	.45	427	21.6	2	88	86	105	.065	.024	1.07	E150	E1.7
	12/29/2003	401	14.2	11.3	7.7	.15	638	3.4	3	122	119	169	.035	1.16	.369	5,860	54.2
	01/13/2004	61	2.16	12.4	7.2	.22	1,050	1.1	23	133	110	422	.152	11.0	1.42	2,220	66.3
	03/10/2004	177	6.24	12.1	7.7	.22	717	7.7	8	120	112	248	.066	3.66	.761	3,790	68.6
	06/07/2004	28	.99	5.7	7.0	.29	716	24.8	14	136	122	254	1.44	1.00	2.19	610	11
MC-3.3S	09/11/2003	.03	.001	5.9	2.8	.73	4,940	25.3	304		-304	3,970	3.47	107	10.8	10	.31
MC-4.9S	09/11/2003	.03	.001	4.2	3.0	.72	4,680	22.3	298		-298	3,810	5.78	107	14.1	9.9	.33
SC-8S	09/10/2003	13	.47	7.6	7.6	.43	449	19.4	1	103	102	103	.021	.010	.572	120	.68

Table 4.	Values for selected physical properties and dissolved constituent concentrations, and calculated loads for stream water and acidic mine drainage.
[L/s, liters p	per second; ft ³ /s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; kg/d, kilograms per day;, no data; E, estimated; <, less than;
>, greater th	han]

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[[]L/s, liters per second; ft³/s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; ^oC, degrees Celsius; kg/d, kilograms per day; --, no data; E, estimated; <, less than; >, greater than]

Site number ^a (fig. 1)	Date	Discharge, instanta- neous (L/s)	Discharge, ^b instanta- neous (ft ³ /s)	Dissolved oxygen (mg/L)	pH (SU)	Eh (volts)	Specific conduct- ance (µS/cm)	Temper- ature (°C)	Acidity, ^c as calcium carbonate (computed) (mg/L)	Alkalinity, as calcium carbonate (mg/L)	Net Alkalinity, ^d as calcium carbonate (mg/L)	Sulfate (mg/L)	Aluminum (mg/L)	lron (mg/L)	Manganese (mg/L)	Sulfate Load ^e (kg/d)	Metal Load ^f (kg/d)
								Stream	n water—Con	tinued							
CS-2S	09/09/2003	0.17	0.01	2.1	3.9	0.50	2,520	15.1	309		-309	2,230	12.4	126	4.33	33	2.1
CS-3S	09/09/2003	.40	.01	7.2	5.9	.35	2,240	19.6	37	17	-21	1,860	2.84	4.47	7.08	64	.50
CS-4S	09/09/2003	E.51	E.02	7.5	6.7	.39	2,150	18.8	13	60	47	1,500	<.150	2.38	4.14	E66	E.29
CS-6S	09/09/2003	1.7	.06	5.8	5.5	.32	3,270	14.9	638	30	-608	3,140	.826	344	9.55	460	52
CS-7S	09/08/2003	1.2	.04	4.8	3.5	.65	3,000	19.5	211		-211	2,510	.532	94.9	11.9	260	11
CS-8S	09/08/2003	.71	.03	>20.0	10.7	.29	752	27.0	0	139	139	154	E.028	E.005	.003	9.4	E.002
	01/12/2004	1.5	.05	19.0	9.4	.35	1,030	5.3	1	219	218	244	.005	.038	.311	32	.05
	03/08/2004	2.6	.09	15.6	8.9	.28	786	11.6	2	214	212	208	.004	.090	.874	47	.22
	06/09/2004	.93	.03	3.8	8.4	.35	880	25.5	1	146	145	225	.009	.008	.367	18	.03
CS-9S	09/08/2003	2.2	.08	8.0	4.5	.54	2,100	21.6	26		-26	1,370	.243	6.70	5.96	260	2.5
	01/12/2004	5.4	.19	10.2	6.8	.21	2,270	3.9	130	56	-75	1,300	<.150	67.8	4.53	610	<34
	03/08/2004	12	.41	9.9	6.9	.20	1,490	9.1	77	89	12	863	E.001	40.2	3.02	890	E45
	06/09/2004	5.4	.19	4.9	4.6	.44	2,290	21.8	176		-176	3,000	E5.00	74.5	7.14	1,400	E40
SC-9S	09/08/2003	15	.54	6.4	7.5	.35	605	19.8	2	95	93	199	.065	.026	.881	260	1.3
	01/12/2004	58	2.04	9.9	7.1	.25	1,160	.6	23	103	80	470	.002	10.6	2.05	2,360	63.4
	03/08/2004	451	15.9	11.6	7.7	.30	615	6.5	2	115	113	178	.012	.352	.542	6,940	35.3
	06/09/2004	26	.90	4.9	7.2	.33	931	22.5	4	128	124	320	.006	.216	1.74	720	4.4
MM-2S	09/05/2003	1.1	.04	8.2	7.9	.27	542	19.6	0	158	158	109	.008	.020	.025	10	.01
MM-4S	09/05/2003	3.7	.13	6.4	6.5	.18	1,630		125	86	-39	884	.009	68.0	1.66	280	22
MM-5S	09/04/2003	5.9	.21	5.9	7.4	.22	1,370	17.7	3	68	65	717	E.001	.366	1.46	370	E.93
MM-6S	09/04/2003	E23	E.81	6.6	8.8	.40	706	23.9	1	142	141	114	E.018	.023	.269	E230	E.62
	12/08/2003	4.0	.14	8.9	7.6	.25	877	6.0	1	209	208	140	.005	.029	.476	48	.18
	01/15/2004	E4.0	E.14	2.9	8.0	.25	950	4.2	2	250	248	151	.005	.114	.959	E52	E.37
	03/09/2004	9.9	.35	5.1	8.1	.31	913	10.2	1	281	280	113	.005	.066	.663	97	.63
	06/08/2004	E5.9	E.21	4.6	7.9	.34	835	31.1	1	145	144	164	.011	.039	.348	E84	E.20
MM-7S	09/04/2003	28	1.0	5.8	8.4	.26	1,060	20.7	1	114	113	E240	.010	.020	.719	E580	1.8
	12/08/2003	12	.43	11.8	6.9	.26	1,600	6.8		117							
	01/15/2004	12	.42	10.7	7.7	.18	1,530	1.7		138							
	03/09/2004	30	1.1	3.8	7.7	.17	1,180	8.9		166							
	06/08/2004	12	.42	5.2	6.6	.20	1,530	24.4		49							

Table 4. Values for selected physical properties and dissolved constituent concentrations, and calculated loads for stream water and acidic mine drainage.—Continued

Site number ^a (fig. 1)	Date	Discharge, instanta- neous (L/s)	Discharge, ^b instanta- neous (ft ³ /s)	Dissolved oxygen (mg/L)	pH (SU)	Eh (volts)	Specific conduct- ance (µS/cm)	Temper- ature (°C)	Acidity, ^c as calcium carbonate (computed) (mg/L)	Alkalinity, as calcium carbonate (mg/L)	Net Alkalinity, ^d as calcium carbonate (mg/L)	Sulfate (mg/L)	Aluminum (mg/L)	lron (mg/L)	Manganese (mg/L)	Sulfate Load ^e (kg/d)	Metal Load ^f (kg/d)
							A	cidic mine	drainage (Gr	ound water)							
HG-2M	09/11/2003	0.28	0.01	1.0	4.6	0.44	3,350	15.5	1,090		-1,090	3,850	E43.8	461	10.30	93	E12
	12/09/2003	.40	.01	.5	4.4	.40	4,030	11.9	1,620		-1,620	4,610	75.5	659	9.62	160	26
	12/29/2003	.42	.02	1.0	4.6	.42	3,490	11.0	1,080	21	-1,060	3,550	42.2	463	9.35	130	19
	01/14/2004	.40	.01	1.1	4.7	.47	3,470	10.7	1,080		-1,080	3,800	42.4	460	9.64	130	18
	03/11/2004	.42	.01	.6	4.7	.60	3,650	10.5	1,000	24	-976	3,620	41.1	422	8.84	130	17
	06/08/2004	.31	.01	1.9	4.5	.51	2,970	13.5	969	25	-944	3,920	E31.3	422	9.17	100	E12
	07/21/2004	.28	.01	.0	4.6	.42	3,700	15.0	975	22	-954	4,250	33.3	431	9.02	100	11
	08/30/2004	.32	.01	.0	4.5	.39	3,470	15.2	926	17	-909	2,590	29.6	416	8.36	72	13
HG-4M	09/11/2003	.11	.004	13.2	2.7	.60	6,320	19.8	6,060		-6,060	10,300	E488	1,780	28.9	98	E22
	12/30/2003	.08	.003	3.3	2.9	.59	7,180	9.9	5,300		-5,300	9,040	378	1,720	27.7	62	15
	01/14/2004	.10	.003	.3	2.8	.57	7,310	9.2	5,600		-5,600	9,760	395	1,820	29.0	84	19
	03/11/2004	.11	.004	1.2	2.7	.60	6,160	9.1	4,660		-4,660	9,380	298	1,600	19.4	89	18
	06/08/2004	.10	.003	3.8	2.7	.59	5,960	15.3	6,700		-6,700	13,800	428	2,320	33.5	120	24
CS-5M	09/09/2003	1.2	.04	6.8	5.2	.33	3,540	13.8	965	34	-931	4,130	E.727	525	11.1	430	E56
	12/09/2003	1.4	.05	5.3	5.2	.32	4,870	13.5	1,040	40	-1,000	4,500	.874	566	9.65	540	70
	01/13/2004	1.7	.06	3.5	5.2	.32	4,260	13.4	1,010	35	-975	2,990	1.06	553	9.51	440	83
	03/09/2004	1.5	.05	4.2	5.6	.35	2,990	13.5	934	43	-891	4,380	<2.50	504	9.35	570	<67
	06/09/2004	1.9	.07	5.0	5.2	.33	2,670	14.0	1,010	38	-972	4,900	.683	551	9.94	800	92
MM-3M	09/05/2003	E2.6	E.09	<.1	5.9	.21	2,580		328	160	-168	1,920	E.050	179	3.47	E430	E41
	12/09/2003	4.2	.15	.4	6.0	.19	2,880	13.6	302	168	-134	839	<.150	165	3.05	300	<61
	01/15/2004	2.5	.09	.4	6.4	.44	2,450	13.5	280	160	-121	1,900	.037	153	2.97	410	34
	03/10/2004	7.3	.26	.6	6.2	.33	1,980	13.2	258	178	-81	1,920	.053	141	2.79	1,200	91
	06/08/2004	E2.7	E.10	.0	5.9	.24	1,960	13.4	276	157	-119	2,300	.036	151	3.06	E540	E36

Table 4.	Values for selected physica	al properties and dissolved constituent concentrations, a	, and calculated loads for stream water and acidic mine drainage.—Co	ontinued
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[L/s, liters per second; ft³/s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ^oC, degrees Celsius; kg/d, kilograms per day; --, no data; E, estimated; <, less than; >, greater than]

^aComplete data for sampled sites are given in table 5.

^bFor convenience instantaneous discharge is given in English and metric units. 1 ft³/s = 28.3168 L. ^cComputed acidity per equation, Acidity_{computed} (mg/L as CaCO₃) = $50[10^{(3-pH)} + 2C_{Fe}/55.85 + 2C_{Mn}/55.94 + 3C_{Al}/26.98]$; C_i, concentration of constituent i in mg/L. ^dNet alkalinity = measured alkalinity - computed acidity. Samples with negative net alkalinities are net acidic.

^eSulfate loads computed per equation, Load = $0.0864(C_{sulfate}) Q; C_{sulfate}$, concentration of sulfate in mg/L; Q, discharge in L/s. ^fMetal loads computed per equation; Load = $0.0864[(C_{Fe} + C_{Mn} + C_{A1}) Q]; C_i$, concentration of constituent i in mg/L; Q, discharge in L/s.



Figure 12. Comparison of pH and calculated net alkalinity for acidic mine drainage measured at mine springs and receiving streams, Sugar Creek, and sewage effluent.

samplings are shown in figure 13 at receiving stream sites. From mine spring site HG-2M to downstream site HG-8S, fieldmeasured pH values generally decreased to 2.6 to 3.9 because the AMD was exposed to the atmosphere, promoting rapid oxidation of Fe²⁺ and precipitation of Fe^{III} oxy-hydroxides. Further downstream in the limestone-lined channel and between site HG-10S and HG-11S, the pH and alkalinity increased as iron concentrations decreased. Downstream from site HG-2M to site HG-7S, net alkalinity decreased (or conversely, net acidity increased) and specific conductance, dissolved metals, and sulfate concentrations increased, but decreased substantially from site HG-7S to downstream site HG-11S. At site HG-11S, smaller sulfate concentration in the March 2004 sample indicate dilution effects from larger discharge. Based on instantaneous discharge and values in table 4, the combined AMD discharge at site HG-7S for the four synoptic sampling events of sulfate and dissolved metals had average loads of 455 and 78 kg/d. If the sulfate concentration value adjusted for analytical error (table 2) is substituted for the June 2004 sample, the average sulfate load is 410 kg/d. The average sulfate load between sites HG-7S and HG-11S decreased only 20 percent to 366 kg/d, or 11 percent, using the adjusted sulfate concentration. At downstream site HG-11S, the effects of carbonate buffering, pH increase, and precipitation of oxy-hydroxides combined to decrease the average metal load by more than 50 percent to 37 kg/d, and the water remained net acidic. The estimated average discharge at site HG-11S of 2.4 L/s was more than double the estimated average discharge upstream at site HG-7S. Because of dilution from unmeasured discharges, sulfate concentrations decreased from an average 4,600 to 2,480 mg/L between the two sites. The increase in discharge accounts for most of the increase in sulfate load.

On June 10, 2004, at the conclusion of a quarterly sampling event, stormflow samples were collected at the peak and on the declining leg of a run-off event resulting from 6.35 cm of rain. Discharge was not measured. A conservative estimate of discharge (based on culvert dimensions and estimated velocity) at site HG-11S of 14,000 L/s at the peak and 2,800 L/s on the declining leg of the hydrograph yields estimates for dissolved metal loads of 1,860 kg/d at the peak and 1,120 kg/d on the declining leg (data for constituent concentrations in table 5). Most of these metal loads were received by Sugar Creek.

The larger loads during stormflow compared to baseflow may be evidence for the acidification of surface runoff by the dissolution of hydrated iron sulfate minerals as well as loading from additional sources such as ephemeral mine seeps. Acidic mine water can precipitate a large variety of soluble and insoluble iron and iron sulfate minerals depending on pH, moisture content, and solution composition. Nordstrom (1982) reported that iron sulfate hydrates such as melanterite [Fe^{II}SO₄:7H₂O], rozenite [Fe^{II}SO₄:4H₂O], szomolnokite [Fe^{II}SO₄:H₂O], and copiapite [Fe^{II}Fe^{III}₄(SO₄)₆(OH)₂:2H₂O] that are associated

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Figure 13. Discharge, specific conductance, pH, and net alkalinity, and iron, manganese, aluminum, and sulfate concentrations for Huntsville Gob subbasin with distance downstream.

with coal are deposited during dry periods as soluble salts because of evaporation. These soluable salts may be at least partially responsible for increased acidity in receiving streams during precipitation events (Nordstrom and Dagenhart, 1978). Olyphant and others (1991) determined surface runoff during precipitation events could be a major source of acidic outflow from unreclaimed mine spoil in a warm-temperate climate, and Bigham and Nordstrom (2000) reported that rapid dissolution of accumulated soluble salts may release stored acidity and "pulses" of contaminants.

Missouri's Water Quality Standards for the protection of aquatic life were often exceeded in samples from the Huntsville Gob subbasin. Mine spring site HG-2M was the largest single source of AMD in the Huntsville Gob subbasin based on contributing discharge, and although its discharge was small (<0.11 L/s), mine spring site HG-4M, with its large metal concentrations (tables 4 and 5), contributed a large percentage of the total acidity during low baseflow conditions in the drainage. All samples from these two mine springs had concentrations of aluminum [> (greater than) 750 μ g/L (micrograms per liter)] and iron (>1,000 µg/L) greater than Missouri's Water Quality Standards for protection of aquatic life, and site HG-4M exceeded the aquatic life standards for nickel (>770 µg/L) and zinc (>2,073 µg/L) (Missouri Department of Natural Resources, 2000). At downstream sites HG-7S and HG-11S, after the mine spring discharges had mixed with stream water, aquatic life standards were exceeded for aluminum and iron for all samples, except the iron analysis in January 2004 from site HG-11S. In June 2004 at site HG-7S the aquatic life standard for zinc was exceeded. The combined metal load (aluminum, iron, and manganese) from mine spring sites HG-2M and HG-4M varied little from 34 to 37 kg/d for the four synoptic sampling events. However, for two of the four synoptic sampling events in January and March 2004, this load represented only 37 to 38 percent of the metal load at downstream site HG-7S. During high baseflow conditions, discharge from diffuse seeps and surface runoff collected to OLCs draining the remediated areas (fig. 6) and the diffuse seeps to the west of site HG-2M (fig.1) can contribute a majority of AMD in the Huntsville Gob subbasin.

Calfee Slope Subbasin

AMD from mine spring site CS-5M (fig. 1) and numerous smaller seeps upstream from this site contribute discharge to the Calfee Slope drainage. Continuous discharge from site CS-5M was recorded during this study and also by Blevins and Ziegler (1992). In the early 1990's a pipe was installed as part of an abandoned mine land remediation project to direct the discharge from a flooded underground mine from which mine spring site CS-5M emerged to a stream approximately 25 m away, which prevented the collection of samples directly from the mine spring for this study. An improperly designed wet seal for the pipe has allowed air infiltration into the abandoned mine (Paul Behum, U.S. Department of the Interior, Office of Surface Mining, written commun., 2005) so that samples are oxygen-

ated at the sample collection point at the outfall of the pipe. Samples were collected, discharges measured or estimated, and field physical properties measured at seven AMD sources upstream from site CS-5M during the September 2003 synoptic sampling event (table 5). Based on data from Blevins and Ziegler (1992) and the September 2003 sampling event, downstream sampling site CS-9S (fig. 1) was deemed appropriate to capture all AMD sources and sewage effluent in the subbasin.

