Total Maximum Daily Load (TMDL) Development

- pH (H^+ Ion Mass) -

For

Cane Run Watershed

(Hopkins County, Kentucky)

Kentucky Department for Environmental Protection

Division of Water

Frankfort, Kentucky

December 2003

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This report has been approved for release:

Jeffrey W. Pratt, Director
Division of Water

12/8/03
Date

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Cane Run, Kentucky

TMDL Fact Sheet

Project Name: Cane Run

Location: Hopkins County, Kentucky

Scope/Size: Cane Run, watershed 2474 acres (3.87 mi^2)
The listed segment is from river mile 0.0 to 3.4

Land Type: Forest, agricultural, barren/spoil

Type of Activity: Acid Mine Drainage (AMD) caused by Strip/Abandoned Mines

Pollutant(s): H^+ Ion mass (Low pH)

TMDL Issues: Non-point sources

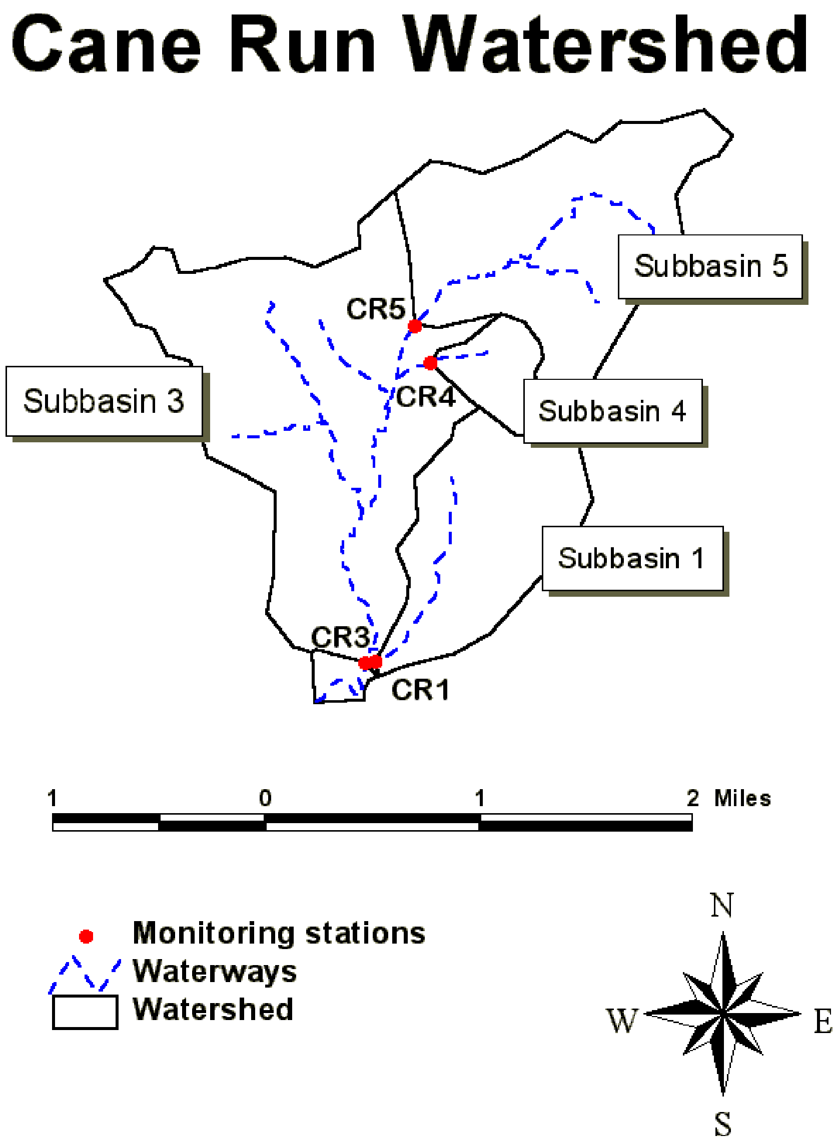
Water Quality Standard/Target: pH shall not be less than six (6.0) or more than nine (9.0) and shall not fluctuate more than one and zero-tenths (1.0) pH unit over a 24-hour period. This standard is found within regulation 401 KAR 5:031.

Data Sources: KPDES Permit Historical Sampling Data, Murray State University Sampling Data

Control Measures: Kentucky non-point source TMDL implementation plan, Kentucky Watershed Framework

Summary: Cane Run was determined as not supporting the designated uses of primary and secondary contact recreation (swimming and wading), and warm water aquatic habitat (aquatic life). Therefore, the creek was placed on the 1998 and 2002 303(d) list for Total Maximum Daily Load (TMDL) development. The creek segment is characterized by a depressed pH, the result of acid mine drainage from strip and abandoned mining sites. The period of lowest pH is at low-flow conditions; however, the period of greatest hydrogen ion load has been determined at a critical flow condition for selected subbasins of Cane Run. For pH violations on such streams, the Kentucky Division of Water has determined that maximum daily mean flow having a 3-

year exceedance frequency be used for setting the appropriate TMDL and associated load reduction. However, for this TMDL the critical flow was defined from the observed data. This flow will be used for this TMDL.



TMDL Development: Total maximum daily loads in grams H^+ ions per day were computed based on the allowable minimum pH value (6.0) for creeks and streams to meet primary and secondary contact (swimming and wading) and aquatic life uses. The TMDL was done for grams of ions (subsequently converted to pounds per day) because the units for pH do not allow for the computation of a quantitatively useful load or reduction amount.

Total TMDL for Cane Run = 0.45 lbs H+ Ions/day				
	Critical Incremental Flow Rate (cfs)	Incremental TMDL for a pH of 6.0 (lbs/day)	Maximum Incremental Load (lbs/day)	Incremental Reduction Needed (lbs/day)
Subbasin 1	14.50	0.088	69.80	69.71
Subbasin 3	46.50	0.282	257.40	257.12
Subbasin 4	1.00	0.006	0.08	0.07
Subbasin 5	12.00	0.073	28.95	28.88
Total	74.00	0.448	356.23	355.78

Permitting in the Cane Run Watershed.

New Permits: New permits (except for new remining permits) for discharges to streams in the Cane Run watershed could be allowed anywhere in the watershed contingent upon end-of-pipe pH permit limits in the range of 7.0 to 9.0 standard units. Water quality standards state that the pH value should not be less the 6.0 nor greater than 9.0 for meeting the designated uses of aquatic life and swimming. This range of 6.0 to 9.0 for pH is generally assigned as end-of-pipe effluent limits. However, because a stream impairment exists (low pH), new discharges cannot cause or contribute to an existing impairment. A pH of 7.0 represents a neutral state between an acidic and a non-acidic condition. A discharge having a pH of 7.0 to 9.0 standard units will not cause or contribute to the existing impairment. Based on limited pH data from streams in undisturbed watersheds in the area, a pH of 7.0 is generally representative of the value of background pH. New permits having an effluent limit pH of 7.0 to 9.0 will not be assigned a hydrogen ion load as part of a Waste Load Allocation (WLA). There are no active permits in the Cane Run Watershed that would contribute to the pH impairment.

Remining Permits: Remining permits may be approved on a case-by-case basis where streams are impaired because of low pH from abandoned mines. Permit approval is contingent on reclamation of the site after mining activities are completed. Existing water quality conditions must be maintained or improved during the course of remining. The permittee is required to monitor in-stream conditions during remining to make sure that current water quality conditions are maintained or improved. Reclamation of the site is the ultimate goal, but water quality standards (pH of 6.0 to 9.0 standard units) may not necessarily be met in the interim if the Commonwealth issues a variance to the discharger. The variance allows an exception to the applicable water quality standard as well as the TMDL. Remining therefore constitutes a means whereby a previously disturbed and unreclaimed area can be reclaimed. The authority for remining is defined in Section 301(p) of the Federal Clean Water Act; Chapter 33, Section 1331(p) of the U.S. Code – Annotated (the Rahall Amendment to the Federal Clean Water Act); and the Kentucky Administrative Regulations (401 KAR 5:029 and 5:040).

The remediation of the remining site will result in a reduction of the non-point source ion load of the subbasin where the remining is done. When remining is completed, the remediation should result in a reduction in the load allocation (LA). Follow-up, in-stream monitoring will need to be done at the subbasin outfall to determine the effect of reclamation activities following remining on the overall ion load coming from the subbasin.

Distribution of Load: Because there were no point source discharges during the study period, the existing Hydrogen Ion load for the watershed was defined entirely as a nonpoint source load. Because new permits (pH 7.0 to 9.0) would not cause or contribute to the existing impairment and remining permits would be exempt from the TMDL requirements, no load has been provided for the waste load allocation category.

Waste Load and Load Allocation for Each Subbasin in the Cane Run Watershed

	Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Waste Load Allocation (lbs/day)	Load Allocation (lbs/day)
Subbasin 1	14.50	0.088	0.000	0.088
Subbasin 3	46.50	0.282	0.000	0.282
Subbasin 4	1.00	0.006	0.000	0.006
Subbasin 5	12.00	0.073	0.000	0.073

Implementation/ Remediation Strategy:

Remediation of pH-impaired streams as a result of current mining operations is the responsibility of the mine operator. The Kentucky Division of Field Services of the Kentucky Department of Surface Mining Reclamation and Enforcement is responsible for enforcing the Surface Mining Control and Reclamation Act of 1977 (SMCRA). The Kentucky Division of Abandoned Mine Lands (DAML) is charged with performing reclamation to address the impacts from pre-law mine sites in accordance with priorities established in SMCRA. SMCRA sets environmental problems as third in priority in the list of AML problem types.

There are currently no planned remediation activities for the Cane Run watershed. However, reclamation activities are underway at other locations within the state where water quality is affected by acid mine drainage (AMD). Since 1985, the Kentucky Division of Abandoned Mine Lands has spent approximately $17 million dollars on various reclamation projects in western Kentucky. These projects are summarized below.

Kentucky Division of Abandoned Mine Lands Reclamation Projects

Watershed	Project Name	**Cost**
Brier Creek	Brier Creek	$522,041
	Buttermilk Road	$403,320
Crab Orchard Creek	Crab Orchard Mine	$1,038,203
	Zugg Borehole	$11,974
Pleasant Run	Pleasant Run	$2,162,085
	Pleasant Run II	$421,384
Pond Creek	Pond Creek I	$50,118
	Pond Creek II	$3,801,740
	Pond Creek III	$4,011,514
Flat Creek	East Diamond Mine	$535,000
	Flat Creek	$720,572
Rock Creek	Paint Cliff	$554,623
	Rock Creek I	$630,158
	Rock Creek II	$760,930
Render Creek	McHenry Coop. Agreement	$130,165
	McHenry II	$1,075,340
	Vulcan Mine	$585,359
Total		**$17,414,526**

The success of the reclamation activities in these watersheds was to be evaluated before developing remediation strategies for other watersheds affected by AMD. The KDAML developed a reclamation project in response to documented sedimentation and flooding problems in the nearby Brier Creek Watershed. The project included reclamation of approximately 120 acres of barren or poorly vegetated areas affected by past strip mining. The project also entailed six acres of channel restoration to minimize sedimentation caused by erosion. The restoration of streams included construction of ditches and PVC coated gabion baskets utilized as velocity reducers and energy dissipaters; bale silt checks and silt trap dugouts were also utilized for sediment control. The reclamation project consisted of 67 acres of gradework to remove erosion gullies, redistribute sediment deposits, and prepare a surface to receive a soil cover. The area under consideration received a two foot soil cover layer, taken from 20 acres of watershed area designated for borrow. Gradework areas were treated with an application of agricultural limestone to neutralize acidic conditions and all areas were revegetated using a combination of seedbed preparation, agricultural limestone, fertilizer, seed, mulch, and crimping. The agricultural limestone provided a variety of particle sizes so that it dissolved at different rates and mobilized under a range of flow conditions. The strategy employed at Brier Creek is similar in some respects to a project that is currently underway on Rock Creek and a tributary, White Oak Creek in McCreary County, Kentucky. This 12-acre project is part of the Kentucky Clean Water Action Plan. It involves the removal of coal refuse from the banks of Rock Creek, the establishment of a vegetative cover on other refuse areas in the watershed, and the application of limestone sand at selected locations to neutralize the effects of AMD.

The total cost for the Brier Creek project was $913,000.00 (i.e. $7600/acre) while the total cost of the Rock Creek project is estimated to be approximately $650,000 (i.e. $54,200/acre). For 2000, the total federal Kentucky AML budget allocation was approximately $17 million. However the bulk of these funds were used to support Priority 1 (extreme danger of adverse effects to public health, safety, welfare, and property) and Priority 2 (adverse effects to public health, safety, and welfare) projects. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the AML projects, particularly Priority 3 projects, would be required in order for the AML program to play a significant part in meeting the TMDL implementation requirement associated with pH impaired streams in the state of Kentucky.

Just recently (June 2003), 319 Clean Water Action Plan funds were awarded to the KDAML. This grant is the Homestead Refuse Reclamation Project and includes reclamation of a 92-acre area of the upper Pleasant Run watershed. The total cost of the reclamation project is $1.26 million, of which 60% is federal funds and 40% is supplied by the KDAML. The reclamation activities channel restoration, re-vegetation, and the use of agricultural limestone.

Introduction

Section 303(d) of the Clean Water Act and EPA's Water Quality Planning and Management Regulations (40 CFR Part 130) require states to develop total maximum daily loads (TMDLs) for water bodies that are not meeting designated uses under technology-based controls for pollution. The TMDL process establishes the allowable loadings of pollutants or other quantifiable parameters for a water body based on the relationship between pollution sources and in-stream water quality conditions. This method exists so that states can establish water-quality based controls to reduce pollution from both point and nonpoint sources and restore and maintain the quality for their water resources (USEPA, 1991a).

Location:

The Cane Run watershed is entirely contained within Hopkins County, in southwestern Kentucky (Figure 1). Hopkins County is bounded by the Tradewater River in the west, the Pond River in the east, Webster County in the northwest, and Christian County in the south.

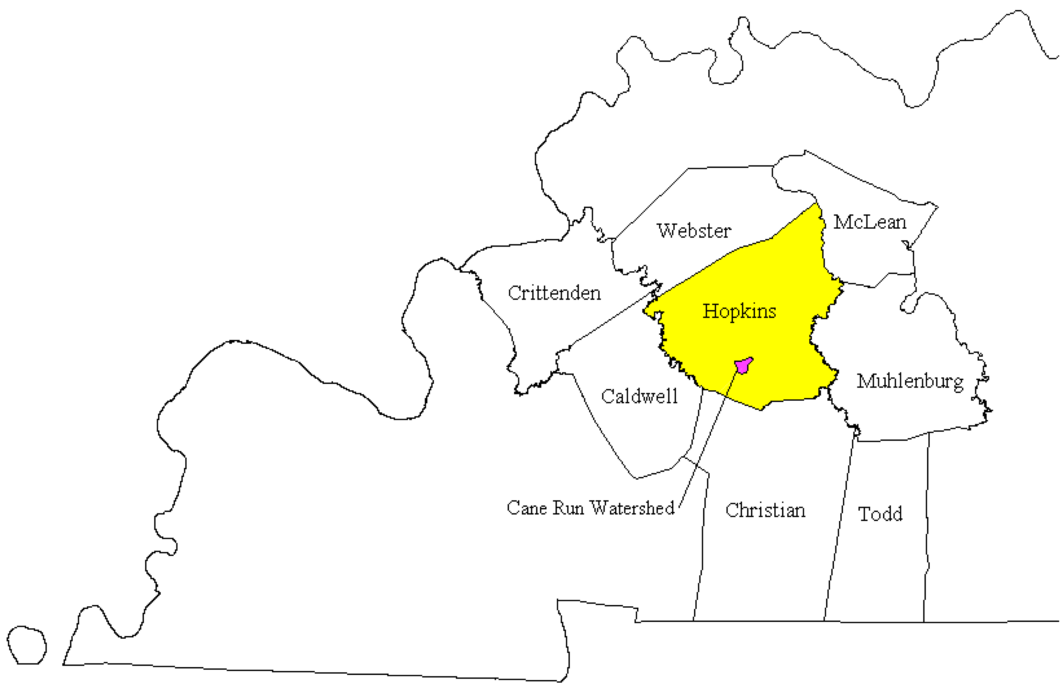


Figure 1. Location of the Cane Run Watershed

Hydrologic Information:

Cane Run, a third order stream, originates in southwest Hopkins County and flows south to discharge into Caney Creek 7.2 miles upstream of its confluence with the Tradewater River. The Tradewater River, along with Pond and Green River, carry the runoff from the county northward to discharge into the Ohio River.
Cane Run's mainstem is approximately 3.4 miles long and drains an area of 2473 acres (3.87 sq. miles). The average gradient is 18.5 feet per mile. Elevations for Cane Run range from 600 ft above mean sea level (msl) in the headwaters to 420 ft above msl at the mouth. Like most of the smaller watersheds, many of the tributary streams are intermittent.

Geologic Information:

The Cane Run watershed is in the Western Coal field physiographic region. The surface bedrock is of Pennsylvanian age. Formations of the Pennsylvanian age are mostly sandstone, siltstone, coal, and interbedded limestone and shale; alluvial deposits of siltstone and crossbedded sand or sandstone underlie the extensive lowland areas (USDA, 1977). The relief of the Cane Run watershed ranges from nearly level to steep. Gently sloping to steep soils are found in the uplands and nearly level soils are found on the floodplain.

Landuse Information:

Coal, oil, and natural gas are among the natural resources of Hopkins County. Coal is the county's most important revenue-producing natural resource. The Cane Run watershed contains two main landuses: resource extraction (mining and disturbed land area) and agriculture.