Discharge from mine spring site CS-5M accounted for 13 to 55 percent of the combined discharge at downstream site CS-9S for four synoptic sampling events, and ranged from 1.2 to 1.9 L/s. Median pH for site CS-5M was 5.2, average dissolved oxygen 5.0 mg/L, and the water was net acidic for all measurements (table 4). At site CS-9S, sewage effluent discharging at site CS-8S accounted for 17 to 33 percent of the discharge. After sewage effluent from CS-8S, which had a median pH of 9.2, discharged into the Calfee Slope drainage the median pH at downstream site CS-9S was 4.6. Net acidity at site CS-9S was decreased substantially from values upstream, even at small pH values, and was net alkaline in March 2004.

Samples for dissolved metals (aluminum, iron, and manganese) and sulfate were collected at mine spring sites CS-5M, CS-8S (sewage effluent), and at downstream site CS-9S during four synoptic sampling events. Dissolved metal and sulfate samples for the other sites in the Calfee Slope subbasin were collected in September 2003. Changes in field measurements of physical properties and dissolved metal and sulfate concentrations with distance downstream are shown in figure 14 at receiving stream sites. Field measured pH in the Calfee Slope subbasin increased from site CS-2M, a small mine seep 5 m downstream from the origin of flow, to site CS-3S, 270 m further downstream (fig. 14). Values for pH then decreased because of seepage from small AMD sources, but remained circumneutral until the point where AMD from mine spring site CS-5M discharged to the stream. The stream channel is lined with limestone for approximately 300 m downstream from site CS-5M (fig. 1). The pH continued to decline downstream from site CS-6S in September 2003 and June 2004, whereas it increased slightly in January and March 2004 (fig. 14). AMD from site CS-5M contains some alkalinity, but is net acidic because of the elevated Fe^{2+} content of the water (table 4). Net acidity concentration increased immediately downstream from the discharge from site CS-5M, but then decreased as the AMD flowed through the limestone-lined channel and was diluted with sewage effluent from site CS-8S. Specific conductance increased downstream from site CS-5M and then declined slightly because of dilution by sewage effluent that discharges into the drainage at site CS-8S. Dissolved metal and sulfate concentrations decreased downstream from site CS-5M in samples from the September 2003 sampling event. Samples collected for the other three sampling events at downstream site CS-9S had similar decreases downstream from site CS-5M.

For the combined discharge at downstream site CS-9S, calculated sulfate and dissolved metal loads had average values from four synoptic sampling events of 792 and 30 kg/d. The AMD remained net acidic at site CS-9S on three occasions and

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Figure 14. Discharge, specific conductance, pH, and net alkalinity, and iron, manganese, aluminum, and sulfate concentrations for Calfee Slope subbasin with distance downstream.

was marginally net alkaline in March 2004. The effects of carbonate buffering, precipitation of oxy-hydroxides, and dilution from sewage effluent combined to decrease the average dissolved metal load by approximately 60 percent from 74 kg/d calculated for the discharge from site CS-5M. The average sulfate load increased with discharge downstream from mine spring site CS-5M, except in September 2003, when the lowest discharge was recorded for the Calfee Slope drainage (table 4).

A sample also was collected to characterize the Calfee Slope subbasin on the declining leg of the June 10, 2004, runoff event at surface-water site CS-6S. Discharge was not measured, but was calculated to be 1,400 L/s, based on estimated velocity and cross-sectional area of the stream channel on the declining leg of the hydrograph. Using this discharge yielded estimates for dissolved metal loads of 540 kg/d (data for constituent concentrations in table 5). As was the case for the Huntsville Gob drainage, a dilution effect from runoff was indicated for smaller dissolved metal concentrations, whereas increased loads were apparent from the introduction of dissolved solids with the runoff as well as loading from additional sources such as ephemeral mine seeps. Increased metal loads from runoff enter Sugar Creek a short distance downstream from site CS-9S (fig. 1).

Mine spring site CS-5M contributes the majority of AMD and accounted for more than 90 percent of the metal loads discharging from the Calfee Slope drainage during this study. The metal load at upstream site CS-2S was 2.1 kg/d, or approximately 4 percent of the metal load of 56 kg/d, at mine spring site CS-5M in September 2003. The metal load was 52 kg/d at site CS-6S, approximately 50 m downstream from site CS-5M, a decrease of approximately 7 percent. Metal loads at downstream site CS-9S were 4.5 to 67 percent of the metal loads calculated at site CS-5M, indicating no other substantial inputs of AMD. Aquatic life standards (Missouri Department of Natural Resources, 2000) were exceeded for iron from mine spring site CS-5M in December 2003 and all four synoptic sampling events, and for aluminum in December 2003 and January 2004. At downstream site CS-9S, after mixing with sewage effluent from site CS-8S with small metals concentrations, aquatic life standards for iron were exceeded in January, March, and June 2004.

Sugar Creek

Instantaneous discharge in Sugar Creek ranged from 16 to 394 L/s at sites upstream from the confluence with the Huntsville Gob drainage (fig. 1, SC-3S and SC-6S) and from 15 to 451 L/s downstream from the confluence with the Calfee Slope drainage (fig.1, SC-9S). Discharge in Sugar Creek has been observed to decrease to zero during abnormally dry summers (D.W. Blevins, U.S. Geological Survey, oral commun., 2004). The corresponding combined discharge of AMD from the Huntsville Gob and Calfee Slope drainages ranged from 2.8 to 18.2 L/s. The highest measured discharges for Sugar Creek occurred in March 2004, and the lowest in September 2003. The discharge for September 2003 is considered to be representative of high baseflow conditions. Larger discharges than those measured in March 2004 would be expected following large precipitation events. The median pH measured at sites in Sugar Creek upstream from AMD discharging from the Huntsville Gob and Calfee Slope drainages (fig. 1, SC-3S and SC-6S) was 7.6, and values ranged from 7.3 to 8.1. At site SC-9S (fig.1), downstream from the two drainages, pH values ranged from 7.1 to 7.7 with a median of 7.4. The smallest pH value measured for Sugar Creek was 7.0 in June 2004, at site SC-7S downstream from the confluence with the Huntsville Gob drainage (fig.1). The average net alkalinity for upstream site SC-6S for three concurrent sampling events was 145 mg/L, whereas downstream at site SC-9S alkalinity averaged 106 mg/L, a decrease of 39 mg/L, but still larger than the TMDL goal of 90 mg/L established by the state of Missouri. All samples from Sugar Creek for which alkalinity was measured were net alkaline. Sulfate concentrations increased for the same three sampling events from an average of 233 mg/L upstream to an average of 323 mg/L at the downstream site. The maximum concentration of sulfate for Sugar Creek was 470 mg/L in January 2004 at downstream site SC-9S (fig. 1). Changes in field measurements of physical properties and dissolved metal and sulfate concentrations with distance downstream are shown in figure 15.

The average sulfate and dissolved metal loads for the discharge at upstream site SC-6S during three synoptic sampling events (January, March, and June 2004) were 1,850 and 4.9 kg/d. At site SC-9S, downstream from the confluence with the Calfee Slope drainage, the average sulfate load in Sugar Creek increased to 3,340 kg/d and dissolved metals load increased to 34 kg/d. The sum of the loads from Sugar Creek upstream at site SC-6S and the two AMD affected tributary stream sites (HG-11S and CS-9S) yield average values of 3,250 kg/d for sulfate and 91 kg/d for dissolved metals. The similarity between the calculated value at site SC-9S and the summed value for loads from sites SC-6S, HG-11S, and CS-9S for sulfate indicate that these three sites account for nearly all of the discharge and AMD contamination at site SC-9S. The field reconnaissance in September 2003 also verified that there are no other inputs or losses of discharge in Sugar Creek during periods without runoff. Nevertheless, the average metals load calculated at SC-9S is 63 percent less than the combined loads for SC-6S, HG-11S, and CS-9S. Precipitation of iron, aluminum, and possibly manganese oxy-hydroxides is likely occurring in Sugar Creek downstream from the AMD sources because of the effects of mixing AMD with oxygenated and buffered stream water.

Aquatic life standards (Missouri Department of Natural Resources, 2000) were exceeded for iron at site SC-7S, downstream from the confluence with the Huntsville Gob drainage, in December 2003 and January, March, and June 2004. Downstream from the confluence with the Calfee Slope drainage the iron standard was exceeded once, in January 2004. The aquatic life standard for aluminum was exceeded in June 2004 at site SC-7S.
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→ SEPTEMBER 2003 → MARCH 2004 → JUNE 2004

Figure 15. Discharge, specific conductance, pH, and net alkalinity, and iron, manganese, aluminum, and sulfate concentrations for Sugar Creek Basin with distance downstream.

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Despite modest effects from AMD on the water quality of Sugar Creek during the current (2003–2004) study, Sugar Creek remains vulnerable to effects from AMD during periods of low discharge. The effects of AMD on water quality in Sugar Creek become much larger during drought conditions because AMD discharges from mine springs in the basin are more sustained and contribute a larger proportion of discharge during dry periods than main-channel discharge in Sugar Creek. In fact, as has been observed in the past, all discharge in Sugar Creek can be AMD (D.W. Blevins, oral commun., 2005).

Mitchell Mine Basin

Mine spring site MM-3M (fig. 1) and several nearby diffuse and small seeps discharge AMD to the Mitchell Mine drainage. Perennial discharge from site MM-3M was noted by Blevins and Ziegler (1992) and the spring exhibited continuous discharge during the current (2003–2004) study. Discharge from the small individual seeps could not be measured because of low volumes. Blevins and Ziegler (1992) sampled extensively in the Mitchell Mine Basin during 1987–1988. Surfacewater sampling site MM-4S was located for the study to capture AMD from the combined discharge from site MM-3M and upstream site MM-2S. Sewage effluent discharges to the Mitchell Mine drainage at site MM-6S. Downstream site MM-7S was located to sample the combined AMD and sewage effluent discharges downstream from site MM-6S (fig. 1).

Discharge from site MM-3M ranged from an estimated 2.6 to 7.3 L/s and accounted for 70 to 92 percent of the discharge at downstream site MM-4S, and 9 to 35 percent of the combined discharge farther downstream at site MM-7S for five synoptic sampling events. Sewage effluent discharging at site MM-6S accounted for 33 to 82 percent of the discharge at site MM-7S. The water discharging from site MM-3M was net acidic with a median pH value of 6.0 and average dissolved oxygen concentration of 0.3 mg/L for all samples (table 4). After mixing with sewage effluent from site MM-6S with a median pH value of 8.0, the median pH value at downstream site MM-7S was 7.7. Water from site MM-7S was analyzed for dissolved metals and sulfate in September 2003, and was net alkaline for that sample.

Changes in field measurements of physical properties and dissolved metal and sulfate concentrations with distance downstream are shown in figure 16 at receiving stream sites. Field measured pH decreased downstream from mine spring site MM-3M, but maintained circumneutral values until sewage effluent from site MM-6S discharged to the stream where the pH increased, sometimes abruptly (fig. 16). AMD from mine spring site MM-3M contained from 157 to 178 mg/L alkalinity (table 4), but was net acidic. Specific conductance increased downstream from site MM-3M, and then decreased because of dilution from unmeasured discharges and the sewage effluent that discharges into the drainage at site MM-6S.

Mine spring site MM-3M contributes most of the AMD discharging into the Mitchell Mine drainage. Site MM-3M had an average metal load of 53 kg/d for five sampling events (four

synoptic sampling events and December 2003) and an average sulfate load of 576 kg/d [568 kg/d if the September 2003 adjusted value for sulfate concentration is substituted (table 2)] for the same five events. Aquatic life standards (Missouri Department of Natural Resources, 2000) of 1,000 µg/L were exceeded for iron for all samples from mine spring site MM-3M. In September 2003, the sulfate and dissolved metal loads for the combined discharge at site MM-7S had values of 580 and 1.8 kg/d. The effects of dilution and buffering from sewage effluent and precipitation of oxy-hydroxides combined to decrease the metal load at site MM-7S by approximately 96 percent from 41 kg/d at mine spring site MM-3M. The sulfate load increased for site MM-7S approximately 35 percent from 430 kg/d [49 percent from 390 kg/d using the adjusted sulfate concentration (table 2)] at mine spring site MM-3M.

Water-Quality Trends

Generation of AMD occurs in three phases: initiation, propagation, and termination. The initiation phase begins when mining activities expose pyritic material to the atmosphere. During the propagation phase acid production increases rapidly; during the termination phase, acid production gradually declines as the available pyritic material is consumed. The actual times associated with these phases are uncertain, but generally are on the order of years to decades (Sams and Beer, 2000). A statistical comparison of water-quality samples from this study and two preceding studies (Blevins and Ziegler, 1992; Missouri Department of Natural Resources, 2002) indicate some significant increases in pH and decreases in specific conductance, and indicate that AMD generating processes in the Sugar Creek Basin are in the termination phase. However, there are not enough data to quantify any definite trends or time frame.

Sampling sites with multiple samples from the current (2003–2004) study were compared with maps, coordinate data, and site descriptions from previous studies. Two previous studies collected multiple samples with time at some of the same or similar sites that were sampled for this study. Blevins and Ziegler (1992) collected water-quality data for AMD sources and receiving streams in the Calfee Slope subbasin, and Sugar Creek Basin and Mitchell Mine Basin during 1987-1988. Additional water-quality data were collected by the Missouri Department of Natural Resources during 2000-2002 from the Calfee Slope subbasin and Sugar Creek Basin, and were used in the development of the TMDL for Sugar Creek (Missouri Department of Natural Resources, 2002). A total of 14 common sites were identified (eight from the Calfee Slope subbasin, three from Sugar Creek Basin, and three from the Mitchell Mine Basin) with sufficient data for comparison for all or some of three key physical properties; pH, specific conductance, and alkalinity, and one constituent, sulfate.

Boxplots presented in figures 17 through 19 summarize the available data for evaluating long-term changes at the 14



Figure 16. Discharge, specific conductance, pH, and net alkalinity, and iron, manganese, aluminum, and sulfate concentrations for Mitchell Mine Basin with distance downstream.

common sites for the current (2003-2004) study and the two previous studies. The boxplots for all eight sites in the Calfee Slope subbasin (fig. 17) show increased pH values and decreased specific conductances for the 17 years represented by the available data. At downstream site CS-9S (fig. 1) median pH was 3.4 for 1987-1988, 4.1 for 2000-2002, and 5.7 for 2003-2004. Median specific conductance decreased from 3,200 to 2,180 µS/cm during the same time period at site CS-9S. Downstream site CS-9S was the only site in the Calfee Slope subbasin that had multiple samples analyzed for alkalinity and sulfate concentration during two different studies, but the number of samples was small. Median alkalinity increased from 10 to 72 mg/L as CaCO₃ and the median sulfate concentration decreased from 1,430 to 1,340 mg/L. However, pH and specific conductance at site CS-9S, as well as alkalinity and sulfate concentrations, are greatly affected by the discharge of sewage effluent from site CS-8S (fig. 1) a short distance upstream. The effluent discharge from site CS-8S fluctuates; and therefore, its effect on stream discharge and water quality is variable. The pH values recorded at upstream sites, particularly at mine spring site CS-5M (fig. 1), may be more useful for characterizing AMD in the Calfee Slope subbasin for possible remediation. Discharge from site CS-5M had a more modest increase in median pH from 4.8 to 5.2 and a decrease in median specific conductance from 5,000 to 3,540 µS/cm. The Wilcoxan rank-sum test indicates pH is significantly larger and specific conductance is significantly smaller (p < 0.05) in samples collected from 2003 to 2004 than those collected from 1987 to 1988 from mine spring site CS-5M. These changes in water quality at the mine spring and similar modest effects downstream (fig. 17) may be caused by regrading and reclamation projects completed in the early 1990's at the underground mine opening near CS-5M, slower rates of acid generation by pyrite oxidation in the underground mines during the AMD termination phase, or differences in discharge and hydrology during the sampling periods.

Specific conductance, alkalinity, sulfate concentration, and to a lesser degree, pH in water from Sugar Creek are dependent on the quantity of baseflow, upstream releases from Sugar Creek Lake (fig. 1), AMD affected discharges from the Huntsville Gob and Calfee Slope drainages, and the relative proportions of these three components to the total discharge in Sugar Creek. Smaller discharges than those observed in this study have been recorded in the past. Blevins and Ziegler (1992) reported one instance of zero discharge in 1988. At smaller discharges, proportional discharge from AMD sources and associated effects on the water quality of Sugar Creek is greater than at larger discharges. The boxplots for Sugar Creek (fig. 18) show increased pH values and decreased specific conductances for the three sites during the 17 years represented in the boxplots. The small pH values reported in 1987 (3.7) and 1988 (3.8) for site SC-9S (fig. 1) were recorded before the remediation projects in the Huntsville Gob and Calfee Slope subbasins of the early 1990's. During the two most recent sample collection periods, pH values at site SC-9S increased from a median of 6.8 in 2000-2002, to a median of 7.4 in 2003-2004. Samples from upstream site SC-6S, located above the confluence with the

Huntsville Gob drainage (fig. 1), had a small increase in pH values from 7.4 to 7.6, and decreases in median alkalinity and sulfate concentrations. Samples from downstream site SC-9S had an increase in median alkalinity and a large decrease in median sulfate concentration from 794 to 260 mg/L. Reclamation and remediation projects in the Huntsville Gob and Calfee Slope subbasins likely contributed to the increase in pH values and the decrease in sulfate concentrations.

The boxplots for the Mitchell Mine Basin (fig. 19) show increased pH values and decreased specific conductances at three sites for the 17-year period. Multiple analyses for alkalinity and sulfate concentrations from the historic data were not available. At mine spring site MM-3M (fig.1) median pH values increased from 5.6 for 1987–1988 to 6.0 for 2003–2004; specific conductance decreased from a median of 3,050 to 2,450 µS/cm. The Wilcoxan rank-sum test indicates a significantly larger pH and significantly smaller specific conductance (p <0.05) between samples collected in 1987–1988 and 2003– 2004 from mine spring site MM-3M. Samples from site MM-7S downstream from the sewage effluent discharge (fig. 1) had median pH values of 5.5 for 1987-1988 and 7.7 for 2003-2004. Median specific conductance decreased from 2,090 to 1,530 µS/cm. There have been no apparent remediation activities in the Mitchell Mine Basin since 1987 that would account for these changes. In a situation analogous to the Calfee Slope drainage, pH and specific conductance at site MM-7S are heavily impacted by the discharge of sewage effluent from MM-6S (fig.1). The pH values recorded at upstream sites, particularly mine spring MM-3M, are more useful for characterizing AMD in the Mitchell Mine Basin for possible remediation.

Characterization and Options for Remediation of Acidic Mine Drainage

Acidity and metals (iron, manganese, and aluminum) can be removed from AMD by using various passive-treatment options and systems to increase pH and alkalinity and aid in the oxidation and precipitation of iron. The primary types of passive systems currently (2005) being considered as options in the United States for remediation of AMD include oxic and anoxic limestone drains (OLDs and ALDs), open limestone channels (OLCs), constructed wetlands, and vertical flow systems, such as successive alkalinity producing systems (SAPS).

Many systems pass AMD through packed beds of limestone fragments to neutralize the acidity and generate alkalinity. As pH increases towards near-neutral values, dissolved Fe³⁺, Al³⁺, and some other metal concentrations in AMD usually decline because of precipitation or adsorption (Blowes and Ptacek, 1994; Cravotta and Trahan, 1999). Limestone in OLCs can become coated or "armored" with the precipitation of Fe^{III} oxyhydroxides, aluminum solid phases such as gibbsite and, possibly, precipitates containing calcium and sulfate, potentially decreasing the rate of limestone dissolution and alkalinity production (Watzlaf and Hedin, 1993; Hedin and Watzlaf, 1994).



Figure 17. Boxplots of pH, specific conductance, and alkalinity, and sulfate concentration for sampling sites with multiple samples collected from 1987 to 2004 in the Calfee Slope subbasin.



Figure 17. Boxplots of pH, specific conductance, and alkalinity, and sulfate concentration for sampling sites with multiple samples collected from 1987 to 2004 in the Calfee Slope subbasin—Continued.



Figure 17. Boxplots of pH, specific conductance, and alkalinity, and sulfate concentration for sampling sites with multiple samples collected from 1987 to 2004 in the Calfee Slope subbasin—Continued.

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Figure 18. Boxplots of pH, specific conductance, and alkalinity, and sulfate concentration for sampling sites with multiple samples collected from 1987 to 2004 in the Sugar Creek Basin.

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Figure 19. Boxplots of pH, specific conductance, and alkalinity, and sulfate concentration for sampling sites with multiple samples collected from 1987 to 2004 in the Mitchell Mine Basin.

ALDs often are effective for generating alkalinity (Hedin and Watzlaf, 1994; Hedin and others, 1994b; Watzlaf and others, 2000). An ALD consists of a buried bed of limestone fragments placed to intercept net-acidic AMD before exposure to atmospheric oxygen. Excluding oxygen minimizes the potential for oxidation of Fe^{2+} to Fe^{3+} and the resultant precipitation of ferrihydrite and related solid phases, minimizes "armoring" of the limestone in the channels, and limits further decreases in pH (Cravotta and Trahan, 1999).

A pe-pH diagram of the system Fe-O-H₂O-S-CO₂, using representative iron and sulfate concentrations for AMD in the Huntsville area, and assuming amorphous ferrihydrite as the Fe^{III} oxy-hydroxide phase, is shown in figure 20. Diagrams such as these are a useful way of showing stability relations when reduction-oxidation reactions are involved. A pe-pH diagram shows equilibrium relations, but does not show the departures from equilibrium that are common in natural waters (Drever, 1997). Precipitation of ferrihydrite, siderite, and pyrite are thermodynamically feasible at a pH value larger than about 5.5 (fig. 20). At pH values less than 5.5, Fe^{2+} is stable in the aqueous state, forms complexes with sulfate, and is shown as FeSO₄ on the diagram. Calculated pe values for AMD from mine springs are based on Fe²⁺/Fe³⁺ ratios ranging from 9.9 to 12.8. Field measured oxidation-reduction potential (Eh) yielded a wider range of calculated pe values of 3.2 to 12.3. Mine spring pH values ranged between 2.1 and 6.4. If a pe of 3.2 is considered as the lower limit for AMD from the mine springs before it is exposed to the atmosphere, the pH range for AMD falls within the upper left quadrant of the pe-pH diagram (pH of 2 to 7) (fig. 20). Precipitation of ferrihydrite [FeOH₃(a)] and hydronium-jarosite (Jarosite-H) are possible.



Figure 20. pe-pH diagram of the system Fe-O-H₂O-S-CO₂ at 25 degrees Celsius, assuming ferrihydrite as the Fe(III) oxy-hydroxide phase, activity of SO_4^{2-} equal to 0.05, and *P*CO₂ equal to 10 kilopascals. Solid-solution boundaries are drawn for an activity of dissolved Fe species of 0.01.

By decreasing the availability of oxygen, ALDs may decrease the possibility or rate of precipitation of Fe^{III} oxyhydroxides during treatment. Continuous inundation with AMD and carbon dioxide retention in an ALD also may increase alkalinity production because the rate and amount of limestone dissolution tends to increase with increased PCO2 and/or decreased pH (Plummer and others, 1979). By mechanisms such as those indicated by reactions 6 and 7, and increased PCO_2 , a larger quantity of alkalinity can be generated in an enclosed ALD than in an OLC (Ziemkiewicz and others, 1994; Ziemkiewicz and others, 1997; Cravotta and Weitzel, 2001). However, field experiments indicate that OLCs can be a cost effective means of increasing alkalinity in AMD (Ziemkiewicz and others, 1994), even with "armored" limestone (Ziemkiewicz and others, 1997; Cravotta and Trahan, 1999). Consequently, OLCs have met with some success for the long-term treatment of AMD (Skousen and others, 1998).

Various passive-treatment systems, including constructed aerobic and anaerobic wetlands and vertical flow systems such as SAPS, have been designed to increase residence time so metals (usually iron, manganese, and aluminum) have time to precipitate in addition to adding alkalinity (Skousen and others, 1998). Aerobic wetlands usually require net-alkaline water (fig. 9) and are not applicable for the treatment of AMD in the Huntsville area. Anaerobic wetlands are designed to facilitate the interaction of influent water with organic material and limestone to generate alkalinity. The surface water in an anaerobic wetland is oxidizing, so the precipitation of metals is enhanced in the presence of the increased alkalinity generated in the wetland (Skousen and others, 1998).

SAPS, as well as other vertical flow systems, are designed to increase the interaction of the influent water with the organic matter and limestone compared to the horizontal flow of water in an anaerobic wetland. Systems similar to SAPS are variously referred to as vertical flow systems, vertical flow ponds, vertical flow wetlands and more generically as reducing and alkalinityproducing systems (RAPS) (Watzlaf and others, 2000). The intent of a vertical flow wetland usually is to optimize sulfate reduction to increase alkalinity. The bacterial conversion of sulfate to sulfide (H₂S) produces bicarbonate alkalinity according to:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^{-}$$
 (16)

where CH_2O generically represents organic carbon (Skousen and others, 1998). Both anaerobic wetlands and SAPS enhance the precipitation of metals thereby decreasing the metal load discharged to receiving streams.

Cubitainer Experiment Results

The cubitainer experiments conducted for this study were designed to provide site-specific information to aid in the determination of the feasibility of the use of ALDs, OLCs, or other passive-treatment options for the treatment of AMD at the Huntsville Gob mine spring and a downstream surface-water site, the Calfee Slope mine spring, and three monitoring wells (fig. 1, sites HG-2M, HG-7S, CS-5M, MW 04-01, MW 04-02, and MW 04-03, respectively). The makeup of the cubitainers for individual experiments, as well as the initial (influent) and final (effluent) concentrations for some key physical properties and constituents, are presented in table 6. The results of closed cubitainer experiments with influent water from mine springs and one surface-water site are presented in figure 21; results for the open cubitainer experiments are presented in figure 22.

Effluent from open and closed cubitainers had larger pH values and alkalinity and calcium concentrations, and smaller aluminum concentration and net acidity than influent for open and closed cubitainer experiments (table 6). The pH values and alkalinity for the individual closed-circulated cubitainer experiments increased asymptotically; the pH attained maximum values between 6.2 and 6.3, and the alkalinity between 276 and 325 mg/L (fig. 21). The apparent decline in alkalinity at the end of the experiment for the uncirculated cubitainer (fig. 21, C) could result because of stratification or precipitation of minerals within the cubitainer. Alkalinity reached 80 percent of maximum concentrations in 8 to 24 hours. The pH for the three open cubitainer experiments reached maximum values between 7.2 and 7.4 (fig. 22). The largest alkalinity concentrations for the open cubitainer experiments, 102 to 214 mg/L, were reached between 8 and 24 hours and declined thereafter to the end of the experiment (fig. 22). Most influent for open and closed cubitainer experiments contained some dissolved oxygen, with concentrations ranging from 1.9 to 5.8 mg/L, with the exception of the anoxic influent sample collected at Huntsville Gob in August 2004 (table 6, fig. 21, E and F) and two of the monitoring wells (table 6, fig. 23, M and N).

Water from all cubitainers had a decrease in net acidity. Experiments performed with cubitainers that were open to the atmosphere for all or part of the experiments produced net-alkaline effluent (table 6, figs. 21 and 22, F, I, J, and K). The initial increase and subsequent decrease in alkalinity for the water in open cubitainer experiments can be explained by the mechanisms indicated in reactions 2, 3, and 6 and reactions involving aluminum and manganese. Initially the oxidation of Fe^{2+} to Fe³⁺ and the subsequent precipitation of Fe^{III} oxy-hydroxides by reactions 2 and 3 release H⁺ that is made available for dissolution of calcite (reaction 6), thereby increasing alkalinity. Similar mechanisms involving the precipitation of various compounds of aluminum also provide additional H⁺ (reaction 9). As the rate of precipitation reactions slow as the available Fe^{3+} and aluminum are consumed, so does the rate of alkalinity generation. The subsequent decrease in alkalinity could be the result of the exsolution of CO₂ and the consequent precipitation of carbonate or hydroxide minerals. Any remaining Fe²⁺ can be precipitated as siderite [FeCO₃(s)] (reaction 17) at a pH larger than approximately 5.5 (fig. 20).

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3(s) + H^+$$
 (17)

Manganese can precipitate as rhodochrosite (MnCO₃) (reaction 18) and manganite (MnOOH) (reaction 19).

$$Mn^{2+} + HCO_3^- \to MnCO_3(s) + H^+$$
 (18)

$$Mn^{2+} + 0.25O_2 + 0.75 H_2O \rightarrow MnOOH + 2H^+$$
 (19)

The removal of one mole of manganese can result in the release of two moles of H⁺ (or an equivalent decrease in bicarbonate), in combination with the hydrolysis of manganite (Hedin and others, 1994a). Investigations by Hedin and Watzlaf (1994) indicate that under aerobic conditions, the removal of manganese proceeds at a slower rate and sequentially after the removal of Fe²⁺.

Some "armoring" of the limestone fragments and deposition of red or rust-colored precipitates was observed in all the cubitainer experiments indicating processes involving the precipitation or formation of mineral solid phases. Although not quantified, the amount of precipitation and "armoring" for the cubitainer experiments open to the atmosphere appeared to be greater than those experiments that were closed to the atmosphere. Cloudiness or a "milky" appearance of the water in the open cubitainer experiments also was noted.

Experiments with two closed cubitainers produced netalkaline water (table 6, fig. 21, E and H). Large declines in iron concentrations were recorded in water from two cubitainers with net-alkaline water, but no mechanism is apparent to explain the decline, other than unintentional and perhaps repeated introduction of oxygen to the system, and release of carbon dioxide during sample withdrawal resulting in the precipitation of ferrihydrite (reaction 1) and possibly siderite (reaction 17). Clouding of the water and "armoring" of the limestone fragments in the cubitainer was observed.

Three cubitainer experiments also were conducted using underground mine water collected from monitoring wells (table 6, fig. 23, L, M, and N). Effluent from all three cubitainers had increased pH values and net alkalinity, and decreased aluminum and iron concentrations compared to influent mine water for the closed condition experiments (table 6). Monitoring well 04-01 (site MW 04-01) is an upgradient well located near the drainage divide, whereas monitoring wells 04-02 (site MW 04-02) and 04-03 (site MW 04-03) are located further downgradient and just upgradient from an area with diffuse AMD seepage and mine spring site HG-2M (fig. 1). Samples from monitoring well 04-01 had only marginal increases in pH values (6.2 to 6.4) and alkalinity concentrations because of reaction with limestone (from an already large value of 508 to 568 mg/L), indicating the water may be nearing equilibrium with underground mine conditions. Both influent and effluent were net alkaline. Consequently, limestone treatment of mine void water similar to that sampled from monitoring well 04-01 is not warranted; rather, direct treatment with a settling pond or aerobic wetland is indicated (fig. 9). Samples from monitoring wells 04-02 and 04-03 had pH values increases from 4.2 to 5.9 and 4.8 to 6.3. Samples from monitoring well 04-02 had an alkalinity increase to 356 mg/L, but the effluent remained net

[mg/L, milligrams per liter; --, no data; <, less than; LS, limestone; wo, without]

						Calci-	Calci-	Alkalinity, influent, as	Alkalinity, effluent, as	Net Alkalinity, influent, as calcium	Net Alkalinity effluent, as calcium			Alumi-	Alumi-			Manga-	Manga-	
	Site		Dissolved			um,	um,	calcium	calcium	carbonate,	carbonate,	Sulfate,	Sulfate,	num,	num,	Iron,	Iron,	nese,	nese,	
Cubi-	number	Sample	oxygen	pH,	pH,	influent	effluent	carbonate	carbonate	computed ^a	computed ^a	influent	effluent	influent	effluent	influent	effluent	influent	effluent	
tainer	(fig. 1)	date	(mg/L)	influent	effluent	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	Description
А	CS-5M	03/09/2004	4.2	5.6	6.3			43	285	-877	-274	4,370	3,470	<2.50	< 0.050	504	303	9.35	9.11	LS/Circulated/Closed
В	CS-5M	03/09/2004	4.2	5.6	6.3			43	304	-877	-252	4,370	3,540	<2.50	<.050	504	302	9.35	8.60	LS/Circulated/Closed
С	CS-5M	03/09/2004	4.2	5.6	6.2			43	256	-877	-448	4,370	3,600	<2.50	.052	504	383	9.35	9.56	LS/Static/Closed
D	HG-2M	06/08/2004	1.9	4.5	6.2	433	787	25	325	-946	-108	3,060	2,290	35.1	<2.5	423	233	9.15	8.89	LS/Circulated/Closed
Е	HG-2M	08/30/2004	.0	4.5	6.2	445	800	16.8	304	-909	44	2,590	2,010	29.6	.034	416	137	8.36	8.15	LS/Circulated/Closed
F	HG-2M	08/30/2004	.0	4.5	7.2	445	772	16.8	60	-909	52	2,590	2,010	29.6	.064	416	.043	8.36	3.98	LS/Circulated/Closed ^c
G	HG-7S	06/08/2004	5.1	3.0	5.9	485	795	0	193	-2,470	-595	5,120	3,190	138	<2.5	904	419	20.3	20.5	LS/Circulated/Closed
Н	HG-7S	08/30/2004	5.8	3.5	6.3	382	874	0	276	-1,130	247	2,650	1,790	67.0	.017	406	7.51	10.1	8.46	LS/Circulated/Closed
Ι	CS-5M	03/09/2004	4.2	5.6	7.3			43	107	-877	98	4,370	2,880	<2.50	<.050	504	.375	9.35	4.76	LS/Circulated/Open
J	HG-7S	06/08/2004	5.1	3.0	7.1	485	568	0	50	-2,470	32	5,120	2,300	138	<2.5	904	<.320	20.3	9.97	LS/Circulated/Open
Κ	HG-7S	06/08/2004	5.1	3.0	7.3	485	578	0	61	-2,470	45	5,120	2,250	138	<2.5	904	<.320	20.3	8.75	LS/Circulated/Open
L	MW 04-01	08/31/2004	.1	6.2	6.4	543	566	508	568	357	566	2,620	2,740	10.6	<.003	49.7	.032	1.74	1.32	LS/Circulated/Closed
М	MW 04-02	08/31/2004	.0	4.2	5.9	434	668	0	356	-3,680	-2,400	6,030	4,970	151	.219	1,560	1,510	23.5	28.1	LS/Circulated/Closed
Ν	MW 04-03	08/31/2004	.0	4.8	6.3	454	697		340		66	3,240	2,530	9.75	.151	483	147	7.46	5.54	LS/Circulated/Closed
Х	CS-5M	03/0920/04	4.2	5.6	4.0			43	24	-877	-901	4,370	4,070	<2.50	3.34	504	494	9.35	9.52	wo LS/Circulated/Closed
Y	HG-7S	06/08/2004	5.1	3.0	2.8	485		0	0	-2,470		5,120		138		904		20.3		wo LS/Circulated/Closed
Z	HG-2M	08/30/2004	.0	4.5	3.5	445	443	16.8	0	-909	-831	2,590	2,730	29.6	27.6	416	361	8.36	8.23	wo LS/Static/Closed

^aNet alkalinity as milligrams per liter $CaCO_3$ = measured alkalinity - computed acidity; Acidity_{computed} (milligrams per liter as $CaCO_3$) = $50[10^{(3-pH)} + 2C_{Fe}/55.85 + 2C_{Mn}/55.94 + 3C_{Al}/26.98]$; C_i, concentration of constituent i in milligrams per liter.

^bCirculation with peristaltic pump at variable rates 0.1–0.5 liter per second; static, uncirculated; open/closed, exposed or sealed to the atmosphere.

^cCubitainer opened after 43 hours.



Figure 21. Changes in effluent pH and alkalinity concentration with elapsed time for cubitainer experiments conducted under closed or open conditions with acidic mine drainage in contact with limestone from mine spring sites HG-2M (A-C) and CS-5M (D-F) and surface-water site HG-7S (G, H).



Figure 22. Changes in effluent pH and alkalinity concentration with elasped time for cubitainer experiments conducted under open conditions with acidic mine drainage in contact with limestone from mine spring site CS-5M (I) and surface-water site HG-7S (J, K).

Figure 23. Changes in effluent pH and alkalinity concentration with elasped time for cubitainer experiments conducted under closed conditions with water in contact with limestone from monitoring well sites MW 04-01 (L), MW 04-02 (M), and MW 04-03 (N).

acidic. Samples from monitoring well 04-03 had an alkalinity increase to 340 mg/L, and were marginally net alkaline, partially because of a large decrease in iron concentrations. Because influent water had a dissolved oxygen concentration of zero and the cubitainer experiments were conducted using closed conditions, the mechanism indicated for precipitation of Fe^{III} oxy-hydroxides is by reactions 3 and 4 and the precipitation of siderite by reaction 17. "Armoring" of the limestone fragments in the cubitainer was observed. The stratigraphy, measured water levels, and dissolved oxygen measurements (table 5) indicate that the voids screened for monitoring well 04-02 were completely flooded and anoxic. However, the large Fe³⁺ concentrations indicated at a pH value of 4.8 implies atmospheric contact and smaller pH values having occurred in the recent past. If water in the vicinity of monitoring wells 04-02 and 04-03 is to be captured for treatment, greater knowledge of the hydrology and the underground mines will be required.