Soils Information:

Cane Run watershed is dominated by nearly level loamy and clayey soils near to the mouth and level to steep loamy soils in the headwaters. The area is comprised mostly of Zanesville soils, with acidic tendencies and moderate to low permeability.

Mining History

Mining activities in the Cane Run Watershed have occurred since 1966. A list of the various mining permits that have been issued for Cane Run is provided in Table 1. Mining permits in Kentucky are classified on the basis of whether the original permit was issued prior to May 3, 1978 (pre-law permit), after January 18, 1983 (post-Kentucky primacy) or in-between these dates (interim period). An explanation of the permit numbering system is provided in Appendix A (at the back of the report).

Table 1. Recent Mining Permits in the Cane Run Watershed

Permits	Beginning Date	Release Date	Area (ac)	Associated Company
939-66	8/30/66	9/18/69	92	Badgett, Russell Jr. Coal Co.
939-72	9/13/72	2/12/76	100	Badgett, Russell Jr. Coal Co.
2960-73	10/26/73	12/9/77	3	Owl Creek Coal Co.
4415-75	2/5/76	2/10/83	5	CN Coal Co.
054-0080	1/14/81	6/29/84	36	Miracle Mining Co.
054-0084	3/12/81	9/16/82	61	Magic Colleries Inc.
054-0117	10/27/81	10/4/85	84.4	Christian Coal Corp.
054-0130	1/29/82	10/30/85	11	DCLE Coal Corp.
054-0143	6/30/82	4/11/85	229	Christian Coal Corporation
854-0060	7/18/84	6/25/92	2	Emerald Energy Corporation
854-0068	5/20/85	12/15/86	94	H&G Construction Co. Inc.
854-0089	5/13/86	12/15/86	96.8	Charolais Corp.
854-0112	10/11/86	1/29/99	96.8	H&G Construction Co. Inc.

All permits are secured through reclamation bonds. A reclamation bond is a financial document submitted to the Office of Surface Mining prior to mine permit issuance. A bond guarantees mining and reclamation operations will be conducted by mining companies according to regulations and the terms of the approved permit. If a coal company cannot comply with these conditions, the bond is "forfeited" (paid to the Office of Surface Mining) for eventual use by the Division of Abandoned Mine Lands in reclaiming the mined area. Reclamation bonds may be submitted in the forms of cash, certificate of deposit, letter of credit or surety (insurance policy).

A reclamation bond may be returned to a coal company by either of two methods: administrative or phase (on-ground reclamation). Administrative releases occur when new bonds are substituted for the original bonds. Administrative releases are also given for areas of a mine site which are permitted but never disturbed by mining or for areas which are included under a second more recently issued permit.

Phase releases occur in three stages and according to specific reclamation criteria: Phase One – all mining is complete, and backfilling, grading and initial seeding of mined areas has occurred; Phase Two – a minimum of two years of growth on vegetated areas since initial seeding, the vegetation is of sufficient thickness to prevent erosion and pollution of areas outside the mine area with mine soils, and any permanent water impoundments have met specifications for future maintenance by the landowner; and Phase Three – a minimum of five years of vegetative growth since initial seeding and the successful completion of reclamation operations in order for the mined area to support the approved postmining land use. Up to 60 percent of the original bond amount is released at Phase One. An additional 25 is returned at Phase Two, with the remainder of the reclamation bond released at Phase Three. Once a permit is released and the reclamation bond returned, the state cannot require additional remediation action by the mining company unless it is documented that fraudulent documentation was submitted as part of the remediation process.

Monitoring History

Impairment of the Cane Run waters was documented as early as 1978. In April, 1981, the Kentucky Department for Natural Resources and Environmental Protection under the Division of Water (DOW) in agreement with the Kentucky Department for Natural Resources and Environmental Protection Division of Abandoned Lands published The Effects of Coal Mining Activities on the Water Quality of Streams in the Western and Eastern Coalfields of Kentucky. The work cited a pH less than 6.0 for Cane Run as gathered by the DOW in 1978. The USGS Water-Data Report KY-78-1 sampled Cane Run in the 1978 water year, documenting a pH level of 4.0.

The degradation of Cane Run is the consequence of acid mine drainage in the watershed as noted by the DOW. In 1966, the first permit was issued which allowed mining activities in the Cane Run watershed. Table 1 lists the historical permits that have been opened and released in the Cane Run watershed.

In 1997, the DOW conducted a survey of streams in the Western Kentucky Coal Fields, including Cane Run, to determine the bodies of water in Kentucky to be placed on the 1998 303(d) List of Waters for TMDL development. On July 3, 1997, a site visit was made to Cane Run. The creek failed to support recreational swimming and aquatic life uses because of a low pH due to acid mine drainage. The pH was recorded as 5.1. Cane Run was subsequently placed on the 1998 303(d) list as a second priority stream.

Problem Definition

The 1998 and 2002 303(d) Lists of waters for Kentucky (Ky. Dept. for Environmental Protection DOW, 1998 and 2003) indicate that 3.4 miles of Cane Run, from the headwaters to the confluence with Caney Creek in Hopkins County, do not meet the designated uses of primary and secondary contact recreation (swimming and wading) and aquatic life. The Cane Run watershed provides a classic example of impairment caused by acid mine drainage (AMD). Bituminous coal mine drainage, like that found in the Cane Run watershed, generally contains very concentrated sulfuric acid and may contain high concentrations of metals, especially iron, manganese, and aluminum.

Acid mine drainage can: (1) ruin domestic and industrial water supplies; (2) decimate aquatic life; and (3) cause waters to be unsuitable for swimming and wading (primary and secondary contact recreation). In addition to these problems, a depressed pH interferes with the natural stream self-purification processes. At low pH levels, the iron associated with AMD is soluble. However, in downstream reaches where the pH begins to improve, most of the ferric sulfate [$Fe_2(SO_4)_3$] is hydrolyzed to essentially insoluble iron hydroxide [$Fe(OH)_3$]. The stream bottom can become covered with a sterile orange or yellow-brown iron hydroxide deposit that impacts benthic algae, invertebrates, and fish.

The sulfuric acid in AMD is formed by the oxidation of sulfur contained in the coal and/or the rock or clay found above and below the coal seams. Most of the sulfur in the unexposed coal is found in a pyritic form as iron pyrite and marcasite (both having the chemical composition FeS_2).

In the process of mining, the iron sulfide (FeS_2) is uncovered and exposed to the oxidizing action of oxygen in the air (O_2), water, and sulfur-oxidizing bacteria. The end products of the reaction are as follows:

$$4\ FeS_2 + 14\ O_2 + 4\ H_20 + \text{bacteria} \rightarrow 4\ Fe + SO_4 + 4\ H_2SO_4 \qquad (1)$$

The subsequent oxidation of ferrous iron and acid solution to ferric iron is generally slow. The reaction may be represented as:

$$4\ FeSO_4 + O_2 + 2\ H_2SO_4 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O \qquad (2)$$

As the ferric acid solution is further diluted and neutralized in a receiving stream and the pH rises, the ferric iron [Fe^{3+} or $Fe_2(SO_4)_3$] hydrolyses and ferric hydroxide [$Fe(OH)_3$] may precipitate according to the reaction:

$$2\ Fe_2(SO_4)_3 + 12\ H_2O \rightarrow\ 4\ Fe(OH)_3 + 6\ H_2SO_4 \qquad (3)$$

The brownish yellow ferric hydroxide ($Fe(OH)_3$) may remain suspended in the stream even when it is no longer acidic. Although the brownish, yellow staining of the streambanks and water doesn't cause the low pH, it does indicate that there has been production of sulfuric acid. The overall stoichiometric relationship is shown in equation (4):

$$4\ FeS_2 + 15\ O_2 + 14\ H_2O \longleftrightarrow 8\ H_2SO_4 + 4\ Fe(OH)_3 \qquad (4)$$

This reaction (eqn. 4) indicates that a net of 4 moles of H+ are liberated for each mole of pyrite (FeS_2) oxidized, making this one of the most acidic weathering reactions known.

Target Identification

The endpoint or goal of the TMDL is to achieve a pH concentration and associated hydrogen ion load in lbs/day that supports aquatic life and recreation uses. The pH criteria to protect these uses are in the range of 6.0 to 9.0 (Title 401, Kentucky Administrative Regulations, Chapter 5:031). For a watershed impacted by AMD, the focus will be on meeting the lower criterion. In the case of violations caused by non-point sources on small intermittent streams, such standards must be evaluated based on an appropriate critical exceedance frequency (return interval) as opposed to a critical period or flow (e.g. 7Q10). For pH violations on such streams, the Kentucky DOW has determined that the maximum daily mean flow having a 3-year exceedance frequency be used for setting the appropriate TMDL and associated load reduction. In cases where the load and the resultant target indicator (i.e. pH) are directly proportional to discharge (flow rate), the exceedance frequency of the associated discharge can be directly related to the exceedance frequency of the target value (e.g. pH). As a result, the critical daily discharge and associated critical load may be obtained as a function of a specified flow exceedance frequency (e.g. 3 years).

In some watersheds, however, as is the case of the Cane Run watershed (see Figures 7-9), it has been observed that the ion load tends to increase as a function of flow, reach a maximum, and then decrease as the flow increases. It is hypothesized that these results reflect two competing physical processes. At lower flows and as a result of a first flush effect, it is hypothesized that ion loads are initially leached out of the spoil areas resulting in increasing ion loads. A maximum value of ion load is reached, and as the runoff volumes increase, it is hypothesized that the ion load in the spoil areas become depleted and therefore reduced because of flow dilution in the stream. As a result, ion load increases with increasing flow, reaches a maximum, and then decreases as flow continues to increase. Based on the observed data, a conservative estimate of the resulting maximum ion loads can now be obtained by selecting the maximum observed ion load at each station.

Source Assessment

Point Source Loads

There are no known permitted point source loads contributing to the existing pH violations in the watershed.

Non-Point Source Loads

The monitoring performed previously in the Cane Run watershed by the DOW indicates substantial impairment to the Cane Run waters. In order to provide a more recent characterization of the pH levels in the watershed, the University of Kentucky (as part of the study contract with the DOW) subcontracted with Murray State University to collect additional data from the watershed at the sites shown in Figure 2. A summary of the results obtained from these sites is shown in Table 2. This data set indicates significant pH degradation in the watershed and serves as a basis for the development of a TMDL.

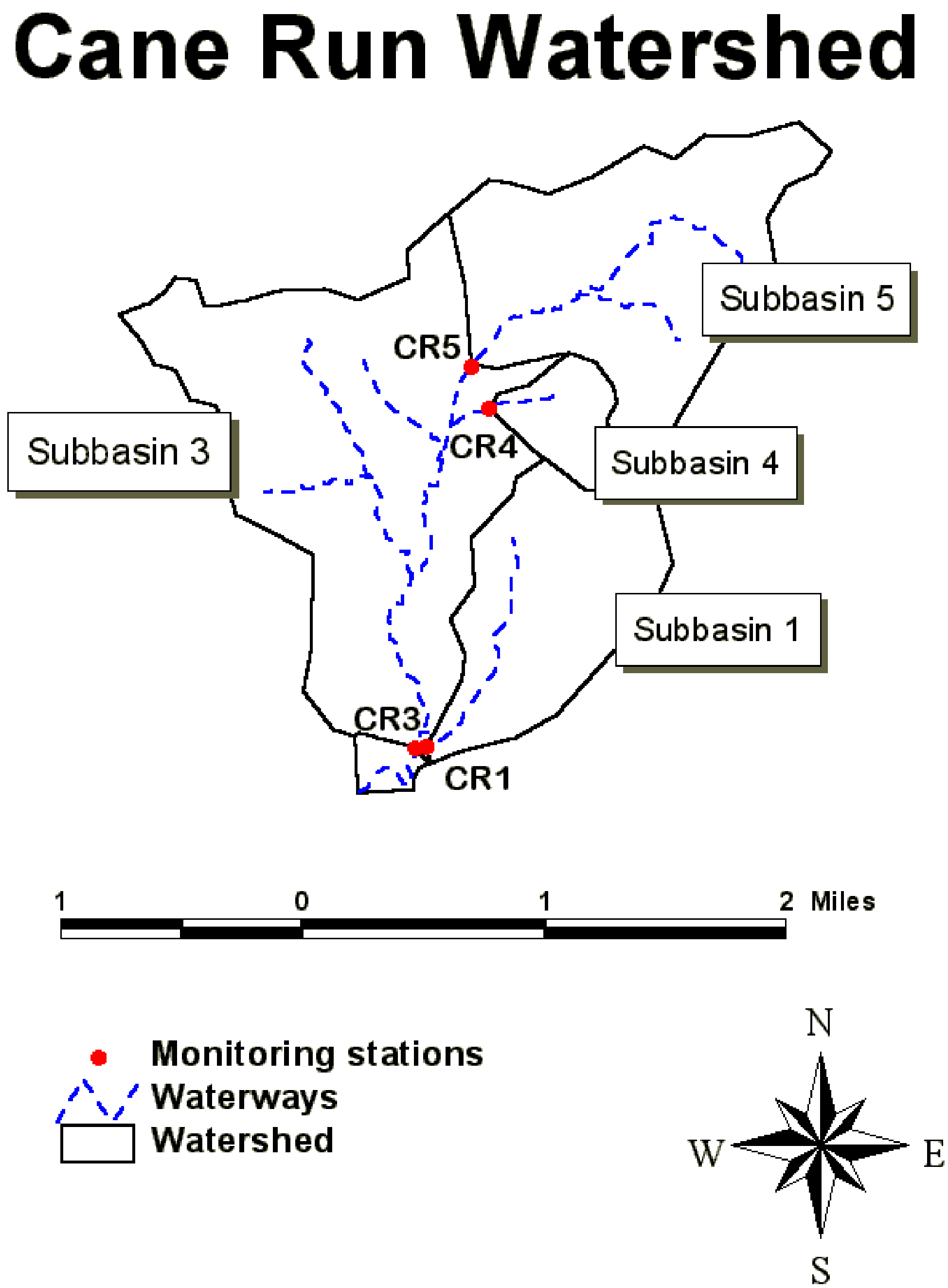


Figure 2. Sampling sites monitored by Murray State personnel

Table 2. Murray State Sampling Results, 1998-2000

	Site 1 (CR1 at mouth of UT to Cane Run at RM 0.52)		Site 3 (CR3 at RM 0.50)		Site 4 (CR4 at RM 0.2 of UT to Cane Run at RM 2.0)		Site 5 (CR5 at RM 2.3)	
Date	Flow Rate (cfs)	pH	Flow Rate (cfs)	pH	Flow Rate (cfs)	pH	Flow Rate (cfs)	pH
10/7/98	7.0	4.7	18.0	5.6	No Flow	No Value	1.8	4.1
10/16/98	11.0	3.3	65.0	3.5	No Flow	No Value	7.0	3.6
10/25/98	3.5	1.4	45.0	1.2	No Flow	No Value	1.0	1.4
11/8/98	3.5	3.3	60.0	3.1	No Flow	No Value	1.8	3.4
11/13/98	3.5	3.4	17.0	3.5	No Flow	No Value	12.0	3.9
11/24/98	14.5	3.1	74.0	3.1	No Flow	No Value	12.0	3.4
12/13/98	14.5	4.1	100.0	4.8	No Flow	No Value	2.5	3.4
12/18/98	14.0	4.9	98.0	4.2	No Flow	No Value	2.5	3.5
12/26/98	No Flow	No Value	No Flow	No Value	No Flow	No Value	12.0	3.5
1/17/99	23.0	5.3	147.0	5.6	0.5	5.2	1.8	3.5
1/24/99	23.0	6.0	90.0	5.5	1.0	4.9	7.0	3.8
1/31/99	28.0	5.7	160.0	5.7	1.0	5.9	17.0	4.1
1/13/00	-	-	-	-	0.5	5.1	-	-

Model Development

The magnitude of the associated hydrogen ion load in a water column (in terms of activity) can be determined by measuring the pH of the water. The relationship between hydrogen load and pH can be expressed as follows:

$$\{H_3O^+\} = 10^{-pH} \quad \text{or more commonly} \quad \{H^+\} = 10^{-pH} \qquad (5)$$

where pH is the negative log of the H^+ ion activity in mol/L. To convert between the measured activity $\{H^+\}$ and the actual molar concentration $[H^+]$, the activity is divided by an activity coefficient, γ.

$$[H^+] = \{H^+\}/\gamma \qquad (6)$$

The activity coefficient γ is dependent on the ionic strength μ of the source water under consideration. The ionic strength of a given source water can be approximated by estimating the TDS (total dissolved solids in mg/liter or ppm) and applying the following relationship:

$$\mu = (2.5 * 10^{-5}) * TDS \qquad (7)$$

In the absence of actual measured values of TDS, a conservative estimate of TDS for Acid Mine Drainage can be obtained using the cumulative probability distribution of typical terrestrial waters (Figure 3) with an associated conservative probability of exceedence of 95%.