Geochemical Modeling Results

The potential for increasing alkalinity by reaction of AMD with limestone in cubitainers or treatment systems is supported by saturation indices computed with PHREEQCI (Parkhurst and Appelo, 1999). Saturation indices computed for AMD and water sampled from underground mine cavities (table 3) indicate mostly undersaturated conditions with respect to CaCO₂ and other carbonate minerals. Mine spring site MM-3M and monitoring well 04-01, with larger pH values, are undersaturated with respect to calcite and dolomite, but supersaturated with siderite (FeCO₃) and are indicative of anoxic conditions for the underground mine water. Siderite saturation could indicate the production of bicarbonate by processes such as calcite dissolution (reaction 6) occurring at a faster rate than the rate of siderite precipitation (reaction 17). Alternatively, it would be expected that while the precipitation of siderite tends to decrease pH initially, the additional H⁺ generated would cause more calcite to dissolve (reaction 6) thus buffering pH values. The operation of these or similar processes are supported by the relatively large alkalinities for the two sites (table 2). Gypsum (CaSO₄:2H₂O), which may react to equilibrium relatively quickly (reaction 12), had saturation indices with small negative values or zero for all sites, and is indicative of near-equilibrium conditions with respect to gypsum.

Precipitation of Fe^{III} and aluminum oxy-hydroxides are of particular concern in the design of passive-treatment systems because of their potential to inhibit flow by clogging flowpaths and "armoring" limestone in OLCs and ALDs (Ziemkiewicz and others, 1994; Skousen and others, 1998; Watzlaf and others, 2000). Saturation indices for goethite (FeOOH) were supersaturated for mine spring and samples from monitoring wells, while ferrihydrite was saturated or near saturation except for samples collected from mine spring site HG-4M, which had pH values less than 3.0. Gibbsite [Al(OH)₃] also was near saturation or saturated except for samples collected from site HG-4M. Amorphous aluminum oxy-hydroxide, which also can "armor" limestone and clog flowpaths in limestone beds and channels, was undersaturated for all mine spring and mine void samples (table 3).

One of the proposed methods for treating AMD at Huntsville was to mix AMD discharges with available surface water or sewage effluent from sewage lagoons located adjacent to the Calfee Slope drainage and the Mitchell Mine drainage (fig. 1). A mixing model with PHREEQCI was used to compute the composition of the resultant solutions based on equation 13. Resultant solutions for three mixing scenarios were computed: mixing AMD from the surface-water site HG-7S with upstream Sugar Creek water from site SC-6S; mixing AMD from mine spring site CS-5M with sewage effluent from site CS-8S; and mixing AMD from mine spring site MM-3M with sewage effluent from site MM-6S (fig. 1). The results are presented in table 7 as mixes 1 through 3. The three mixtures also were modeled to simulate treatment with limestone and contact with the atmosphere.

A 1:25 ratio of AMD from site HG-7S to Sugar Creek water from site SG-6S was required to obtain the targeted pH value of 6.5 based on modeled results. Alkalinity of 95.7 mg/L was larger than the targeted value of 90 mg/L, and the final mixture was net alkaline. Calcite, gypsum, and siderite were undersaturated in both the AMD and stream water, and remained so in the final mixture. Larger values of supersaturation were present in the mixture than in the AMD for the various Fe^{III}, manganese, and aluminum solid phases (table 7). During the three sampling events, when discharge was measured at both sites, the ratio of AMD to stream water was less than 1:25, indicating that Sugar Creek could receive AMD from the Huntsville Gob drainage with minimal levels of water-quality degradation during most periods. However, in drier times, when discharge in Sugar Creek is smaller than was observed for this study, the mixing ratio would likely be less than 1:25, and targeted values for pH and alkalinity would not be achieved based on the modeled results.

Passive treatment of AMD in a settling pond was simulated for the Huntsville Gob drainage by modeling the behavior of less conservative and non-conservative constituents in contact with the atmosphere while maintaining a pH of 6.5 or larger. The mixing ratio of AMD to stream water was reduced to approximately 1:11, but the alkalinity decreased to 2.3 mg/L, largely because of the exsolution of carbon dioxide. The 1:11 mixture was then equilibrated with calcite to simulate an OLC or OLD. Alkalinity increased to 48.3 mg/L and pH to a value of 8.1. Calculated acidity was zero because of the modeled precipitation of Fe^{III}, aluminum, and manganese oxy-hydroxides so that although the mixture had alkalinity less than the targeted 90 mg/L, the mixture was net alkaline.

A 1:9 ratio of AMD from site CS-5M to sewage effluent from site CS-8S was required to obtain the targeted pH value of 6.5 based on modeled results. Alkalinity of 64.8 mg/L was less than the targeted value of 90 mg/L, and the final mixture was net acidic. Calcite, gypsum, and siderite are undersaturated in the final mixture. Fe^{III} oxy-hydroxides, manganese, and the aluminum solid phase gibbsite, are supersaturated, while amor-

Table 7. Selected physical properties, dissolved constituent concentrations, and saturation indices of selected minerals dissolved in surface water and acidic mine drainage used in geochemical mixing experiments and results.

[E, estimated; <, less than; --, insufficient data; a(m), amorphous]

				Site number, results	of mixing, and o	late sample collecte	d		
	HG-7S	SC-6S	MIX 1 ^b	CS-5M	CS-8S	MIX 2 ^b	MM-3M	MM-6S	MIX 3 ^b
Parameter or constituent ^a	12/30/2003	12/29/2003		09/09/2003	09/08/2003		09/05/2003	09/04/2003	
Mixing ratio	1	25	1:25	1	9	1:9	1	5.25	1:5.25
Dissolved oxygen	7.6	14.9	10.5	6.8	20.0	.6	.1	6.6	.0
pH	4.4	7.8	6.5	5.2	10.7	6.5	5.9	8.8	6.5
pe	8.8	6.3	16.1	5.6	4.8	13.7	3.5	6.8	5.6
Calcium	314	65.6	75.1	448	69.6	108	323	63.9	106
Magnesium	112	16.3	20.0	279	17.1	43.4	156	15.8	38.3
Potassium	E6.78	4.36	4.45	31.8	11.1	13.2	23.6	12.6	14.4
Sodium	38.6	9.3	10.4	207	38.9	55.8	87.4	47.4	53.9
Acidity, as calcium carbonate, computed ^c	1,260	1	49	965	0	97	327	1	53
Alkalinity, as calcium carbonate	11	118	95.7	34	139	64.8	160	142	126
Net Alkalinity ^d , as calcium carbonate	-1,250	117	47	-931	139	-32	-167	141	73
Chloride	9.62	8.10	8.16	16.6	51.7	48.2	21.5	65.6	58.6
Silica	24.1	2.13	5.28	47.7	13.9	17.3	25.2	12.8	14.8
Sulfate ^e	2,480	112	202	3,530	154	493	1,750	114	295
Aluminum	64.2	.056	2.44	.727	.028	.098	.05	.018	.023
Barium	<.100	.052	.050		.022	.020		.013	.011
Iron	494	.049	18.9	525	.005	52.8	179	.023	28.7
Manganese	9.88	.284	.650	11.1	.003	1.12	3.47	.269	.783
Strontium	.609	.198	.214	.762	.230	.284	1.36	.193	.380
Zinc	1.01	.005	.043	.062		.006	.048		.008
Saturation index ^f									
Calcite (CaCO ₃)	-4.2	-0.1	-1.5	-2.8	1.8	-1.3	-1.4	1.2	-0.9
Gypsum (CaSO ₄ :2H ₂ O)	2	-1.5	-1.3	01	-1.5	9	2	-1.6	-1.0
Birnessite (MnO ₂)	-12.6	-5.4	9.5	-15.9	.19	5.0	-17.7	9	-11
Manganite (MnOOH)	-7.6	-1.2	5.1	-8.4	3.0	3.0	-8.9	1.7	-5.1
Siderite (FeCO ₃)	-1.8	-3.0	-8.6	4	-13.0	-7.4	.6	-7.5	.5
Ferrihydrite [Fe(OH) ₃ (a)]	.9	2.9	4.7	.4	-1.3	4.1	01	1.1	3.6
Goethite (FeOOH)	5.9	8.0	9.8	5.9	4.7	10.0	5.5	7.0	9.4
Jarosite-K [KFe ₃ (SO ₄) ₂ (OH) ₆]	3.3	-2.9	6.9	1.3	-21.5	7.7	-2.6	-9.1	5.8
Jurbanite (AlOHSO ₄)	1.4	-3.9	1.1	.1	-15.5	-2.0	5	-9.8	-2.5
Gibbsite [Al(OH) ₃]	5	5.1	4.4	.6	-2.3	2.3	1.5	4	1.8
Al-hydroxide (am) [Al(OH) ₃ (a)]	-3.4	7	1.4	-2.2	-4.9	4	-1.3	-3.1	9

^aUnits are milligrams per liter unless otherwise noted.

^bThe composition of the mixtures is the result of computations with a mixing model using PHREEQCI (Parkhurst and Appelo, 1999) of two water samples in the proportions given. Thermodynamic data are from the data base WATEQ4F (Ball and Nordstrom, 1991).

^cComputed acidity per equation; Acidity_{computed} (milligrams per liter as CaCO₃) = $50[10^{(3-pH)} + 2C_{Fe}/55.85 + 2C_{Mn}/55.94 + 3C_{Al}/26.98]$; C_i, concentration of constituent i in milligrams per liter.

^dNet alkalinity = measured alkalinity - computed acidity.

^eSulfate values for HG-7S, CS-5M, and MM-3M adjusted to achieve charge balance within plus or minus (\pm) 1 percent. If the initial charge balance was within \pm 5 percent the sulfate concentration was not adjusted. ^fSaturation index (SI), SI = log(IAP/Ksp). Computations performed using PHREEQCI (Parkhurst and Appelo, 1999) for samples and mixtures, version 2.10, with thermodynamic data for IAP (ion activity product) and Ksp (species

equilibrium constant) from the data base WATEQ4F (Ball and Nordstrom, 1991). Saturation indices are unitless.

phous aluminum oxy-hydroxides and jurbanite (AlOHSO₄) are undersaturated (table 7). Discharge from site CS-5M exceeded discharge from the sewage treatment ponds during all four sampling events by 13 to 100 percent. Based on these observed volumes of sewage effluent and modeled results, the discharge of sewage effluent alone would seldom be large enough to improve water quality to meet water-quality targets.

Passive treatment of AMD in a settling pond was simulated for the Calfee Slope drainage by modeling the mixture in contact with the atmosphere, while maintaining a pH of 6.5 or larger. The mixing ratio of AMD to sewage effluent was reduced to approximately 1:8, but the alkalinity decreased to 1.9 mg/L because of the exsolution of carbon dioxide. The 1:8 mixture was then equilibrated with calcite. Alkalinity increased to 30.0 mg/L and pH to a value of 8.0. While the original mixture before treatment was net acidic (table 7), after simulated treatment calculated acidity was zero for the mixture and net alkalinity equaled total alkalinity because of the precipitation of Fe^{III}, aluminum, and manganese oxy-hydroxides.

AMD from mine spring site MM-3M (fig. 1) was mixed at a 4:21 ratio with sewage effluent from site MM-6S to obtain the targeted pH value of 6.5. The resultant mixture was net alkaline (alkalinity of 126 mg/L), which is larger than the targeted value of 90 mg/L. Calcite, gypsum, and manganite (MnOOH) are undersaturated in the final mixture. Fe^{III} solid phases and gibbsite are supersaturated, while amorphous aluminum oxyhydroxide and jurbanite are undersaturated (table 7). During the five sampling events when discharge was measured at both sites, the ratio of AMD to sewage effluent was larger than 1:5 on all but one occasion, indicating that mixing with sewage effluent alone would seldom increase pH and alkalinity enough to meet water-quality targets.

Passive treatment of AMD in a settling pond was simulated for the Mitchell Mine drainage by modeling the mixture in contact with the atmosphere while maintaining a pH value of 6.5 or larger. The mixing ratio of AMD to sewage effluent was reduced to approximately 2:3, but the alkalinity decreased to 1.4 mg/L because of the exsolution of carbon dioxide. The 2:3 mixture was then equilibrated with calcite. Alkalinity increased to 31.4 mg/L and pH to a value of 8.0. The original mixture before treatment was net alkaline (table 7). After simulated treatment, net alkalinity decreased from 73 to 31.4 mg/L, but acidity decreased 53 mg/L to zero.

Remediation Options

Selection and design of an appropriate passive-treatment system is based on water chemistry, discharge rate, topography, and other site-specific characteristics. Discharge rates for mine springs and their receiving streams generally were small, ranging from less than 0.1 to 7.9 L/s (table 5). The three major sources of AMD in the Sugar Creek Basin; mine spring site HG-2M and nearby seeps, mine spring site CS-5M, and mine spring site MM-3M, are located on private land. Constructed passive-treatment options and the various water-chemistry

characteristics for which they are appropriate are summarized in figure 9. Generally, to meet Missouri Water Quality Standards for pH, all the AMD sources would require the construction of settling ponds, construction of wetlands, or a combination of the two to facilitate iron oxidation, hydrolysis, and precipitation of iron oxy-hydroxides, and to provide a system for increasing alkalinity. Feasibility studies can determine which options are economically possible and to what extent landowner cooperation may be required for construction of settling ponds and wetlands.

To establish criteria for wetland construction, a minimum wetland size was calculated for each site using the values for maximum discharge and iron concentration measured during the study at AMD sites. These values are representative of influent flow volume and chemistry at the point of treatment. An iron removal rate of $0.02 \text{ kg/m}^2/\text{d}$ (kilogram per square meter per day) was used unless otherwise noted (Hedin and others, 1994a) according to:

$$W_{\rm m} = [C_{\rm Fe}Q/0.02]F$$
 (20)

where W_m is the wetland size in square meters,

- C_{Fe} is the iron concentration in milligrams per liter,
 - Q is the discharge in liters per second, and
- F equals 0.0864, the conversion factor to kilogram per day.

The calculated minimum wetland sizes assume prior generation of adequate alkalinity and do not take into consideration the large aluminum concentrations typical at some sites. Therefore, wetlands used for remediation in the Sugar Creek Basin and Mitchell Mine Basin may need to be constructed larger than the minimum calculated size.

Passive-treatment options that were considered for the mine springs and nearby seeps are based on three major considerations: that the AMD is net acidic, the AMD has large metal concentrations, and the water will be oxic. Based on these considerations, treatment of the AMD initially would be directed to one of three options (fig. 9); an anaerobic wetland, a settling pond followed by a SAPS, or an OLC/OLD followed by a settling pond and possibly a SAPS. There likely is enough hydraulic head at the three mine spring sites to implement any of these options, but this needs to be confirmed by survey before planning, construction, and implementation. AMD from the three mine springs, in all cases, was observed to be less than 62 percent of the total discharge at downstream sites, so it may be possible to add alkalinity and dilute the AMD by regulating the discharge from potential constructed impoundments and sewage effluent from treatment lagoons to augment low discharges. The effect of AMD on Sugar Creek, which is greatest when discharges are low, also could be lessened by regulating and extending discharge from Sugar Creek Lake (fig. 1) during dry periods. However, mixing AMD with other solutions, either water from streams or constructed impoundments and sewage effluent, in the stream does not remove metals from the stream environment. Mixing in wetlands or settling ponds, in contrast, removes metals by precipitation outside the stream environment

while potentially reducing pH variation within the stream by providing time for equilibration of the AMD and mixed water and/or effluent. AMD from the three mine springs might be directly routed to ALDs before the water becomes oxygenated, but large ferric iron and aluminum concentrations may make this option questionable, and clogging of the drains likely.

All the major sources of AMD in the Huntsville Gob subbasin are upstream from sampling site HG-7S, and approximately 200 m downstream from mine spring site HG-2M (fig. 1). The observed pH values from downstream site HG-11S during this study were 5.0 or less, and were less then 3.0 for two samples (table 4). AMD discharging to Sugar Creek from the Huntsville Gob drainage has the potential to degrade the entire 4.35-km impaired reach of Sugar Creek (fig. 1) and is an important remedial priority. Water from site HG-2M emerges from a pipe and flows down slope through a constructed OLC, with substantial topographic relief adequate to support passive treatment, and across private land for approximately 2 km, where it joins Sugar Creek. All identified sources of AMD are located in the upper 750 m of the Huntsville Gob drainage. AMD at site HG-7S is net acidic and has large iron, manganese, aluminum, and sulfate concentrations. Diluting AMD at this site with releases from a potential constructed upstream impoundment would require sustained discharge of more than 15 L/s from the impoundment based on the geochemical mixing experiments with water from Sugar Creek. Because releases that large likely could not be sustained for extended periods at this site, this option would only be an intermittent or partial solution to meeting water-quality goals for pH and alkalinity, and would not remove metals from the stream environment. The minimum calculated wetland size at site HG-7S is 0.83 hectare.

Metal concentrations decrease substantially as the AMD flows through an OLC downstream from site HG-7S (fig. 7), but the pH remained 5.0 or less and the water was net acidic at downstream site HG-11S during this study (fig. 13). By the time combined discharge from site HG-2M and the diffuse seeps collected in OLCs reaches site HG-7S, the water is oxic. If treatment of the AMD is implemented at site HG-7S or further downstream, small pH and large metal concentrations indicate the appropriate initial treatment would include using either a settling pond or OLC, but not an anaerobic wetland. Large aluminum concentrations also may preclude the use of an ALD because of the potential for clogging caused by the precipitation of aluminum oxy-hydroxides. The pH was observed to remain low after AMD flowed through the existing limestone channel; therefore, utilization of a SAPS downstream from the limestone channel would be indicated.

The primary source of AMD in the Calfee Slope subbasin is mine spring site CS-5M. AMD discharging to Sugar Creek from the Calfee Slope drainage could degrade the lower 1.7 km of the impaired reach of the creek (fig. 1). The Calfee Slope drainage originates within the city limits of Huntsville, and is easily accessible to domestic animals and children, making remediation of the Calfee Slope drainage a high priority. Water from site CS-5M is piped 25 m from an abandoned mine entrance to a limestone channel that also is the drainage ditch for a county road. Relief from the mine entrance to the drainage ditch is approximately 3 m, and should be adequate to support passive treatment at that point. The ditch is lined with limestone for 300 m downstream, and follows the road for another 900 m before turning west and flowing across private property for an additional 100 m to Sugar Creek. Total relief from site CS-5M to the mouth of the Calfee Slope drainage is approximately 10 m. All other identified sources of AMD are located upstream from mine spring site CS-5M.