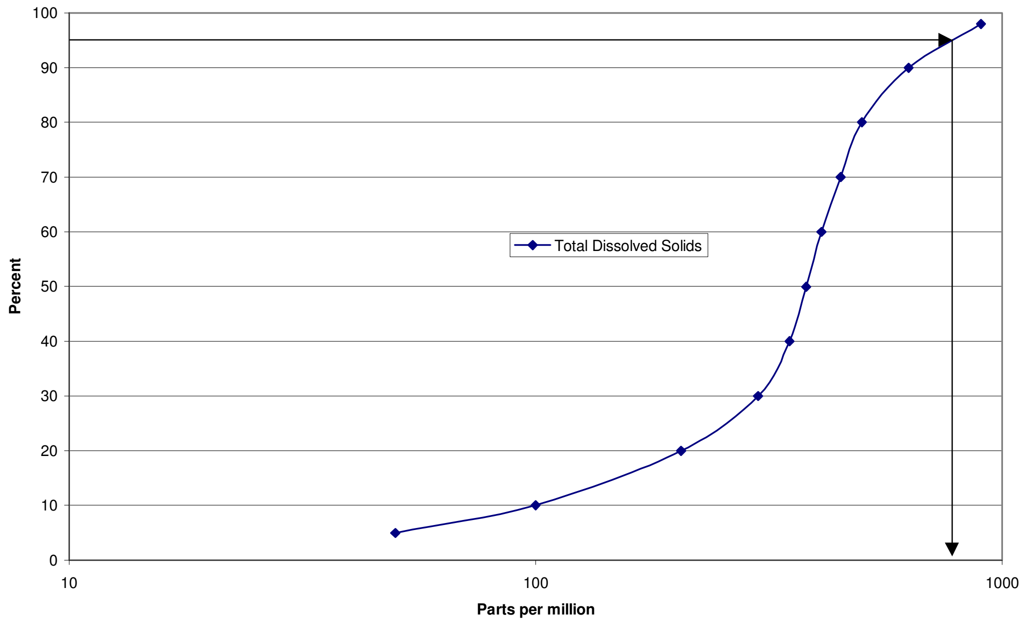


Figure 3: Distribution function of total dissolved solids concentration for terrestrial waters (Snoeyink, 1980)

Use of Figure 3 along with an exceedence probability of 95% yields a TDS value of approximately 900 ppm. Substitution of a TDS concentration of 900 ppm into equation 7 yields an ionic strength of 0.0225. Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Figure 4. Use of an ionic strength of 0.0225 yields an activity coefficient of 0.89.

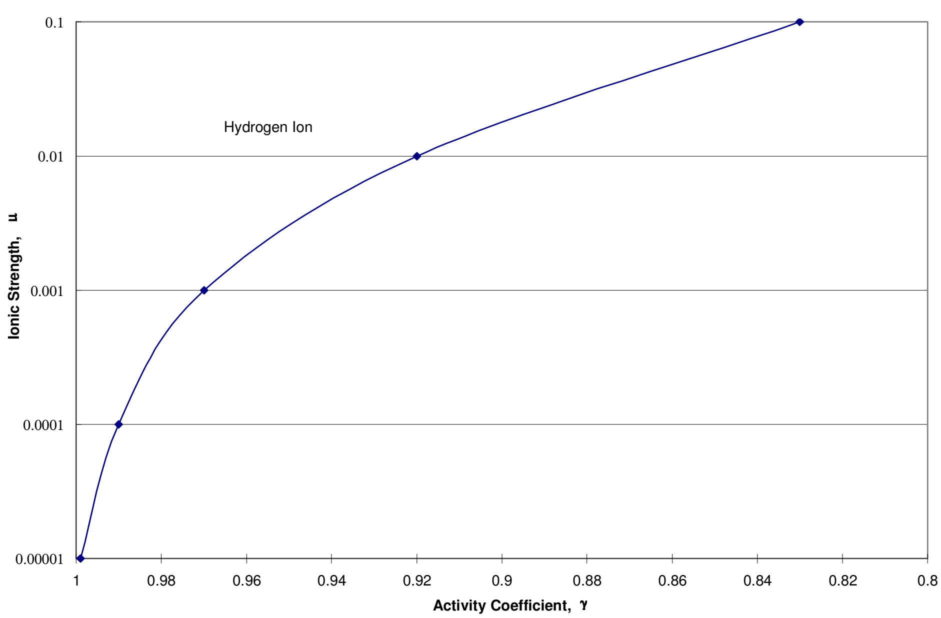


Figure 4: Activity coefficients of H+ as a function of ionic strength (Snoeyink, 1980)

The atomic weight of hydrogen is one gram per mole so the concentration of hydrogen ions in mol/L is also the concentration in g/L. Multiplying the concentration of hydrogen ions by the average flow rate for a given day results in a hydrogen ion load for that day in grams/day. As a result, for any given flow rate, there is a maximum ion load that the stream can assimilate before a minimum pH value of 6.0 is violated. Thus for any given day a TMDL may be calculated for that day using the average daily flow and a minimum pH standard of 6 units.

Hydrogen Loading Sample Calculation

In order to demonstrate the hydrogen loading conversion procedure, use the following monitoring data:

- Critical discharge (Q) = 74.0 cfs
- Measured pH = 6.0

The pH can be converted to a mole/liter measurement (i.e. moles $[H^+]$/liter) by applying the following relationship:

$$pH = -\log \{H^+\}$$

The resulting moles of hydrogen are the anti-log of -6.0, which is 0.000001 moles/liter. The units need to be converted into grams/cubic ft. This is accomplished by applying the following conversion factors:

- There is one gram per mole of Hydrogen.
- 1 liter = 0.035314667 cubic feet

(0.000001 moles/liter)*(1 gram/mole)*(1liter/0.035314667 ft^3) = 0.0000283168 g/ft^3

The goal is to achieve a loading rate in terms of g/day. If the amount of hydrogen in grams/cubic foot is multiplied by the given flow rate in cubic feet/second and a conversion factor of 86,400 s/day, then the load is computed as:

(0.0000283168 g/ft^3)*(74.0 ft^3/s)*(86400s/1day) = 181.05 g/day or .40 lbs/day

Assuming an activity correction factor of 0.89, the final load is 203.42 g/day, or 0.45 lbs/day:

181.05 g/day / 0.89 = 203.42 g/day, or .45 lbs/day

This load is based on a pH of 6.0. The pH determination is based on a logarithmic scale such that as the pH decreases by one unit, the number of moles per liter of hydrogen increases by 10. This obviously has a significant effect on the load and subsequent load reduction needed to attain a pH of 6.0. Using the Q = 74.0 cfs, the load needed to attain a pH of 6.0 if the observed pH is 5.0 is 4.04 lbs/day. For an observed pH of 4.0 the reduction needed is 40.36 lbs/day.

Because pH and equivalent hydrogen ion load can be related as a function of discharge (flow) and ionic strength, a functional relationship can be developed between discharge and the associated ion loading for a given pH value. By specifying a minimum pH value (e.g. 6) and a minimum activity correction factor (e.g. 0.89), an envelope of maximum ion loads may be obtained as a function of discharge (Figure 5). This figure thus provides a basis for establishing the maximum ion load for a given discharge.

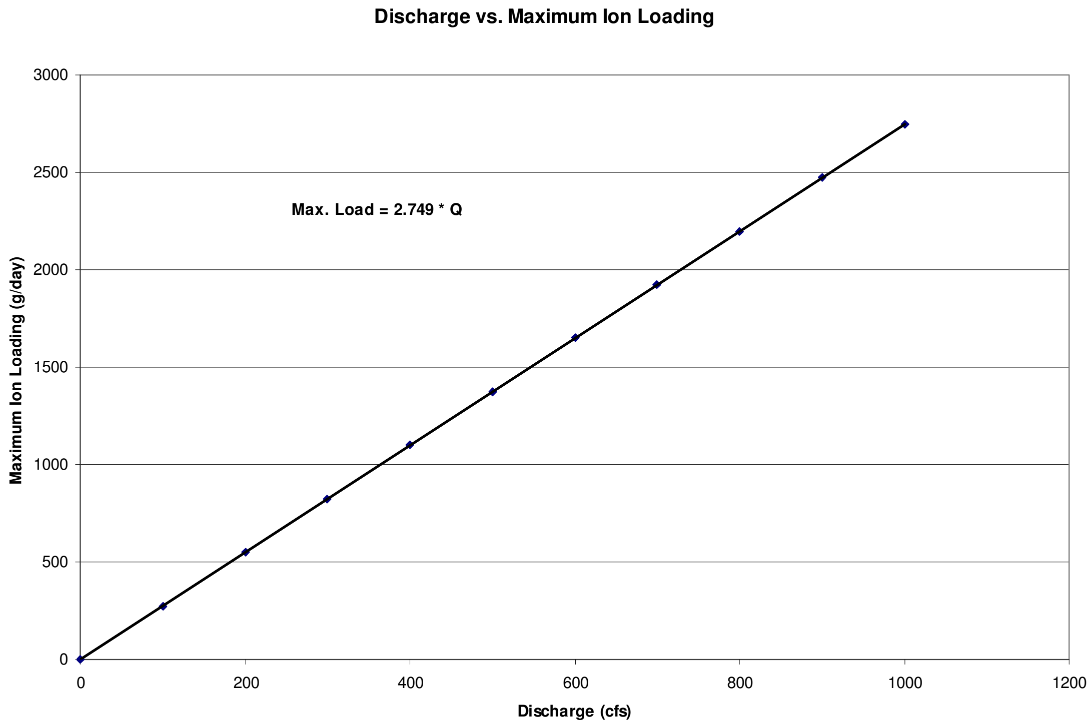


Figure 5. Relation between discharge and maximum ion loading for a pH of 6.0

TMDL Development

Theory

The Total Maximum Daily Load (TMDL) is a term used to describe the maximum amount of a pollutant a stream can assimilate without violating water quality standards, and it includes a margin of safety. The units of a load measurement are mass of pollutant per unit time (i.e. mg/hr, lbs/day). In the case of pH there is no associated mass unit (pH is measured in Standard Units).

Total maximum daily loads (TMDLs) are comprised of the sum of individual waste load allocations (WLAs) for point sources, and load allocations (LAs) for both nonpoint sources and natural background levels for a given watershed. The sum of these components may not result in exceedance of water quality standards (WQSs) for that watershed. In addition, the TMDL must include a margin of safety (MOS), that is either implicit or explicit, that accounts for the uncertainty in the relation between pollutant loads and the quality of the receiving water body. Conceptually, this definition is denoted by the equation:

$$\text{TMDL} = \text{Sum (WLAs)} + \text{Sum (LAs)} + \text{MOS} \quad (8)$$

Margin of Safety

The margin of safety (MOS) is part of the TMDL development process (Section 303(d)(1)(C) of the Clean Water Act). There are two basic methods for incorporating the MOS (USEPA, 1991a):

1) Implicitly incorporate the MOS using conservative model assumptions to develop allocations, or

2) Explicitly specify a portion of the total TMDL as the MOS using the remainder for allocations.

In the current TMDL, the MOS is incorporated implicitly through the properties of water chemistry that determine the relationship between pH and hydrogen ion concentration and through the use of the maximum observed ion loads at each station as the basis of the TMDL load reduction. In an electrically neutral solution (such as all natural systems), the activity coefficient (γ in eqn. 6) is assumed to be equal to 1.0, meaning that there is no quantitative difference between activity and molar concentration. In the case of AMD there obviously exists the possibility of additional ions in the water column that may affect the relationship between the measured activity and the associated ion load. Therefore, taking a conservative approach, a minimum activity correction factor of 0.89 is assumed. This means that for all values of pH the calculated hydrogen ion concentration is assumed to be higher than would normally be calculated under the assumption of a nominal activity correction factor. Overestimation of the potential loading rate requires a greater reduction and thus allows for an implicitly defined margin of safety. Finally, all pH degradation below the minimum threshold of 6 is assumed to be totally attributable to acid mine drainage. As a result, any load reductions for the watershed will be made irrespective of any natural background sources and thus provide a further conservative reduction strategy.

TMDL Determination

The TMDL for a given stream segment may be determined on the basis of a critical discharge and the use of Figure 5. These values are then converted to pounds per day. In determining the TMDLs for stations CR1, CR3, CR4, and CR5 (Figure 2), the flow value corresponding to the maximum observed ion load for each station was used as the critical discharge. Site CR3 is the most downstream site and therefore incorporates the ion load from the other three sites. For this reason, an incremental value of flow and load is given in Table 3 for site CR3. Therefore, the flow for Subbasin 3 is 46.5 cfs (74.0 - 14.5 - 1.0 - 12.0 = 46.5). Using these discharges, the TMDLs in Table 3 were obtained.

Table 3. Incremental Critical Flow and Corresponding TMDL (lbs/day)

Subbasin	Incremental Flow Rate (cfs)	Incremental TMDL (lbs/day)
1	14.50	0.088
3	46.50	0.282
4	1.00	0.006
5	12.00	0.073

Hydrogen Ion Loading Model

Once a TMDL is developed for a watershed, the associated load reduction must be spatially allocated. One way to accomplish this objective is through unit load reductions as associated with different land uses within the watershed. The impacts of such reductions on the associated water quality standard can then be verified through mathematical simulation. Alternatively, separate TMDLs and associated load reductions can be developed for individual subbasins within the watershed. In the current study, separate TMDLs and associated load reductions were developed for each of the subbasins identified in Figure 2. Attainment of the individual load reductions should therefore meet the TMDL requirement for the complete watershed.

Based on a physical inspection of the watershed, it is hypothesized that the degradation of the pH in the stream is directly related to oxidation of sulfur that occurs as runoff flows over the spoil areas associated with previous mining activities in the basin. Plots of ion loads versus flows from the four monitoring stations shown in Figure 2 are shown in Figures 6-9.