AMD at site CS-5M was net acidic, and had large iron, manganese, and sulfate concentrations. During the September 2003 sampling event, iron and already small aluminum concentrations decreased as the AMD flowed through an OLC downstream from site CS-5M, but manganese remained elevated until the point where sewage effluent from site CS-8S discharges to the stream (fig. 15). Water discharging from the pipe at site CS-5M to the unnamed tributary in the Calfee Slope subbasin is oxic. If treatment of the AMD is implemented at site CS-5M or further downstream, small pH and large metal concentrations would indicate initial treatment using either a settling pond or OLC. However, if a poorly designed wet seal is repaired to exclude air contact with the underground mine water at mine spring site CS-5M, treatment with an ALD may be possible (Paul Behum, written commun., 2005). The pH values observed downstream from mine spring site CS-5M were variable, but can be as small as 3.5 (table 4). Diluting AMD at this site with sewage effluent from the nearby treatment facility would require discharge from the sewage lagoons of more than 40 L/s, based on the geochemical mixing experiments. Observed discharges from the treatment facility ranged from 0.7 to 2.6 L/s (table 4). Consequently, alkaline additions and dilution from sewage effluent would be only a partial solution to meeting water-quality goals for pH and alkalinity, and would not remove metals from the stream environment. After mixing with sewage effluent at downstream site CS-9S, the AMD was net acidic for three of four sampling events, with pH values ranging between 4.5 and 6.9, but was marginally net alkaline for the March 2004 sample. Because approximately only 300 m out of 1.3 km between sites CS-5M and CS-9S of the Calfee Slope drainage is lined with limestone, the potential exists to increase alkalinity and pH by lining more of the channel. Treatment with a SAPS for additional alkalinity also may be warranted. The minimum calculated wetland size for treatment at site CS-5M is 0.46 ha. If the wetland is constructed for the combined discharge of AMD and sewage effluent at downstream site CS-9S, the minimum calculated size is 0.39 ha.

Mine spring site MM-3M is the primary source of AMD in the Mitchell Mine Basin. Water from site MM-3M emerges from an abandoned mine entrance, drops approximately 2 m to the unnamed tributary in the Mitchell Mine Basin, and flows 4.2 km to the East Fork Little Chariton River (fig. 1). The upper one-half of the drainage is located within the city limits of Huntsville, and is mostly unaltered except at road crossings. However, AMD discharging to the unnamed tributary from mine spring site MM-3M has the potential to degrade the entire 4.5 km length of the stream (fig. 1) during low discharges. Although classification of the Mitchell Mine drainage as impaired does not fall within the scope of the Sugar Creek TMDL document (Missouri Department of Natural Resources, 2002), remediation of the Mitchell Mine drainage is an important remedial priority because the unnamed tributary originates within the city limits of Huntsville, and is easily accessible to domestic animals and children. The upper part of the drainage between sites MM-3M and MM-4.4S (fig. 1) has a relief of approximately 3 m, and should be adequate to support passive treatment at that point. The majority of identified AMD sources discharge into this upper reach of the Mitchell Mine drainage. Total relief from site MM-3M to the sewage treatment facilities discharging to the unnamed tributary at site MM-6S, 1.6 km downstream, is approximately 12 m.

AMD at site MM-3M was net acidic, despite having alkalinities of 157 mg/L or larger (table 4). Mine spring site MM-3M also had large iron and sulfate concentrations. During the September 2003 sampling event, iron and already small aluminum concentrations decreased between sites MM-4S and MM-5S, but manganese remained elevated until the point where sewage effluent from site MM-6S discharged to the stream (fig. 16). When AMD emerges from the ground at mine spring site MM-3M, the dissolved oxygen concentration is small (less than 1 mg/L). If treatment of the AMD is implemented at site MM-3M, initial treatment with an anaerobic wetland could be geochemically feasible. However, for a given iron-loading rate, an anaerobic wetland will have an area four times larger than an aerobic wetland of the same depth based on a removal rate of 0.005 kg/m²/d (Hedin and others, 1994a). The minimum calculated wetland size at site MM-3M is 2.2 ha. If treatment is implemented further downstream where conditions are oxic, the large iron concentrations would indicate the most appropriate initial treatment would be using either a settling pond or OLC. Geochemical mixing experiments indicate dilution and alkalinity addition to AMD from mine spring site MM-3M with sewage effluent would require a sewage lagoon discharge of more than 35 L/s, and possibly piping the AMD for the 1.6 km distance between the two sites. Observed discharges from the sewage lagoons ranged from 4 to 23 L/s (MM-6S; table 4). Therefore, mixing with sewage effluent would likely be only a partial solution to meeting water-quality goals similar to those in the Sugar Creek TMDL (Missouri Department of Natural Resources, 2002). Diluting AMD from mine spring site MM-3M with releases from a potential constructed upstream impoundment could be used to provide additional alkalinity and dilution, but also would be only a partial solution. After mixing with sewage effluent at downstream site MM-7S, the water had alkalinities that ranged between 49 and 166 mg/L, and pH values between 6.6 and 8.4. The geochemical mixing experiments indicated a computed alkalinity of 126 mg/L at a pH of 6.5 (table 7). The September 2003 sampling event indicated that iron concentrations had decreased by more than 99 percent from mine spring site MM-3M by the time flow reached downstream site MM-7S. Alkalinity concentrations were larger than 90 mg/L for three of the four sampling events, and pH values were larger than 6.5 for all four events at downstream site

MM-7S. Because the Mitchell Mine drainage flows through a mud bottom channel for much of its length, the potential exists to increase the alkalinity by lining the channel with limestone.

Treatment of AMD from the three major mine springs and related discharges using passive treatment is geochemically feasible. Large metal concentrations are balanced by modest discharge volumes. Not all potential loadings on constructed wetlands were considered. Larger discharges and surface runoff can increase loads. Large aluminum and iron concentrations, particularly in the Huntsville Gob subbasin, can affect wetland and limestone drain performance. The minimum calculated wetland sizes of 0.39 to 2.2 ha may be achievable based on topography and current (2005) land use.

Summary and Conclusions

Sugar Creek, some of its tributaries, and the Mitchell Mine drainage near Huntsville, Missouri, receive discharges from abandoned coal mines. The U.S. Geological Survey, in cooperation with the Missouri Department of Natural Resources, conducted an investigation beginning in June 2003 to evaluate the effects of acidic mine drainage (AMD) sources on affected segments of Sugar Creek and Mitchell Mine drainage, detect possible trends in water quality, and to identify possible remedial options. From September 4 to 11, 2003, discharge and waterquality data were collected synoptically at all AMD sites with measurable discharge and selected surface-water sites during a period of stable high baseflow and no precipitation. Additional synoptic sampling was conducted quarterly in January, March, and June 2004 at selected sites to detect any seasonal or temporal variation in discharge or water quality.

The results of this study indicate that discharge from the largest mine spring in the Huntsville Gob subbasin accounted for 31 to 62.5 percent of the combined AMD discharging to its receiving stream and ranged from 0.28 to 0.42 L/s (liter per second). The median pH value for the mine spring was 4.6 and the water was acidic with negative net alkalinities. The dominant source of acidity in the water samples was iron, but a substantial amount of the total acidity concentration was because of large aluminum concentrations. The combined discharge of dissolved metals from the mine spring and other smaller sources of AMD measured downstream had an average load of 78 kg/d (kilograms per day). Under high baseflow conditions, flow from open limestone channels draining the remediated areas of the Huntsville Gob and other diffuse seeps can contribute the majority of AMD discharging to the drainage. All identified sources of AMD are located in the upper 750 meters of the drainage.

Discharge from the largest mine spring in the Calfee Slope subbasin accounted for 13 to 55 percent of the discharge downstream from the AMD confluence during the study, and ranged from 1.2 to 1.9 L/s. Sewage effluent discharging to the stream accounted for 17 to 33 percent of the total discharge. The median pH value for the mine spring was 5.2. Water from the mine spring contains some alkalinity, but is net acidic. After mixing with sewage effluent with a median pH value of 9.2, the median pH downstream was 4.6. The predominant source of acidity in water samples from the mine spring was iron. Aluminum concentrations were small. Calculated dissolved metal loads had an average value of 30 kg/d for the combined discharge at the most downstream sampling site. The effects of carbonate buffering, precipitation of oxy-hydroxides, and dilution from sewage effluent combined to decrease the average dissolved metal load by approximately 60 percent from 74 kg/d calculated for the discharge from the mine spring.

The Huntsville Gob drainage and Calfee Slope drainage affect water quality in Sugar Creek. Discharge in Sugar Creek ranged from 16 to 394 L/s at sites upstream from the confluence with the Huntsville Gob drainage, and from 15 to 451 L/s downstream from the confluence with the Calfee Slope drainage; however, discharge in Sugar Creek has been observed to decrease to zero during abnormally dry summers. The corresponding combined discharge of AMD from the Huntsville Gob and Calfee Slope drainages ranged from 2.8 to 18.2 L/s. Values for pH in Sugar Creek downstream from the AMD discharges had a median value of 7.4, and all measurements had values of 7.0 or larger. The calculated dissolved metal load had an average value of 4.9 kg/d for the discharge upstream from identified AMD sources and increased to 34 kg/d downstream from the discharges from the Huntsville Gob and Calfee Slope drainages. These two tributaries contribute nearly the entire metal load in Sugar Creek under baseflow conditions. Precipitation of iron, aluminum, and possibly manganese oxy-hydroxides is likely occurring in Sugar Creek because of the effects of AMD mixing with unaffected stream water, carbonate buffering, and the resulting near-neutral pH.

Discharge from the largest mine spring in the Mitchell Mine Basin accounted for 9 to 35 percent of the combined discharge at the most downstream sampling site and ranged from an estimated 2.6 to 7.3 L/s. Effluent discharging from sewage treatment lagoons downstream accounted for 33 to 82 percent of the total discharge. The median pH value at the mine spring was 6.0, and the water was net acidic for all samples. After mixing with sewage effluent downstream with a median pH of 8.0, the median pH value was 7.7. The calculated dissolved metal load had a value of 1.8 kg/d for the combined discharge for the September 2003 sampling event, a decrease of approximately 96 percent for the calculated load from the mine spring. The water from the mine spring had an average metal load of 53 kg/d for all five sampling events. Water from the mine spring contained 157 to 178 mg/L (milligrams per liter) alkalinity, but was net acidic.

The pH, specific conductance, alkalinity, and sulfate concentration data collected for this study were compared to data from two previous studies during the past 17 years for mine springs and surface-water sites in the Calfee Slope subbasin, Sugar Creek, and Mitchell Mine Basin. General decreases in specific conductance and sulfate concentrations and increased pH indicate that AMD generating processes have declining rates of acid production, but the data are insufficient to identify any definite trends or time frame. The pH values for mine springs in the Calfee Slope subbasin and Mitchell Mine Basin were significantly larger, and the specific conductance was significantly smaller, than in previous studies (p < 0.05), but the data were insufficient to identify any other trends. Generally, the median pH values in Sugar Creek were larger, and specific conductance and sulfate concentrations smaller, at comparable sample sites for the current (2003–2004) study than in previous studies.

Cubitainer experiments supported the feasibility of alkalinity generation by the dissolution of limestone within passivetreatment systems such as open limestone channels and anoxic limestone drains to meet targeted values for Sugar Creek under the State of Missouri's Total Maximum Daily Load program that also may be applicable to the Mitchell Mine drainage. Geochemical experiments indicate that mixing AMD with sewage effluent and/or dilution with stream water or water from potential constructed impoundments also may provide partial remediation of AMD. Successive alkalinity producing systems (SAPS) or other constructed wetlands will likely be required to meet targeted goals for pH values larger than 6.5 and alkalinities of 90 mg/L, and to remediate AMD in the Huntsville Gob and Calfee Slope subbasins.

Selection and design of an appropriate passive-treatment system generally considers water chemistry, discharge, topography, and other site-specific characteristics. Discharges measured during the study for mine springs and their receiving streams generally were low, ranging from less than 0.1 to 7.9 L/s. To meet Missouri Water Quality Standards for pH, all the AMD sources would require at least the construction of settling ponds, wetlands, or a combination of the two to facilitate iron oxidation, hydrolysis, and precipitation of iron oxyhydroxides, and also some limestone treatment system for increasing alkalinity.

Low pH and large metal concentrations in AMD from mine springs in the Huntsville Gob subbasin indicate an initial treatment using a settling pond and/or an open limestone channel to increase alkalinity. The minimum calculated wetland size to treat the combined AMD in the Huntsville Gob subbasin is 0.83 ha (hectare) based on a removal rate for iron of $0.02 \text{ kg/m}^2/d$ (kilogram per square meter per day). Because pH was observed to remain small after AMD flowed through the existing limestone channel, treatment with a SAPS also may be considered.

If treatment of AMD in the Calfee Slope subbasin is implemented at the mine spring or further downstream, small pH and large metal concentrations would indicate initial treatment using a settling pond and/or open limestone channel to increase alkalinity. The minimum calculated wetland size is 0.46 ha at the mine spring. If the wetland is constructed for the combined discharge of AMD and sewage effluent downstream, the minimum calculated size is 0.39 ha based on an iron removal rate of 0.02 kg/m²/d. Diluting AMD at this site with sewage effluent from the nearby treatment facility would require a larger discharge from the sewage lagoons than the 0.7 to 2.6 L/s measured from the treatment facility. This option likely would be only a partial solution to meeting water-quality goals for pH and alkalinity, and does not remove metals from the stream environment. Because approximately only 300 meters of the 1.3 kilometers of the Calfee Slope drainage is lined with limestone, the potential exists to increase alkalinity and pH by lining more of the channel. Treatment with a SAPS also may be appropriate.

The minimum calculated wetland size at the mine spring site in the Mitchell Mine Basin is 2.2 ha based on a removal rate of 0.005 kg/m²/d for anaerobic wetlands. Diluting AMD at this site with sewage effluent would require a larger discharge from the sewage lagoons than the measured discharges from the treatment facility of 4 to 23 L/s. Because of the 1.6 kilometers distance between the mine spring and the sewage lagoons, piping AMD from the mine spring to the vicinity of the sewage lagoons also might be necessary to implement this option. Metals would still be discharged to the stream environment. Because the Mitchell Mine drainage flows through a mud bottom channel for much of its length, the potential exists to increase the alkalinity by lining the channel with limestone.

Consideration of water chemistry and discharge indicate that passive-treatment options are geochemically feasible for AMD remediation in the Sugar Creek Basin and Mitchell Mine Basin. Topographical relief is sufficient to provide adequate hydraulic head for passive-treatment systems. Economic feasibility studies can determine which systems are best suited for the site and need to consider geochemical feasibility, topographical setting, construction, and long-term maintenance costs. Solutions for treatment of AMD will, to a large extent, be dependent on cooperation of landowners because the primary sources of AMD are located on private land, but actual land requirements for remediation systems should not be large.

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TABLE

[NWIS, National Water Information System; L/s, liters per second; ft³/s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; mV, millivolt; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; µg/L, micrograms per liter; ICP, inductively-coupled plasma; UV-vis, ultraviolet-visible spectroscopy; --, no data; E, estimated; <, less than; >, greater than]

Site number (fig. 1)	NWIS station number	Date	Discharge, instanta- neous (L/s)	Discharge, instanta- neous ^a (ft ³ /s)	Dissolved oxygen, field (mg/L)	pH, field (SU)	Eh, field (mV)	Specific conduc- tance, field (µS/cm)	Temper- ature (°C)	Hardness, as calcium carbonate (mg/L)	Calcium, dissolved (mg/L)	Magnes- ium, dissolved (mg/L)	Potas- sium, dissolved (mg/L)	Sodium, dissolved (mg/L)
SC 18	302827002284601	07/08/2003				7.0			28.4					
SC-13	392827092284001	07/08/2003				7.9 8 0			20.4					
SC-1.15	392817092290201	07/08/2003				0.2			29.7					
SC-2S	392811092291201	07/08/2003				7.7			28.7					
		09/10/2003	17	0.6	1	7.8	400	268	24.1					
		01/14/2004			12.6	8.1	411	359	3					
		03/11/2004			12.5	8.1	340	562	9.8					
		06/09/2004	13	.47	5.2	7.4	404	310	23.4					
SC-3S	392716092312301	07/08/2003				7.7			28					
		09/10/2003	16	.57	4.9	7.5	456	357	20.2					
		01/13/2004	E48	E1.7	13	7.8	341	863	1.5					
		03/10/2004	E125	E4.4	12.5	8.1	298	573	8.1					
		06/07/2004	E22	E.77	4	7.4	374	538	24.7					
SC-4S	392713092281101	09/16/2003				7.6		519	20.2					
SC-4.7S	392703092292701	09/16/2003				7.9		759	20.2					
SC-4.8S	392701092300501	09/16/2003				7.7		722	19.8					
SC-4.9S	392704092303501	09/16/2003				7.9		812	18.4					
SC-5S	392716092312201	09/10/2003	.09	.003	4.7	7.3	431	669	19.8					
		09/16/2003				7.7		776	18.3					
		01/13/2004	16	.55	13	8	244	1,038	1.1					
		03/10/2004	63	2.2	11.6	8.1	264	863	9					
		06/07/2004	4.6	.16	7.1	7.6	371	853	25.3					
SC-6S	392716092312401	12/29/2003	394	14	14.9	7.8	374	508	3	230	65.6	16.3	4.36	9.29
		01/13/2004	63	2.2	13.5	7.6	326	936	1.2					
		03/10/2004	187	6.6	12.1	8.1	220	747	8.7		113.0			
		06/07/2004	26	.93	4.6	7.5	337	615	24.3		91.3			