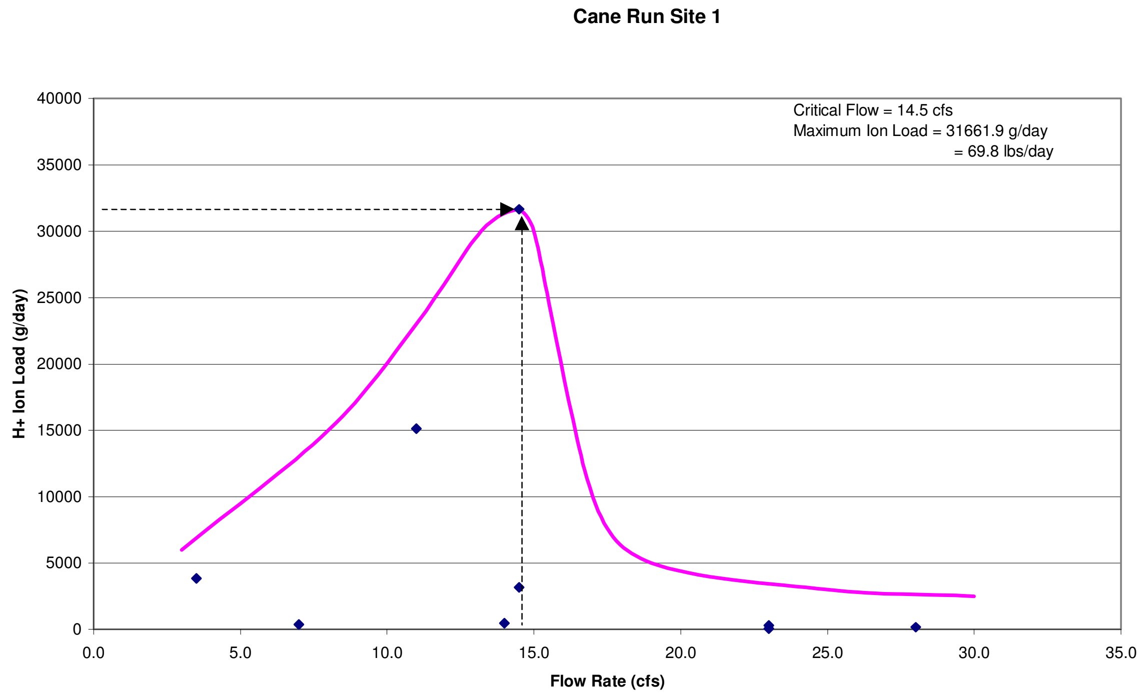


Figure 6. Relation between flow and ion load for site 1

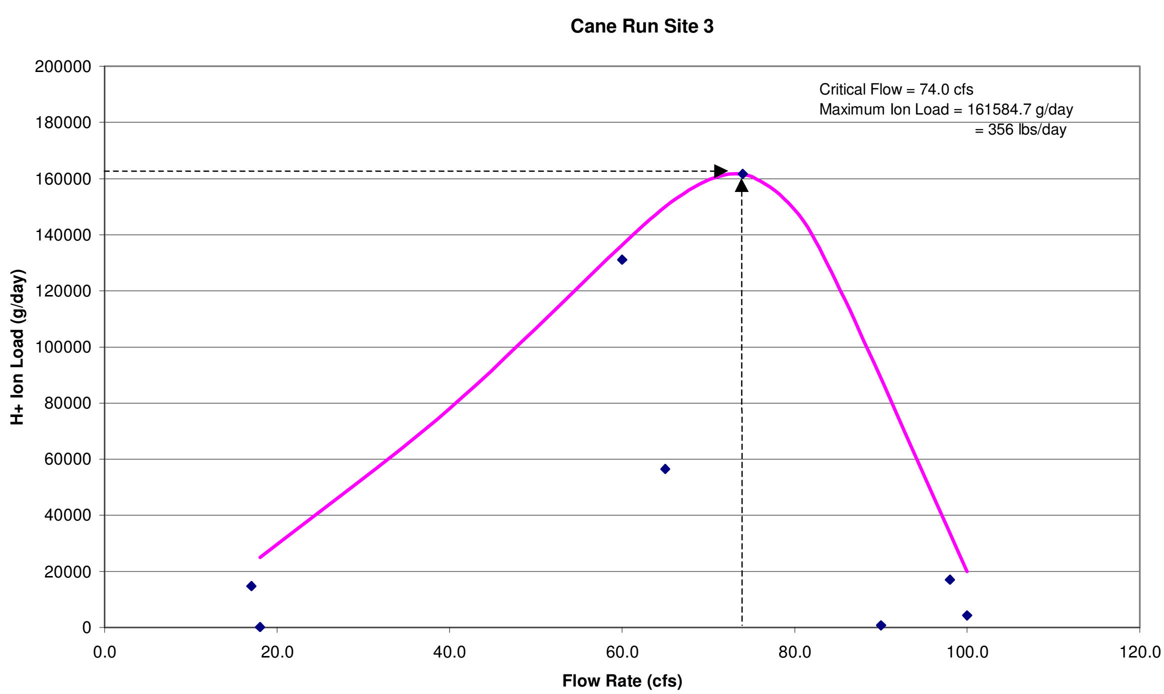


Figure 7. Relation between flow and ion load for site 3

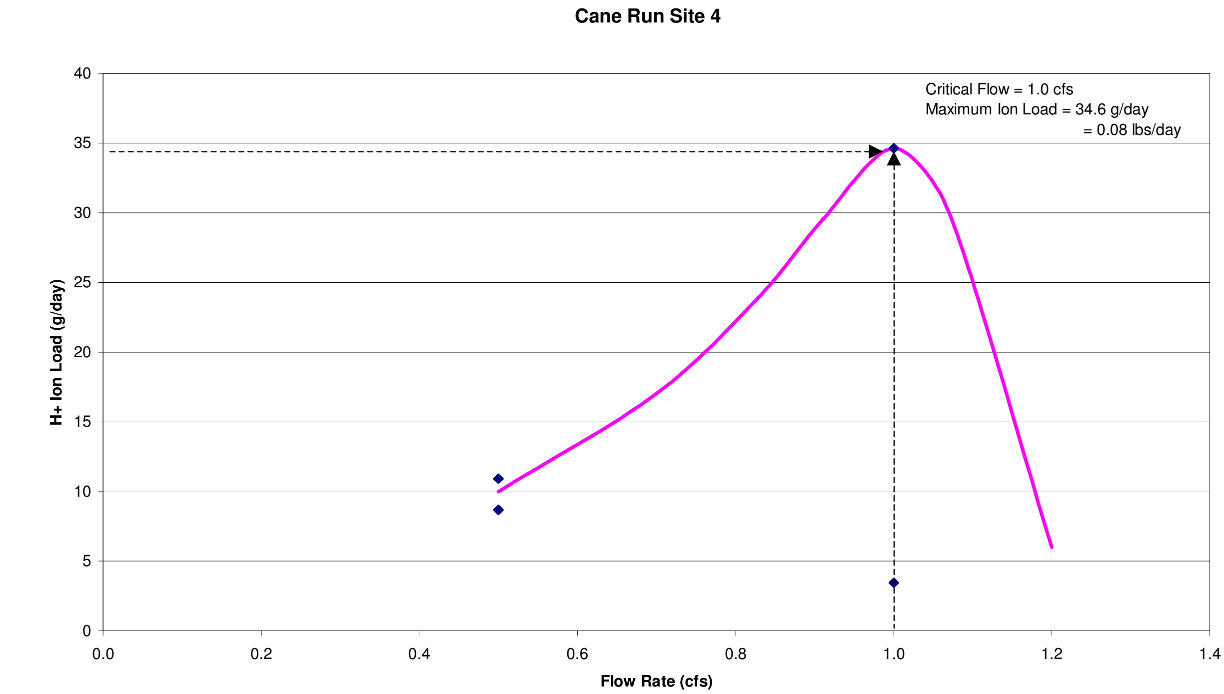


Figure 8. Relation between flow and ion load for site 4

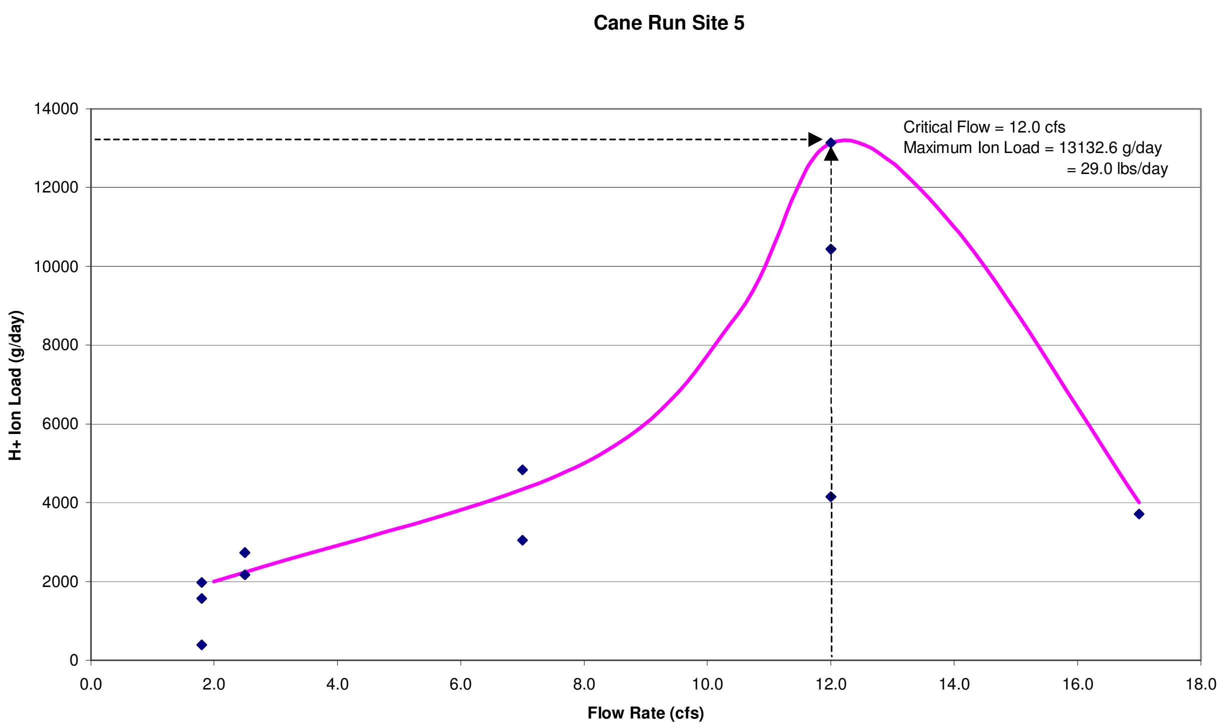


Figure 9. Relation between flow and ion load for site 5

In examining each figure, it is observed that the ion load tends to increase as a function of flow, reach a maximum, and then decrease as the flow increases. It is hypothesized that these results reflect two competing physical processes. At lower flows, it is hypothesized that ion loads are initially leached out of the spoil areas resulting in increasing ion loads. A maximum value of ion load is reached and as the runoff volume increases, it is hypothesized that the ion loads in the spoil areas become depleted and therefore reduced because of flow dilution in the stream. As a result, ion load increases with increasing flow, reaches a maximum, and then decreases as the flow continues to increase. On the basis of the observed data, a conservative estimate of the resulting maximum ion loads can be obtained by selecting the maximum observed ion load at each station.

Predicted Load

The maximum hydrogen ion loads for each site may be obtained from Figures 6-9. Using the data, the total predicted maximum loads were calculated (Table 4)

Table 4. Incremental Critical Flow and Corresponding Predicted Ion Loads (lbs/day)

Subbasin	Incremental Flow Rate (cfs)	Predicted Incremental Ion Load (lbs/day)
1	14.50	69.80
3	46.50	257.40
4	1.00	0.08
5	12.00	28.95

Note again that a mass balance application must be performed to find the incremental load for Subbasin 3. The incremental load at Subbasin 3 is found by subtracting the incremental load for Subbasins 1, 4, and 5 from the cumulative load at Subbasin 3 (356.23 lbs/day - 64.80 lbs/day - 28.95 lbs/day - 0.08 lbs/day = 257.40 lbs/day).

Load Reduction Allocation

Translation of the TMDL in Table 3 into associated daily load reductions for each site may be accomplished by subtracting the incremental TMDL from the incremental predicted load for each of the subbasins. This approach allocates the total load reduction for Cane Run (site CR3) between each of the contributing sites in the watershed so that the entire watershed is rehabilitated and the pH is improved throughout the stream network. Application of this approach yields the values in Table 5.

Table 5. TMDL Summary and Reductions Needed for Cane Run

Total TMDL for Cane Run = 0.45 lbs H+ Ions/day				
	Critical Incremental Flow Rate (cfs)	Incremental TMDL for a pH of 6.0 (lbs/day)	Predicted Maximum Incremental Load (lbs/day)	Incremental Reduction Needed (lbs/day)
Subbasin 1	14.50	0.088	69.80	69.715
Subbasin 3	46.50	0.282	257.40	257.120
Subbasin 4	1.00	0.006	0.08	0.070
Subbasin 5	12.00	0.073	28.95	28.880
Total	74.00	0.448	356.23	355.785

Permitting

New Permits

New permits (except for new remining permits) for discharges to Cane Run could be allowed contingent upon end-of-pipe pH limits in the range of 7.0 to 9.0 standard units. Water quality standards state that the pH value should not be less the 6.0 nor greater than 9.0 for meeting the designated uses of aquatic life and swimming. This range of 6.0 to 9.0 for pH is generally assigned as end-of-pipe effluent limits. However, because a stream impairment exists (low pH), new discharges cannot cause or contribute to an existing impairment. A pH of 7.0 represents a neutral state between an acidic and a non-acidic condition. A discharge having a pH of 7.0 to 9.0 standard units will not cause or contribute to the existing impairment. Based on limited pH data from streams in undisturbed watersheds in the area, a pH of 7.0 is generally representative of background pH. New permits having an effluent limit pH of 7.0 to 9.0 will not be assigned a hydrogen ion load as part of a Waste Load Allocation. . There are no active permits in the Cane Run Watershed that would contribute to the pH impairment.

Remining Permits

Remining permits may be approved on a case-by-case basis where streams are impaired because of low pH from abandoned mines. Existing water quality conditions must be maintained or improved during the course of mining. Permit approval is contingent on reclamation of the site after mining activities are completed. Reclamation of the site is the ultimate goal, but water quality standards (pH of 6.0 to 9.0 standard units) may not necessarily be met in the interim if the Commonwealth issues a variance to the permittee. In instances where the Commonwealth issues a variance for a remining activity consistent with this regulation, hydrogen ion loads from this remining activity are allowed to exceed the waste load allocation. The variance allows an exception to the applicable water quality standard as well as to the TMDL. Remining therefore constitutes a means whereby a previously disturbed and unreclaimed area can be reclaimed. The authority for remining is defined in Section 301(p) of the Federal Clean Water Act; Chapter 33, Section 1331(p) of the U.S. Code – Annotated (the Rahall Amendment to the Federal Clean Water Act); and the Kentucky Administrative Regulations (401 KAR 5:040 and 5:029).

The eventual reclamation of the remining site should result in a reduction of the nonpoint source ion load of the subbasin. The reclamation should also result in an improved stream condition (increased pH) because a previously disturbed and unreclaimed area will be reclaimed. Follow-up, in-stream monitoring would need to be done at the subbasin outfall to determine the effect of reclamation activities following remining on the overall ion load coming from the subbasin. There are currently no active remining permits in the Cane Run watershed.

Distribution of Load

Because there are currently no point source discharges in the watershed that would contribute to the existing low pH impairment and because new permits (pH 7.0 to 9.0) and remining permits would be exempt from the TMDL requirements, no load has been provided for the waste load allocation category (Table 6).

Table 6. Waste Load and Load Allocation for Each Subbasin in the Cane Run Watershed

	Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Waste Load Allocation (lbs/day)	Load Allocation (lbs/day)
Subbasin 1	14.50	0.088	0.000	0.088
Subbasin 3	46.50	0.282	0.000	0.282
Subbasin 4	1.00	0.006	0.000	0.006
Subbasin 5	12.00	0.073	0.000	0.073

Implementation/Remediation Strategy

Remediation of pH-impaired streams as a result of current mining operations is the responsibility of the mine operator. The Kentucky Division of Field Services of the Kentucky Department of Surface Mining Reclamation and Enforcement (DSMRE) is responsible for enforcing the Surface Mining Control and Reclamation Act of 1977 (SMCRA). The Kentucky Division of Abandoned Mine Lands (KDAML), also a part of DSMRE, is charged with performing reclamation to address the impacts from pre-law mine sites in accordance with priorities established in SMCRA. SMCRA sets environmental problems as third in priority in the list of AML problem types.

There are currently no planned remediation activities for the Cane Run watershed. However, reclamation activities are underway at other locations within the state where water quality is affected by acid mine drainage (AMD). Since 1985, the KDAML has spent approximately $17 million dollars on various reclamation projects in western Kentucky. These projects are summarized in Table 7.

Table 7. Kentucky Division of Abandoned Mine Lands Reclamation Projects

Watershed	Project Name	Cost
Brier Creek	Brier Creek	$522,041
	Buttermilk Road	$403,320
Crab Orchard Creek	Crab Orchard Mine	$1,038,203
	Zugg Borehole	$11,974
Pleasant Run	Pleasant Run	$2,162,085
	Pleasant Run II	$421,384
Pond Creek	Pond Creek I	$50,118
	Pond Creek II	$3,801,740
	Pond Creek III	$4,011,514
Flat Creek	East Diamond Mine	$535,000
	Flat Creek	$720,572
Rock Creek	Paint Cliff	$554,623
	Rock Creek I	$630,158
	Rock Creek II	$760,930
Render Creek	McHenry Coop. Agreement	$130,165
	McHenry II	$1,075,340
	Vulcan Mine	$585,359
Total		**$17,414,526**

The success of the reclamation activities in these watersheds was to be evaluated before developing remediation strategies for other watersheds affected by AMD. The KDAML developed a reclamation project in response to documented sedimentation and flooding problems in the nearby Brier Creek Watershed. The project included reclamation of approximately 120 acres of barren or poorly vegetated areas affected by past strip mining. The project also entailed six acres of channel restoration to minimize sedimentation caused by erosion. The restoration of streams included construction of ditches and PVC coated gabion baskets utilized as velocity reducers and energy dissipaters; bale silt checks and silt trap dugouts were also utilized for sediment control. The reclamation project consisted of 67 acres of gradework to remove erosion gullies, redistribute sediment deposits, and prepare a surface to receive a soil cover. The area under consideration received a two foot soil cover layer, taken from 20 acres of watershed area designated for borrow. Gradework areas were treated with an application of agricultural limestone to neutralize acidic conditions and all areas were revegetated using a combination of seedbed preparation, agricultural limestone, fertilizer, seed, mulch, and crimping. The agricultural limestone provided a variety of particle sizes so that it dissolved at different rates and mobilized under a range of flow conditions. The strategy employed at Brier Creek is similar in some respects to a project that is currently underway on Rock Creek and a tributary, White Oak Creek in McCreary County, Kentucky. This 12-acre project is part of the Kentucky Clean Water Action Plan. It involves the removal of coal refuse from the banks of Rock Creek, the establishment of a vegetative cover on other refuse areas in the watershed, and the application of limestone sand at selected locations to neutralize the effects of AMD.

The total cost for the Brier Creek project was $913,000.00 (i.e. $7600/acre) while the total cost of the Rock Creek project is estimated to be approximately $650,000 (i.e. $54,200/acre). For 2000, the total federal Kentucky AML budget allocation was approximately $17 million. However the bulk of these funds were used to support priority 1 (extreme danger of adverse effects to public health, safety, welfare, and property) and priority 2 (adverse effects to public health, safety, and welfare) projects. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the AML projects, particularly priority 3 projects, would be required in order for the AML program to play a significant part in meeting the TMDL implementation requirement associated with pH impaired streams in the state of Kentucky.

For 2000, the total federal Kentucky AML budget allocation was approximately $17 million. However, the bulk of these funds were used to support Priority 1 (extreme danger of adverse effects to public health, safety, welfare, and property) and Priority 2 (adverse effects to public health, safety, and welfare) projects. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the AML program, as well as a rearrangement of priorities as established in SMCRA, would be required in order for the AML program to play a significant part in meeting the TMDL implementation requirement associated with pH impaired streams in the state of Kentucky.

Just recently (June 2003), 319 Clean Water Action Plan funds were awarded to the KDAML. This grant is the Homestead Refuse Reclamation Project and includes reclamation of a 92-acre area of the upper Pleasant Run watershed. The total cost of the reclamation project is $1.26 million, of which 60% is federal funds and 40% is supplied by the KDAML. The reclamation activities channel restoration, re-vegetation, and the use of agricultural limestone.

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USDA, Soil Survey of Hopkins County Kentucky, 1977

APPENDIX A: MINING PERMITS NUMBERING SYSTEM

XXXX-XX Permit issued prior to May 3, 1978. Ex. 1357-76. The first four numbers represent the mine number. The last two numbers represent the year of issuance.

XXX-XXXX Permit issues after May 3, 1978. The first three numbers indicate the location of the mine by county and the timing of the original permit issuance. (Ex. Hopkins County = 54).

If the first three numbers correspond to the county number, the permit was originally issued during the interim program.

If 200 has been added to the county number, the permit was originally issued prior to May 3, 1978, and carried through into the interim program. Ex. 254 (Hopkins)

If 400 has been added to the county number the permit was issued prior to the Permanent Program and was to remain active after January 18, 1983. Ex. 454 or 654 (Hopkins)

If 800 has been added to the county number: (1) the application is for a permit after January 18, 1983 or (2) two or more previously permitted areas have been combined into a single permit. Ex. 854 (Hopkins)

The last four numbers indicate the type of mining activity being permitted.

COAL

0000-4999	Surface Mining
5000-5999	Underground Mine
6000-6999	Crush/Load Facility
7000-7999	Haul Road Only
8000-8999	Preparation Plant
9000-9399	Refuse Disposal

NON-COAL

9400-9499	Limestone
9500-9599	Clay
9600-9699	Sand/Gravel
9700-9799	Oil Shale
9800-9899	Flourspar