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Site number (fig. 1)	NWIS station number	Date	Discharge, instanta- neous (L/s)	Discharge, instanta- neous ^a (ft ³ /s)	Dissolved oxygen, field (mg/L)	pH, field (SU)	Eh, field (mV)	Specific conduc- tance, field (µS/cm)	Temper- ature (°C)	Hardness, as calcium carbonate (mg/L)	Calcium, dissolved (mg/L)	Magnes- ium, dissolved (mg/L)	Potas- sium, dissolved (mg/L)	Sodium, dissolved (mg/L)
HG-2M	392634092310101	07/23/2003				4.1			15.9					
		09/11/2003	0.28	0.01	1	4.6	443	3.350	15.5	1.800	445	171	13.4	72.9
		12/09/2003	.40	.01	.5	4.4	395	4.030	11.9					
		12/29/2003	.42	.02	1	4.6	416	3,490	11	1,600	410	140	12.6	63.8
		01/14/2004	.40	.01	1.1	4.7	466	3,470	10.7					
		03/11/2004	.42	.01	.6	4.7	597	3,650	10.5		419			
		06/08/2004	.31	.01	1.9	4.5	512	2,970	13.5	1,700	431	147	E12	66.4
		07/21/2004	.28	.01	0	4.6	423	3,700	15		434			
		08/30/2004	.32	.01	0	4.5	386	3,470	15.2	1,700	445	139	E5.27	62
HG-3S	392637092310501	09/11/2003	.40	.01	3	3	621	4,890	21.5					
		01/14/2004	.85	.03	8.6	3.5	581	4,650	3.2					
		03/11/2004	.85	.03	8.4	3.5	585	4,050	7.9					
		06/08/2004	.45	.02	3.4	2.9	624	4,300	25.9					
HG-4M	392637092310401	07/23/2003				2.1			17.3					
		09/11/2003	.11	.004	13.2	2.7	597	6,320	19.8	1,200	285	126	<.48	16
		12/09/2003	.11	.004	.1	2.6	582	8,380	11					
		12/30/2003	.08	.003	3.3	2.9	588	7,180	9.9	1,800	420	182	<32	24.3
		01/14/2004	.1	.003	.3	2.8	572	7,310	9.2					
		03/11/2004	.11	.004	1.2	2.7	601	6,160	9.1		320			
		06/08/2004	.1	.003	3.8	2.7	586	5,960	15.3		419			
HG-5S	392636092310301	09/11/2003	E<.28	E<.01	.6	2.6	631	6,760	27					
HG-5.5S	392634092310201	09/11/2003	.06	.002	7.9	2.5	623	5,050	23.7					
		03/11/2004			10.5	3	711	3,930	11.2					
HG-6S	392638092305701	09/11/2003			1.2	4.9	364	5,390						
		03/11/2004			6.4	5.4	256	3,260	11.5					
HG-6.9S	392638092310401	09/11/2003	.06	.002	8.4	6.8	145	3,390	21.1					
		12/30/2003	1.1	.04	6.2	6.9	223	2,360	2					
		01/14/2004	.4	.01	9.2	6	549	4,650	.2					
		03/11/2004	.74	.03	18.8	6.1	454	3,080	4.5					
		06/08/2004	.15	.01	6.4	5.8	262	3,240	23.8					

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Site number (fig. 1)	NWIS station number	Date	Discharge, instanta- neous (L/s)	Discharge, instanta- neous ^a (ft ³ /s)	Dissolved oxygen, field (mg/L)	pH, field (SU)	Eh, field (mV)	Specific conduc- tance, field (µS/cm)	Temper- ature (°C)	Hardness, as calcium carbonate (mg/L)	Calcium, dissolved (mg/L)	Magnes- ium, dissolved (mg/L)	Potas- sium, dissolved (mg/L)	Sodium, dissolved (mg/L)
HG-7S	392638092310501	09/11/2003	0.45	0.02	4.8	3	623	4,540	20.6					
		12/30/2003	E>1.5	E>.05	7.6	4.4	522	3,300	1.3	1,200	314	112	E6.78	38.6
		01/14/2004	1.3	.05	9.2	3.7	549	4,650	.2					
		03/11/2004	1.7	.06	16.8	3.7	578	3,940	4.3		354			
		06/08/2004	.73	.03	5.1	3	613	4,550	22.7	2,000	482	189	E10.8	63.5
		08/30/2004	E>1.2	E>.04	5.8	3.5	585	3,200	25.2		382			
HG-8S	392648092312201	01/13/2004	E>1.9	.07	9.9	3.9	566	3,980	.2					
		03/10/2004			8.8	3.5	588	2,660	11.8					
		06/07/2004			2.7	2.6	698	4,310	31.2					
HG-10S	392648092312301	01/13/2004	.74	.03	10.5	8.2	392	1,771	.4					
		03/10/2004	2	.07	5.5	7.4	380	1,229	6.9					
		06/07/2004	E4	E.01	4.2	7	574	1,679	20.3					
HG-11S	392707092312201	09/10/2003	.65	.02	7.1	2.8	783	3,410	18.5					
		01/13/2004	>2.6	>.09	11.3	4.7	424	2,660	2.3					
		03/10/2004	6.2	.22	8.4	5	450	1,675	11.2					
		06/07/2004	E.28	E.01	5.3	2.9	744	2,760	29.3		394			
		06/10/2004	E14,200	E500	9.3	7.1	433	295	20.5		40.4			
		06/10/2004	E2,830	E100	7.2	6.7		642	23.4		106			
HG-12S	392719092313301	01/13/2004	4.4	.16	10.9	4.4	400	2,470	.1					
		03/11/2004	8.4	.3	10.6	4.8	375	1,520	9.4					
		06/07/2004	.76	.03	6.6	3.1	705	2,350	26.2					
SC-7S	392723092313801	09/10/2003	E17	E.60	5.8	7.2	446	427	21.6					
		12/29/2003	401	14	11.3	7.7	147	638	3.4					
		01/13/2004	61	2.2	12.4	7.2	222	1,050	1.1					
		03/10/2004	177	6.2	12.1	7.7	218	717	7.7					
		06/07/2004	28	1	5.7	7	285	716	24.8		108			
MC-2S	392655092320301	07/24/2003				7.3			18.3					
MC-3M	392658092320001	07/24/2003			0	5.2		4,060	19.4					
MC-3.3S	392659092320001	07/24/2003				2.7			20.9					
		09/11/2003	.03	.001	5.9	2.8	732	4,940	25.3					
MC-4S	392702092315901	07/24/2003				3.9			19.5					

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Site number (fig. 1)	NWIS station number	Date	Discharge, instanta- neous (L/s)	Discharge, instanta- neous ^a (ft ³ /s)	Dissolved oxygen, field (mg/L)	pH, field (SU)	Eh, field (mV)	Specific conduc- tance, field (µS/cm)	Temper- ature (°C)	Hardness, as calcium carbonate (mg/L)	Calcium, dissolved (mg/L)	Magnes- ium, dissolved (mg/L)	Potas- sium, dissolved (mg/L)	Sodium, dissolved (mg/L)
MC-4.9S	392703092320101	07/24/2003				3			19.6					
		09/11/2003	0.03	0.001	4.2	3	724	4.680	22.3					
MC-5S	392704092320001	09/11/2003	.08	.003	6.7	3.2	701	4,500	22.8					
SC-8S	392736092323801	07/08/2003				7.6			27.6					
		07/22/2003				7.7		536						
		09/10/2003	13	.47	7.6	7.6	430	449	19.4					
		01/12/2004	53	1.9	9.1	7.2	217	1,030	1.1					
		03/08/2004	425	15	11.5	7.7	337	609	6.6					
		06/09/2004	27	.96	4.8	7.3	371	710	22.5					
CS-2S	392635092322401	09/09/2003	.17	.01	2.1	3.9	501	2,520	15.1					
		01/13/2004	.23	.01	4.4	3.8	460	2,760	11.9					
		03/09/2004	.31	.01	13.7	4.3	401	2,200	13.1					
		06/09/2004	.12	.004	1.1	3.8	408	2,170	14.5					
CS-2.5M	392636092322601	09/09/2003	E<.28	E<.01	.5	4.6	463	2,670	15.2					
CS-2.6M	392636092322701	09/09/2003	E.08	E.003	.4	4.3	487	2,590	13					
CS-3S	392639092323301	07/09/2003				6.5			23.1					
		09/09/2003	.4	.01	7.2	5.9	349	2,240	19.6					
		01/13/2004	1.5	.05	10.3	6.5	374	2,030	1					
		03/09/2004	2.6	.09	5	7.4	245	1,320	7.2					
		06/09/2004	1.8	.06	7.5	6.5	303	1,120	19.7					
CS-3.1M	392637092323401	09/09/2003	E.28	E.01	.3	4.6	391	2,190	14.1					
CS-3.2M	392640092323401	09/09/2003	.03	.001	3.7	6.3	182	2,340	23					
CS-3.9M	392645092323801	09/09/2003	E<.28	E<.01	2.4	3.7	679	2,640	19.7					
CS-4S	392647092323801	09/09/2003	E.51	E.02	7.5	6.7	386	2,150	18.8					
		01/13/2004	.88	.03	12.1	6.8	278	2,060	.8					
		03/09/2004	3.9	.14	6.2	6.5	339	1,380	7.9					
		06/09/2004	2.5	.09	5.6	6.8	282	1,720	20					
CS-4.9M	392648092324101	09/08/2003	.03	.001	.3	3.3	469	2,340	16					

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Site number (fig. 1)	NWIS station number	Date	Discharge, instanta- neous (L/s)	Discharge, instanta- neous ^a (ft ³ /s)	Dissolved oxygen, field (mg/L)	pH, field (SU)	Eh, field (mV)	Specific conduc- tance, field (µS/cm)	Temper- ature (°C)	Hardness, as calcium carbonate (mg/L)	Calcium, dissolved (mg/L)	Magnes- ium, dissolved (mg/L)	Potas- sium, dissolved (mg/L)	Sodium, dissolved (mg/L)
CS-5M	392647092323701	07/22/2003				53		3 610	13.6					
00 5111	372011072323101	09/09/2003	12	0.04	6.8	5.2	332	3 540	13.8	2 300	448	279	31.8	207
		12/09/2003	1.2	0.01	53	5.2	315	4 870	13.5	2,500				207
		01/13/2004	1.1	.05	3.5	5.2	318	4 260	13.4					
		03/09/2004	1.7	.00	4.2	5.6	348	2 990	13.1		422			
		06/09/2004	1.9	.07	5	5.2	328	2,670	14		442			
		07/08/2004	E1.9	E.07	4.9	5.3	405	4.260	13.8					
CS-6S	392648092323701	09/09/2003	1.7	.06	5.8	5.5	320	3.270	14.9					
		01/13/2004	3.8	.14	8.2	5.9	303	3.010	4.8					
		03/09/2004	E5.4	E.19	8.9	6.6	278	1,915	8					
		06/09/2004	4.1	.15	6	5.7	276	2,200	17.5					
		06/10/2004	E1,420	E50	6.9	6.8	220	564	19.6		77			
CS-7S	392710092323901	09/08/2003	1.2	.04	4.8	3.5	652	3,000	19.5					
		01/12/2004	1.5	.05	8	6.1	250	2,640	4.2					
		03/08/2004	E9.1	E.32	8.9	7	279	1,683	6.5					
		06/09/2004	5.6	.2										
CS-8S	392712092323901	07/22/2003				9.2		862						
		09/08/2003	.71	.03	>20	10.7	286	752	27	240	69.6	17.1	11.1	38.9
		01/12/2004	1.5	.05	19	9.4	349	1,026	5.3					
		03/08/2004	2.6	.09	15.6	8.9	278	786	11.6		129			
		06/09/2004	.93	.03	3.8	8.4	346	880	25.5		104			
CS-9S	392729092323801	09/08/2003	2.2	.08	8	4.5	541	2,100	21.6					
		01/12/2004	5.4	.19	10.2	6.8	210	2,270	3.9					
		03/08/2004	12	.41	9.9	6.9	196	1,490	9.1		236			
		06/09/2004	5.4	.19	4.9	4.6	443	2,290	21.8		381			
SC-9S	392732092324901	09/08/2003	15	.54	6.4	7.5	352	605	19.8	260	73.7	19.2	6.13	13.6
		01/12/2004	58	2	9.9	7.1	247	1,160	.6					
		03/08/2004	451	16	11.6	7.7	295	615	6.5		91			
		06/09/2004	26	.9	4.9	7.2	331	931	22.5		132			
SC-10S	392745092332401	07/08/2003				7.8			29.7					

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MM-2S	392608092323801	09/05/2003	1.1	0.04	8.2	7.9	272	542	19.6					
		12/09/2003	E.6	E.02	11.9	7.5	178	1.080	6.6					
		01/15/2004	E1.0	E.04	13.3	8.5	175	1.050	1					
		03/10/2004	.2	.01	10.6	8	241	1.050	3.8					
		06/08/2004	.51	.02	5.2	7.6	274	709	23.4					
MM-3M	392609092323701	07/22/2003				6		2.820						
		09/05/2003	E2.6	E.09	<.1	5.9	210	2,580			323	156	23.6	87.4
		12/09/2003	4.2	.15	.4	6	191	2,880	13.6					
		01/14/2004	3.7	.13		5.9		2,840						
		01/15/2004	2.5	.09	.4	6.4	438	2,450	13.5					
		03/10/2004	7.3	.26	.6	6.2	326	1,980	13.2		347			
		06/08/2004	E2.7	E.1	0	5.9	244	1,960	13.4		337			
MM-4S	392610092323801	09/05/2003	3.7	.13	6.4	6.4	181	1,630						
		12/09/2003	E5.1	E.18	7	6.3	211	2,580	7.4					
		01/15/2004	3.5	.13	6.6	7	216	2,200	9.4					
		03/10/2004	7.9	.28	8.2	6.7	339	1,660	8.5					
		06/08/2004	3.2	.11	4.6	6.3	228	1,800	16.6					
MM-4.1M	392609092323801	12/09/2003	E.28	E.01	8.1	7	222	1,360	7.4					
MM-4.4S	392614092324701	07/09/2003				5.8			18.1					
MM-5S	392627092333401	09/04/2003	5.9	.21	5.9	7.4	218	1,370	17.7					
		12/08/2003	8.5	.3	12.5	6.8	249	1,970	7.9					
		01/15/2004	7.9	.28	12.3	7.6	200	1,900	.2					
		03/09/2004	14	.51	10.9	7.6	204	1,270	9					
		06/08/2004	5.7	.2	5.3	6.1	289	1,780	21.3					
MM-6S	392627092333301	07/22/2003				8.5		823						
		09/04/2003	E23	E.81	6.6	8.8	400	706	23.9	220	63.9	15.8	12.6	47.4
		12/08/2003	4	.14	8.9	7.6	250	877	6					
		01/15/2004	E4.0	E.14	2.9	8	252	950	4.2					
		03/09/2004	9.9	.35	5.1	8.1	309	913	10.2		107			
		06/08/2004	E5.9	E.21	4.6	7.9	344	835	31.1		82			

[NWIS, National Water Information System; L/s, liters per second; ft³/s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; mV, millivolt; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; µg/L, micrograms per liter; ICP, inductively-coupled plasma; UV-vis, ultraviolet-visible spectroscopy; --, no data; E, estimated; <, less than; >, greater than]

Site number (fig. 1)	NWIS station number	Date	Discharge, instanta- neous (L/s)	Discharge, instanta- neous ^a (ft ³ /s)	Dissolved oxygen, field (mg/L)	pH, field (SU)	Eh, field (mV)	Specific conduc- tance, field (µS/cm)	Temper- ature (°C)	Hardness, as calcium carbonate (mg/L)	Calcium, dissolved (mg/L)	Magnes- ium, dissolved (mg/L)	Potas- sium, dissolved (mg/L)	Sodium, dissolved (mg/L)
MM-7S	392627092333501	09/04/2003	28	1	5.8	8.4	256	1,060	20.7					
		12/08/2003	12	.43	11.8	6.9	255	1,600	6.8					
		01/15/2004	12	.42	10.7	7.7	179	1,530	1.7					
		03/09/2004	30	1.1	3.8	7.7	172	1,180	8.9					
		06/08/2004	12	.42	5.2	6.6	204	1,530	24.4					
MW 04-01	392616092304201	06/29/2004			0	6.1	222	2,750	15					
		07/08/2004			0	6.2	270	3,410	15		529	377	23.1	237
		07/21/2004			0	6.2	335	4,640	15.2					
		08/31/2004			.1	6.2	265	4,600	14.7	2,900	543			
MW 04-02	392629092310101	07/08/2004			.1	4.4	385	3,270	15.9					
		07/21/2004			0	4.6	415	5,270	14.4		350			
		08/31/2004			0	4.2	434	7,250	14.5	2,300	434	294	17.6	81.6
MW 04-03	392626092310101	07/08/2004			0	6.2	253	2,020	14.5					
		07/20/2004			0	6.3	286	3,210	14.4		447			
		08/31/2004			0	4.8	396	4,670	14	2,200	454	268	12.5	71
MW 04-04	392646092323601	07/08/2004			.4	6	445	2,340	14.1		546			

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Site number (fig. 1)	NWIS station number	Date	Acidity, heated, as hydrogen (mg/L)	Alkalinity, field, as calcium carbonate (mg/L)	Bicar- bonate, field (mg/L)	Carbon- ate, field (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Ammonia, dissolved, as nitrogen (mg/L)	Nitrite plus nitrate, dissolved, as nitrogen (mg/L)	Ortho- phosphate, dissolved, as phosphorus (mg/L)	Organic carbon, dissolved (mg/L)
SC-1S	392827092284601	07/08/2003											
SC-1.1S	392817092290201	07/08/2003											
SC-2S	392811092291201	07/08/2003											
		09/10/2003		107	130	0			17				
		01/14/2004											
		03/11/2004											
		06/09/2004											
SC-3S	392716092312301	07/08/2003											
		09/10/2003		63	E77	E0			51				
		01/13/2004											
		03/10/2004											
		06/07/2004											
SC-4S	392713092281101	09/16/2003											
SC-4.7S	392703092292701	09/16/2003											
SC-4.8S	392701092300501	09/16/2003											
SC-4.9S	392704092303501	09/16/2003											
SC-5S	392716092312201	09/10/2003		124	151	0			215				
		09/16/2003											
		01/13/2004											
		03/10/2004											
		06/07/2004											
SC-6S	392716092312401	12/29/2003	0.3	118	143	0	8.1	4.55	112	0.02	< 0.379	0.016	
		01/13/2004		153	186	0			320				
		03/10/2004		133	E159	E2			212				
		06/07/2004		154	187	0			166				

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Site number (fig. 1)	NWIS station number	Date	Acidity, heated, as hydrogen (mg/L)	Alkalinity, field, as calcium carbonate (mg/L)	Bicar- bonate, field (mg/L)	Carbon- ate, field (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Ammonia, dissolved, as nitrogen (mg/L)	Nitrite plus nitrate, dissolved, as nitrogen (mg/L)	Ortho- phosphate, dissolved, as phosphorus (mg/L)	Organic carbon, dissolved (mg/L)
HC AL	202/2/002210101	07/00/0000											
HG-2M	392634092310101	07/23/2003											
		09/11/2003	28				16.3	24.1	3,850	3.48	<0.022	0.016	
		12/09/2003	22						4,610				
		12/29/2003	21	21	E27	E0	14.5	24	3,550	2.69	<.016		
		01/14/2004	21						3,800				
		03/11/2004	22	24	E31	E0			3,620				
		06/08/2004	21	25	E33	E0	14.2	24.5	3,920	2.7	.019		
		07/21/2004	20	22	E28	E0			4,250				
		08/30/2004	17	17	E23	E0	10.1	29.2	2,590	2.68	.18	<.09	
HG-3S	392637092310501	09/11/2003							5,250				
		01/14/2004											
		03/11/2004											
		06/08/2004											
HG-4M	392637092310401	07/23/2003											
		09/11/2003	160				21.1	77.5	10,300	5.9	<.022	.753	
		12/09/2003	130										
		12/30/2003	120				13.8	101	9,040	5.09	<.016	.438	
		01/14/2004	120						9,760				
		03/11/2004	120						9,380				
		06/08/2004	8.5						13,800				
HG-5S	392636092310301	09/11/2003											
HG-5.5S	392634092310201	09/11/2003											
		03/11/2004											
HG-6S	392638092305701	09/11/2003											
		03/11/2004											
HG-6.9S	392638092310401	09/11/2003		152	185	0			2,570				
		12/30/2003		42	E51	E0							
		01/14/2004		51	E62	E0							
		03/11/2004		17	E21	E0							
		06/08/2004											

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Site number (fig. 1)	NWIS station number	Date	Acidity, heated, as hydrogen (mg/L)	Alkalinity, field, as calcium carbonate (mg/L)	Bicar- bonate, field (mg/L)	Carbon- ate, field (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Ammonia, dissolved, as nitrogen (mg/L)	Nitrite plus nitrate, dissolved, as nitrogen (mg/L)	Ortho- phosphate, dissolved, as phosphorus (mg/L)	Organic carbon, dissolved (mg/L)
110 78	202(2002210501	00/11/2002							5 800				
HG-/S	392638092310501	10/20/2002							5,890				
		12/30/2003	28	11	E16	E0	9.62	24.1	2,860	1.95	0.048	0.02	
		01/14/2004	44						5,010				
		03/11/2004	55						3,880				
		06/08/2004	50				12.9	41.4	7,310	4.04	.041		
110 00	202(10002212201	08/30/2004	22						2,650				
HG-85	392648092312201	01/13/2004											
		03/10/2004											
	202610002012201	06/07/2004											
HG-10S	392648092312301	01/13/2004											
		03/10/2004											
		06/07/2004											
HG-11S	392707092312201	09/10/2003							3,070				
		01/13/2004	13						2,260				
		03/10/2004	7	3	E4	E0			1,350				
		06/07/2004	11						3,220				
		06/10/2004							60				
		06/10/2004							296				
HG-12S	392719092313301	01/13/2004											
		03/11/2004											
		06/07/2004											
SC-7S	392723092313801	09/10/2003		88	107	0			105				
		12/29/2003		122	148	0			169				
		01/13/2004		133	162	0			422				
		03/10/2004	.4	120	E145	E0			248				
		06/07/2004		136	165	0			254				
MC-2S	392655092320301	07/24/2003											
MC-3M	392658092320001	07/24/2003											
MC-3.3S	392659092320001	07/24/2003											
		09/11/2003							3,970				
MC-4S	392702092315901	07/24/2003											

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Site number (fig. 1)	NWIS station number	Date	Acidity, heated, as hydrogen (mg/L)	Alkalinity, field, as calcium carbonate (mg/L)	Bicar- bonate, field (mg/L)	Carbon- ate, field (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Ammonia, dissolved, as nitrogen (mg/L)	Nitrite plus nitrate, dissolved, as nitrogen (mg/L)	Ortho- phosphate, dissolved, as phosphorus (mg/L)	Organic carbon, dissolved (mg/L)
MC-4.9S	202202002220101	07/04/2002											
	392703092320101	0//24/2003											
16.50	20270 (00222000)	09/11/2003							3,810				
MC-55	392704092320001	09/11/2003											
50-85	392/36092323801	07/08/2003											
		07/22/2003		119	145	0							
		09/10/2003		103	126	0			103				
		01/12/2004		115	140	0							
		03/08/2004											
		06/09/2004											
CS-2S	392635092322401	09/09/2003							2,230				
		01/13/2004											
		03/09/2004											
		06/09/2004											
CS-2.5M	392636092322601	09/09/2003											
CS-2.6M	392636092322701	09/09/2003											
CS-3S	392639092323301	07/09/2003											
		09/09/2003		17	E20	E0			1,860				
		01/13/2004											
		03/09/2004											
		06/09/2004											
CS-3.1M	392637092323401	09/09/2003											
CS-3.2M	392640092323401	09/09/2003											
CS-3.9M	392645092323801	09/09/2003											
CS-4S	392647092323801	09/09/2003		60	73	0			1,500				
		01/13/2004		69	85	0							
		03/09/2004											
		06/09/2004											
CS-4.9M	392648092324101	09/08/2003											
[NWIS, National Water Information System; L/s, liters per second; ft^3 /s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; mV, millivolt; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; \circ C, degrees Celsius; μ S/L, micrograms per liter; ICP, inductively-coupled plasma; UV-vis, ultraviolet-visible spectroscopy; --, no data; E, estimated; <, less than; >, greater than]

Site number (fig. 1)	NWIS station number	Date	Acidity, heated, as hydrogen (mg/L)	Alkalinity, field, as calcium carbonate (mg/L)	Bicar- bonate, field (mg/L)	Carbon- ate, field (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Ammonia, dissolved, as nitrogen (mg/L)	Nitrite plus nitrate, dissolved, as nitrogen (mg/L)	Ortho- phosphate, dissolved, as phosphorus (mg/L)	Organic carbon, dissolved (mg/L)
CS 5M	202647002222701	07/22/2002		22	E29	EO							
C2-21M	392047092323701	0//22/2003		24	E28	EU		 7					
		12/00/2003	20	54 40	E42	EU	10.0	4/./	4,150	3.32	<0.022		
		12/09/2003	19	40	E49	EU			4,500				
		01/15/2004	19	33	E44	EU			2,990				
		05/09/2004	19	43	E33 E47	EU			4,380				
		07/08/2004	20	30 42	E47	EU			4,900				
CS 65	2026/2002222701	0//08/2004		43 20	E32 27	EU							
03-03	392046092323701	09/09/2003		53	57	0			3,140				
		03/00/2004		33 86	105	0							
		06/09/2004		60 54	105 E66	E0							
		06/10/2004	150	J 4 	E00								
CS-75	392710092323001	00/08/2004							2 510				
0-10	572110072525701	01/12/2004		21	 F25	 F0			2,510				
		03/08/2004											
		06/09/2004											
CS-85	392712092323901	07/22/2004		108	E107	E12							
00 00	572112072525701	09/08/2003	< 1	139	E58	E12 F49	51.7	13.9	154	2.19	292	0.044	47.5
		01/12/2004		219	E239	E14			244				45.7
		03/08/2004		212	E243	E8			208				35.2
		06/09/2004		146	171	3			225				26.8
CS-9S	392729092323801	09/08/2003							1.370				
		01/12/2004	2.4	56	E68	E0			1,300				
		03/08/2004	1.1	89	109	0			863				
		06/09/2004	3.2						3,000				
SC-9S	392732092324901	09/08/2003	.3	95	115	0	8.42	7.8	199	.222	.154	<.007	
		01/12/2004	.4	103	125	0			470				
		03/08/2004	.2	115	139	0			178				
		06/09/2004		128	157	0			320				
SC-10S	392745092332401	07/08/2003											

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Site number (fig. 1)	NWIS station number	Date	Acidity, heated, as hydrogen (mg/L)	Alkalinity, field, as calcium carbonate (mg/L)	Bicar- bonate, field (mg/L)	Carbon- ate, field (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Ammonia, dissolved, as nitrogen (mg/L)	Nitrite plus nitrate, dissolved, as nitrogen (mg/L)	Ortho- phosphate, dissolved, as phosphorus (mg/L)	Organic carbon, dissolved (mg/L)
	202(00002222001	00/05/2002		150	101	0			100				
MM-25	392608092323801	12/00/2003		158	191	0			109				
		12/09/2003											
		01/15/2004											
		05/10/2004											
101 211	202(00002222201	00/08/2004											
WIW-5W	392009092323701	07/22/2003		151	184	0				1.52			
		12/00/2003	4.2	160	195	0	21.5	25.2	1,920	1.53	<0.022	<0.007	
		12/09/2003	5.0	108	205	0			839				
		01/14/2004											
		01/15/2004	5.7	100	195	0			1,900				
		05/10/2004	5.5	1/8	210	0			1,920				
MM 4C	202(10002222801	00/08/2004	1.5	157	E192	EU			2,300				
IVIIVI-45	392010092323801	12/00/2002		80	104	0			884				
		12/09/2003	2.9	164	200	0							
		01/15/2004		100	195	0							
		05/10/2004		170	207	0							
	202(00002222801	12/00/2002	2	140	1/8	0							
MM 4 4S	392609092323801	12/09/2003											
MM-4.45	392614092324701	07/09/2003											
MM-55	392627092333401	12/09/2003		68	83	0			/1/				
		12/08/2003											
		01/15/2004											
		03/09/2004											
MM (C	202(27002222201	00/08/2004											
IVIIVI-05	392627092333301	07/22/2003	7	1/1	201 E152	3 E0		10.9					
		09/04/2003	./	142	E153	E9	65.6	12.8	114	2.47	.05	.99	29.6
		12/08/2003		209	254	0			140				
		01/15/2004		250	305	0			151				20.0
		03/09/2004		281	341	1			113				5/
		06/08/2004		145	175	1			164				17

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Site number (fig. 1)	NWIS station number	Date	Acidity, heated, as hydrogen (mg/L)	Alkalinity, field, as calcium carbonate (mg/L)	Bicar- bonate, field (mg/L)	Carbon- ate, field (mg/L)	Chloride, dissolved (mg/L)	Silica, dissolved (mg/L)	Sulfate, dissolved (mg/L)	Ammonia, dissolved, as nitrogen (mg/L)	Nitrite plus nitrate, dissolved, as nitrogen (mg/L)	Ortho- phosphate, dissolved, as phosphorus (mg/L)	Organic carbon, dissolved (mg/L)
MM 76	202(27002222501	00/04/2002		114	120	4			E240				
MM-/S	392027092333301	09/04/2003		114	150	4			E240				
		12/08/2003		117	142	0							
		01/15/2004		138	168	0							
		03/09/2004		166	202	0							
		06/08/2004		49	E59	E0							
MW 04-01	392616092304201	06/29/2004											
		07/08/2004		527	642	0			2,640				
		07/21/2004		506	617	0							
		08/31/2004	0	508	619	0	16.8	12.5	2,620	3.15	< 0.016	< 0.09	
MW 04-02	392629092310101	07/08/2004											
		07/21/2004	54						8,380				
		08/31/2004	84				10.1	26.6	6,030	5.04	<.016	.235	
MW 04-03	392626092310101	07/08/2004											
		07/20/2004	0	278	340	0			2,020				
		08/31/2004	18				6.37	15.4	3,240	1.97	<.016	<.09	
MW 04-04	392646092323601	07/08/2004		129	157	0			1,470				

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Site number (fig. 1)	NWIS station number	Date	Aluminum, dissolved (µg/L)	Aluminum, total (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobolt, dissolved (µg/L)	Copper, dissolved (µg/L)	lron, dissolved ICP (μg/L)	lron, dissolved UV-vis (µg/L)	lron, ferrous, dissolved UV-vis (µg/L)	lron, ferric, computed ^b (μg/L)
0010		07/00/2002												
SC-1S	392827092284601	07/08/2003												
SC-1.1S	392817092290201	07/08/2003												
SC-2S	392811092291201	07/08/2003												
		09/10/2003	7								17	720	700	20
		01/14/2004												
		03/11/2004												
		06/09/2004												
SC-3S	392716092312301	07/08/2003												
		09/10/2003	7								41	1,150	1,080	70
		01/13/2004												
		03/10/2004												
		06/07/2004												
SC-4S	392713092281101	09/16/2003												
SC-4.7S	392703092292701	09/16/2003												
SC-4.8S	392701092300501	09/16/2003												
SC-4.9S	392704092303501	09/16/2003												
SC-55	392716092312201	09/10/2003	4								23	1 330	1 280	50
5005	0,2,100,2012201	09/16/2003												
		01/13/2004												
		02/10/2004												
		05/10/2004												
00 (0	20271(002212401	12/20/2002												
SC-0S	392716092312401	12/29/2003	50	333	516	<0.4	<3	5	EI	<5	49	50	40	10
		01/13/2004	20								68	80	100	0
		03/10/2004	24								31	30	30	0
		06/07/2004	101								241			

[NWIS, National Water Information System; L/s, liters per second; ft³/s, cubic feet per second; mg/L, milligrams per liter; SU, standard units; mV, millivolt; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; µg/L, micrograms per liter; ICP, inductively-coupled plasma; UV-vis, ultraviolet-visible spectroscopy; --, no data; E, estimated; <, less than; >, greater than]

Site number (fig. 1)	NWIS station number	Date	Aluminum, dissolved (µg/L)	Aluminum, total (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobolt, dissolved (µg/L)	Copper, dissolved (µg/L)	lron, dissolved ICP (µg/L)	lron, dissolved UV-vis (µg/L)	lron, ferrous, dissolved UV-vis (μg/L)	lron, ferric, computed ^b (μg/L)
UC M	202624002210101	07/22/2002												
П О- 2М	392034092310101	0//23/2003												
		12/00/2003		438	<80	<10	<80	<200	<120	<280	461,000	516,000	497,000	19,000
		12/09/2003	/5,500								659,000	623,000	030,000	2 000
		12/29/2003	42,200	40,100	<100	<20	<160	<210	<130	<250	463,000	467,000	464,000	3,000
		01/14/2004	42,400								460,000	464,000	458,000	6,000
		03/11/2004	41,100								422,000	465,000	462,000	3,000
		06/08/2004		31,300	<200	<40	<320	<420	<260	<500	422,000	451,000	451,000	0
		07/21/2004	33,300								431,000	461,000	457,000	4,000
		08/30/2004	29,600	32,200	<100	<20	<160	<210	<130	<250	416,000			
HG-3S	392637092310501	09/11/2003	144,000								862,000	879,000	856,000	23,000
		01/14/2004												
		03/11/2004												
		06/08/2004												
HG-4M	392637092310401	07/23/2003												
		09/11/2003		488,000	36.5	31.5	<6	E7	433	<21	1,780,000	2,440,000	1,920,000	520,000
		12/09/2003										2,090,000	2,090,000	0
		12/30/2003	378,000	364,000	<400	<80	<640	<840	E377	<1,000	1,720,000	1,720,000	1,750,000	0
		01/14/2004	395,000								1,820,000	2,000,000	1,810,000	190,000
		03/11/2004	298,000								1,600,000	1,630,000	1,550,000	80,000
		06/08/2004	428,000								E2,320,000	2,440,000	2,370,000	70,000
HG-5S	392636092310301	09/11/2003												
HG-5.5S	392634092310201	09/11/2003												
		03/11/2004												
HG-6S	392638092305701	09/11/2003												
		03/11/2004												
HG-6.9S	392638092310401	09/11/2003	<150								20,500	24,200	24,000	200
		12/30/2003												
		01/14/2004										410,000	374,000	36,000
		03/11/2004										234,000	215,000	19,000
		06/08/2004												

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Site number (fig. 1)	NWIS station number	Date	Aluminum, dissolved (μg/L)	Aluminum, total (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobolt, dissolved (µg/L)	Copper, dissolved (µg/L)	lron, dissolved ICP (μg/L)	lron, dissolved UV-vis (µg/L)	lron, ferrous, dissolved UV-vis (μg/L)	lron, ferric, computed ^b (μg/L)
110 70	202/20202210501	00/11/2002	207.000								1 120 000	1 120 000	1 000 000	10.000
HG-/S	392638092310501	09/11/2003	207,000								1,130,000	1,120,000	1,080,000	40,000
		12/30/2003	64,200	61,200	<100	<20	<160	<210	E84	<250	494,000	462,000	453,000	9,000
		01/14/2004	109,000								783,000	785,000	752,000	33,000
		03/11/2004	81,100								552,000	578,000	547,000	31,000
		06/08/2004		130,000	<200	<40	<320	<420	E252	<500	894,000	603,000	572,000	31,000
		08/30/2004	67,000								406,000			
HG-8S	392648092312201	01/13/2004												
		03/10/2004												
		06/07/2004												
HG-10S	392648092312301	01/13/2004												
		03/10/2004												
		06/07/2004												
HG-11S	392707092312201	09/10/2003	85,700								86,400	101,000	102,000	0
		01/13/2004	39,500								233	239,000	239,000	0
		03/10/2004	16,400								120,000	125,000	123,000	2,000
		06/07/2004	45,600								40,700	44,900	43,400	1,500
		06/10/2004	130								1,040	1,170	1,160	10
		06/10/2004	60								3,250	4,820	4,650	170
HG-12S	392719092313301	01/13/2004												
		03/11/2004												
		06/07/2004												
SC-7S	392723092313801	09/10/2003	65								24	360	340	20
		12/29/2003	35								1,160	1,680	1,600	80
		01/13/2004	152								11.000	11.500	11.500	0
		03/10/2004	66								3.660	2.730	2.420	310
		06/07/2004	1.44								1.000	990	1.020	0
MC-2S	392655092320301	07/24/2003												
MC-3M	392658092320001	07/24/2003												
MC-3 3S	392659092320001	07/24/2003												
5.55	272037072320001	09/11/2003	3 470								107 000	118 000	118 000	0
MC-4S	392702092315901	07/24/2003												

Table

[NWIS, National Water Information System; L/s, liters per second; tt^3/s , cubic feet per second; mg/L, milligrams per liter; SU, standard units; mV, millivolt; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; $\mu g/L$, micrograms per liter; ICP, inductively-coupled plasma; UV-vis, ultraviolet-visible spectroscopy; --, no data; E, estimated; <, less than; >, greater than]

Site number (fig. 1)	NWIS station number	Date	Aluminum, dissolved (µg/L)	Aluminum, total (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobolt, dissolved (µg/L)	Copper, dissolved (µg/L)	lron, dissolved ICP (µg/L)	lron, dissolved UV-vis (µg/L)	lron, ferrous, dissolved UV-vis (µg/L)	lron, ferric, computed ^b (μg/L)
MC-4.98	302703002320101	07/24/2003												
MC-4.95	372703072320101	09/11/2003	5 780								107.000	115,000	115,000	0
MC 58	202704002220001	09/11/2003	5,780								107,000	115,000	115,000	0
MC-35	392704092320001	09/11/2003												
30-85	392730092323801	07/08/2003												
		0//22/2003												
		09/10/2003	21								10	460	430	30
		01/12/2004												
		03/08/2004												
		06/09/2004												
CS-2S	392635092322401	09/09/2003	12,400								126,000	165,000	159,000	6,000
		01/13/2004												
		03/09/2004												
		06/09/2004												
CS-2.5M	392636092322601	09/09/2003												
CS-2.6M	392636092322701	09/09/2003												
CS-3S	392639092323301	07/09/2003												
		09/09/2003	2,840								4,470	5,330	5,330	0
		01/13/2004												
		03/09/2004												
		06/09/2004												
CS-3.1M	392637092323401	09/09/2003												
CS-3.2M	392640092323401	09/09/2003												
CS-3.9M	392645092323801	09/09/2003												
CS-4S	392647092323801	09/09/2003	<150								2,380	2,560	2,510	50
		01/13/2004										4.260	3,820	440
		03/09/2004												
		06/09/2004												
CS-4.9M	392648092324101	09/08/2003												

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Site number (fig. 1)	NWIS station number	Date	Aluminum, dissolved (µg/L)	Aluminum, total (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobolt, dissolved (µg/L)	Copper, dissolved (µg/L)	lron, dissolved ICP (µg/L)	lron, dissolved UV-vis (µg/L)	lron, ferrous, dissolved UV-vis (μg/L)	lron, ferric, computed ^b (µg/L)
CS 5M	202647002222701	07/22/2002												
C3-51VI	392047092323701	07/22/2003												12 000
		12/00/2002		121	12.7	<1.2	<0	<15	<9	<21	525,000	587,000	575,000	12,000
		12/09/2003	8/4								500,000	500,000	555,000	0.000
		01/13/2004	1,000								555,000	555,000	544,000	9,000
		05/09/2004	<2,500								504,000	572,000	570,000	2,000
		06/09/2004	683								551,000	580,000	548,000	32,000
69.69	202(40002222701	07/08/2004												
CS-6S	392648092323701	09/09/2003	826								344,000	353,000	302,000	51,000
		01/13/2004										222,000	220,000	2,000
		03/09/2004										141,000	137,000	4,000
		06/09/2004										247,000	220,000	27,000
		06/10/2004	110								3,900	14	14	0
CS-7S	392710092323901	09/08/2003	532								94,900	104,000	97,500	6,500
		01/12/2004												
		03/08/2004												
		06/09/2004												
CS-8S	392712092323901	07/22/2003												
		09/08/2003		28	21.8	<.4	<2	E3	<3	<7	E5	600	1,040	0
		01/12/2004	5								38			
		03/08/2004	4								90			
		06/09/2004	9								8			
CS-9S	392729092323801	09/08/2003	243								6,700	7,440	7,430	10
		01/12/2004	<150								67,800	70,600	69,300	1,300
		03/08/2004	E1								40,200	39,600	39,100	500
		06/09/2004	<5,000								74,500	86,800	82,100	4,700
SC-9S	392732092324901	09/08/2003	65	227	50.5	<.4	<2	E3	<3	<7	26	90	90	0
		01/12/2004	2								10,600	10,800	10,700	100
		03/08/2004	12								352	510	470	40
		06/09/2004	6								216	240	220	20
SC-10S	392745092332401	07/08/2003												

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Site number (fig. 1)	NWIS station number	Date	Aluminum, dissolved (µg/L)	Aluminum, total (µg/L)	Barium, dissolved (μg/L)	Beryllium, dissolved (μg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobolt, dissolved (µg/L)	Copper, dissolved (µg/L)	lron, dissolved ICP (µg/L)	lron, dissolved UV-vis (µg/L)	lron, ferrous, dissolved UV-vis (μg/L)	Iron, ferric, computed ^b (μg/L)
MM-2S	392608092323801	09/05/2003	8								20	70	67	3
		12/09/2003												
		01/15/2004												
		03/10/2004												
		06/08/2004												
MM-3M	392609092323701	07/22/2003												
		09/05/2003		50	<50	<10	<50	<125	<9	<175	179,000	166,000	166,000	0
		12/09/2003	<150								165,000	164,000	154,000	10,000
		01/14/2004												
		01/15/2004	37								153,000	156,000	148,000	8,000
		03/10/2004	53								141,000	147,000	143,000	4,000
		06/08/2004	36								151,000	148,000	143,000	5,000
MM-4S	392610092323801	09/05/2003	9								68,000	68,000	72,800	0
		12/09/2003										112,000	108,000	4,000
		01/15/2004										106,000	106,000	0
		03/10/2004										68,500	65,500	3,000
		06/08/2004										98,000	94,600	3,400
MM-4.1M	392609092323801	12/09/2003												
MM-4.4S	392614092324701	07/09/2003												
MM-5S	392627092333401	09/04/2003	E1								366	87	81	6
		12/08/2003												
		01/15/2004												
		03/09/2004												
		06/08/2004												
MM-6S	392627092333301	07/22/2003												
		09/04/2003		18	12.8	<.4	<2	<5	<3	<7	23	150	620	0
		12/08/2003	5								29			
		01/15/2004	5								114			
		03/09/2004	5								66			
		06/08/2004	11								39			

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Site number (fig. 1)	NWIS station number	Date	Aluminum, dissolved (µg/L)	Aluminum, total (µg/L)	Barium, dissolved (µg/L)	Beryllium, dissolved (µg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobolt, dissolved (µg/L)	Copper, dissolved (µg/L)	lron, dissolved ICP (μg/L)	lron, dissolved UV-vis (µg/L)	lron, ferrous, dissolved UV-vis (µg/L)	lron, ferric, computed ^b (µg/L)
MM-7S	392627092333501	09/04/2003	10								20	30	380	0
		12/08/2003										7,010	5,140	1,870
		01/15/2004										8,050	5,090	2,960
		03/09/2004												
		06/08/2004												
MW 04-01	392616092304201	06/29/2004												
		07/08/2004	10								35,400			
		07/21/2004												
		08/31/2004	11	16	<50	<10	<80	<105	<65	<125	49,700			
MW 04-02	392629092310101	07/08/2004												
		07/21/2004	162,000								1,490,000			
		08/31/2004	151,000	171,000	E44	E11	<80	<105	E125	<125	1,560,000			
MW 04-03	392626092310101	07/08/2004												
		07/20/2004	174								85,400			
		08/31/2004	9,750	58,700	E18	<10	<32	<42	E42	<42	483,000			
MW 04-04	392646092323601	07/08/2004	141								5,200			

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Site number (fig. 1)	NWIS station number	Date	lron, total (µg/L)	Lead, dissolved (µg/L)	Lithium, dissolved (µg/L)	Mangan- ese, dissolved (µg/L)	Mangan- ese, total (µg/L)	Molyb- denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Silver, dissolved (µg/L)	Strontium, dissolved (µg/L)	Vanadium, dissolved (µg/L)	Zinc, dissolved (µg/L)
SC-1S	392827092284601	07/08/2003											
SC-1.1S	392817092290201	07/08/2003											
SC-2S	392811092291201	07/08/2003											
		09/10/2003				66							
		01/14/2004											
		03/11/2004											
		06/09/2004											
SC-3S	392716092312301	07/08/2003											
		09/10/2003				405							
		01/13/2004											
		03/10/2004											
		06/07/2004											
SC-4S	392713092281101	09/16/2003											
SC-4.7S	392703092292701	09/16/2003											
SC-4.8S	392701092300501	09/16/2003											
SC-4.9S	392704092303501	09/16/2003											
SC-5S	392716092312201	09/10/2003				201							
		09/16/2003											
		01/13/2004											
		03/10/2004											
		06/07/2004											
SC-6S	392716092312401	12/29/2003	660	< 0.08	5	284	280	7	9	<3	198	<5	5
		01/13/2004				749							
		03/10/2004				383							
		06/07/2004				1,000							

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Site number (fig. 1)	NWIS station number	Date	lron, total (µg/L)	Lead, dissolved (µg/L)	Lithium, dissolved (µg/L)	Mangan- ese, dissolved (µg/L)	Mangan- ese, total (µg/L)	Molyb- denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Silver, dissolved (µg/L)	Strontium, dissolved (µg/L)	Vanadium, dissolved (µg/L)	Zinc, dissolved (µg/L)
HC AL	202/2/002210101	05/00/0000											
HG-2M	392634092310101	07/23/2003											
		09/11/2003	491,000	0.38	196	10,300	10,400	<160	280	<200	1,400	<240	616
		12/09/2003				9,620							
		12/29/2003	396,000	.27	175	9,350	9,330	<200	300	<140	1,230	<230	544
		01/14/2004				9,640							
		03/11/2004				8,840							
		06/08/2004	407,000	.31	E174	9,170	8,810	<400	E140	<280	1,360	<460	482
		07/21/2004				9,020							
		08/30/2004	359,000	.34	179	8,360	7,550	<200	140	<140	1,320	<230	<150
HG-3S	392637092310501	09/11/2003				21,300							
		01/14/2004											
		03/11/2004											
		06/08/2004											
HG-4M	392637092310401	07/23/2003											
		09/11/2003	2,620,000	<.4	671	28,900	47,300	<12	1,590	<15	170	<18	4,400
		12/09/2003											
		12/30/2003	1,700,000	E.16	727	27,700	24,000	<800	2,240	<560	371	<920	5,720
		01/14/2004				29,000							
		03/11/2004				19,400							
		06/08/2004				33,500							
HG-5S	392636092310301	09/11/2003											
HG-5.5S	392634092310201	09/11/2003											
		03/11/2004											
HG-6S	392638092305701	09/11/2003											
		03/11/2004											
HG-6.9S	392638092310401	09/11/2003				5,990							
		12/30/2003											
		01/14/2004											
		03/11/2004											
		06/08/2004											

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Site number (fig. 1)	NWIS station number	Date	lron, total (µg/L)	Lead, dissolved (µg/L)	Lithium, dissolved (µg/L)	Mangan- ese, dissolved (µg/L)	Mangan- ese, total (µg/L)	Molyb- denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Silver, dissolved (µg/L)	Strontium, dissolved (µg/L)	Vanadium, dissolved (µg/L)	Zinc, dissolved (µg/L)
HG-7S	392638092310501	09/11/2003				24,800							
110 75	372030072310301	12/30/2003	421.000	<0.16	100	9.880	8 3/10	~200	440	~140	1	~230	1.010
		01/14/2004	-21,000	<0.10	170	17 300		<200		<140		<250	1,010
		03/11/2004				12 100							
		06/08/2004	871.000	31	380	20,300	19 800	<400	720	<280	986	<460	1 970
		08/30/2004		.51		10,100				~200			
HG-8S	392648092312201	01/13/2004											
110 05	372010072312201	03/10/2004											
		06/07/2004											
HG-108	392648092312301	01/13/2004											
110 100	0,20,00,2012001	03/10/2004											
		06/07/2004											
HG-118	392707092312201	09/10/2003				13,300							
110 115	0,2,0,0,2012201	01/13/2004				7.750							
		03/10/2004				4.420		0					
		06/07/2004				11.400							
		06/10/2004				355							
		06/10/2004				12,800							
HG-12S	392719092313301	01/13/2004											
		03/11/2004											
		06/07/2004											
SC-7S	392723092313801	09/10/2003				1,070							
		12/29/2003				369							
		01/13/2004				1,420							
		03/10/2004				761							
		06/07/2004				2,190							
MC-2S	392655092320301	07/24/2003											
MC-3M	392658092320001	07/24/2003											
MC-3.3S	392659092320001	07/24/2003											
		09/11/2003				10,800							
MC-4S	392702092315901	07/24/2003											

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Site number (fig. 1)	NWIS station number	Date	lron, total (μg/L)	Lead, dissolved (µg/L)	Lithium, dissolved (µg/L)	Mangan- ese, dissolved (µg/L)	Mangan- ese, total (µg/L)	Molyb- denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Silver, dissolved (µg/L)	Strontium, dissolved (µg/L)	Vanadium, dissolved (µg/L)	Zinc, dissolved (µg/L)
MC 4.95	302703002320101	07/24/2003											
MC-4.95	392703092320101	09/11/2003											
MC 58	302704002320001	09/11/2003				14,100							
MC-55	392704092320001	07/08/2003											
30-05	392730092323801	07/08/2003											
		07/22/2003											
		09/10/2003				572							
		01/12/2004											
		03/08/2004											
CE 25	202(25002222401	06/09/2004											
CS-2S	392635092322401	09/09/2003				4,330							
		01/13/2004											
		03/09/2004											
~~ ~ ~ ~ ~		06/09/2004											
CS-2.5M	392636092322601	09/09/2003											
CS-2.6M	392636092322701	09/09/2003											
CS-3S	392639092323301	07/09/2003											
		09/09/2003				7,080							
		01/13/2004											
		03/09/2004											
		06/09/2004											
CS-3.1M	392637092323401	09/09/2003											
CS-3.2M	392640092323401	09/09/2003											
CS-3.9M	392645092323801	09/09/2003											
CS-4S	392647092323801	09/09/2003				4,140							
		01/13/2004											
		03/09/2004											
		06/09/2004											
CS-4.9M	392648092324101	09/08/2003											

<u>∞</u>

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Site number (fig. 1)	NWIS station number	Date	lron, total (μg/L)	Lead, dissolved (µg/L)	Lithium, dissolved (µg/L)	Mangan- ese, dissolved (µg/L)	Mangan- ese, total (µg/L)	Molyb- denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Silver, dissolved (µg/L)	Strontium, dissolved (µg/L)	Vanadium, dissolved (µg/L)	Zinc, dissolved (µg/L)
CG 514	202(12002222201	07/02/2002											
CS-5M	392647092323701	07/22/2003											
		09/09/2003	488,000	<0.16	388	11,100	12,500	<300	E20	<15	762	<18	62
		12/09/2003				9,650							
		01/13/2004				9,510							
		03/09/2004				9,350							
		06/09/2004				9,940							
~~ ~~		07/08/2004											
CS-6S	392648092323701	09/09/2003				9,550							
		01/13/2004											
		03/09/2004											
		06/09/2004											
		06/10/2004				391							
CS-7S	392710092323901	09/08/2003				11,900							
		01/12/2004											
		03/08/2004											
		06/09/2004											
CS-8S	392712092323901	07/22/2003											
		09/08/2003	250	<.8	10	3	342	<4	E6	<5	230	<6	<3
		01/12/2004				311							
		03/08/2004				874							
		06/09/2004				367							
CS-9S	392729092323801	09/08/2003				5,960							
		01/12/2004				4,530							
		03/08/2004				3,020							
		06/09/2004				7,140							
SC-9S	392732092324901	09/08/2003	780	<.08	17	881	878	<4	8	<5	211	<6	<3
		01/12/2004				2,050							
		03/08/2004				542							
		06/09/2004				1,740							
SC-10S	392745092332401	07/08/2003											

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Site number (fig. 1)	NWIS station number	Date	lron, total (µg/L)	Lead, dissolved (µg/L)	Lithium, dissolved (µg/L)	Mangan- ese, dissolved (µg/L)	Mangan- ese, total (µg/L)	Molyb- denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Silver, dissolved (µg/L)	Strontium, dissolved (µg/L)	Vanadium, dissolved (µg/L)	Zinc, dissolved (µg/L)
MM-28	302608002323801	09/05/2003				25.2							
101101-25	572000072525001	12/09/2003											
		01/15/2003											
		03/10/2004											
		06/08/2004											
MM-3M	392609092323701	07/22/2003											
101101 5101	572007072525701	09/05/2003	181 000	<0.16	198	3 470	3 050	<100	E10	<125	1 360	<150	F48
		12/09/2003				3,050							
		01/14/2004											
		01/15/2004				2.970							
		03/10/2004				2,790							
		06/08/2004				3,060							
MM-4S	392610092323801	09/05/2003				1,660							
		12/09/2003											
		01/15/2004											
		03/10/2004											
		06/08/2004											
MM-4.1M	392609092323801	12/09/2003											
MM-4.4S	392614092324701	07/09/2003											
MM-5S	392627092333401	09/04/2003				1,460							
		12/08/2003											
		01/15/2004											
		03/09/2004											
		06/08/2004											
MM-6S	392627092333301	07/22/2003											
		09/04/2003	180	<.08	9	269	410	<4	<7	<5	193	<6	<3
		12/08/2003				476							
		01/15/2004				959							
		03/09/2004				663							
		06/08/2004				348							

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Site number (fig. 1)	NWIS station number	Date	lron, total (µg/L)	Lead, dissolved (µg/L)	Lithium, dissolved (µg/L)	Mangan- ese, dissolved (µg/L)	Mangan- ese, total (µg/L)	Molyb- denum, dissolved (µg/L)	Nickel, dissolved (µg/L)	Silver, dissolved (µg/L)	Strontium, dissolved (µg/L)	Vanadium, dissolved (µg/L)	Zinc, dissolved (µg/L)
MM-7S	392627092333501	09/04/2003				719							
		12/08/2003											
		01/15/2004											
		03/09/2004											
		06/08/2004											
MW 04-01	392616092304201	06/29/2004											
		07/08/2004				1,570							
		07/21/2004											
		08/31/2004	75,470	<0.16	223	1,740	2,600	<100	<50	<70	6,190	<115	<75
MW 04-02	392629092310101	07/08/2004											
		07/21/2004				24.800							
		08/31/2004	1 550 000	< 24	373	23 500	25 400	<100	639	<70	1 820	<230	1 300
MW 04-03	392626092310101	07/08/2004											
WIW 04-05	572020072510101	07/20/2004				1 000							
		07/20/2004				1,900							
		08/31/2004	498,000	<.16	187	7,460	7,800	<40	251	<28	2,040	<115	468
MW 04-04	392646092323601	07/08/2004				4.870							

^aFor convenience instantaneous discharge is given in English and metric units. 1 $\text{ft}^3/\text{s} = 28.3168$ liters.

^bFerric iron, computed = iron, dissolved (UV-vis) - iron, ferrous (UV-vis). If the analyzed value of ferrous iron is greater than the analyzed value for dissolved iron, a zero value is reported for ferric iron.

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