Final

pH (H$^+$ Ion Mass)

Total Maximum Daily Load (TMDL)

for

Beech Creek of Pond Creek Watershed
(Muhlenberg County, Kentucky)

Kentucky Department for Environmental Protection

Division of Water

Frankfort, Kentucky

January 2006

Kentucky
UNBRIDLED SPIRIT™

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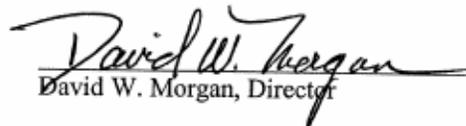# Beech Creek of Pond Creek Watershed
(Muhlenberg County, Kentucky)

Kentucky Department for Environmental Protection

Division of Water

Frankfort, Kentucky

This report has been approved for release:

David W. Morgan, Director

Division of Water

1/13/06

Date

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Beech Creek of Pond Creek

Total Maximum Daily Load (TMDL) Fact Sheet

Project Name: Beech Creek of Pond Creek

Location: Muhlenberg County, Kentucky

Scope/Size: Beech Creek watershed (5.38 mi^2)
         Stream Segment: river mile 0.0 to 3.4

Land Type: forest, agricultural, barren/spoil

Type of Activity: acid mine drainage (AMD) caused by abandoned mines

Pollutant(s): H^+ Ion mass, sulfuric acid

TMDL Issues: nonpoint sources

**Water Quality
Standard/Target:** The 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: Kentucky Pollutant Discharge Elimination System Permit
         Historical Sampling Data, Kentucky Division of Water
         (KDOW) Data Collection

Control Measures: Kentucky nonpoint source TMDL implementation plan,
         Kentucky Watershed Framework

Summary: Beech Creek 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, Beech Creek was placed
         on the 1998 and 2002 303(d) Lists for TMDL development.
         Beech Creek is characterized by a depressed pH, the result
         of AMD from abandoned mining sites. In developing the
         TMDL for Beech Creek, pH readings from two different
         locations along Beech Creek were used. Both locations
         showed impairment, so the TMDL has been developed for
         both subbasins (Subbasins 1 and 2).
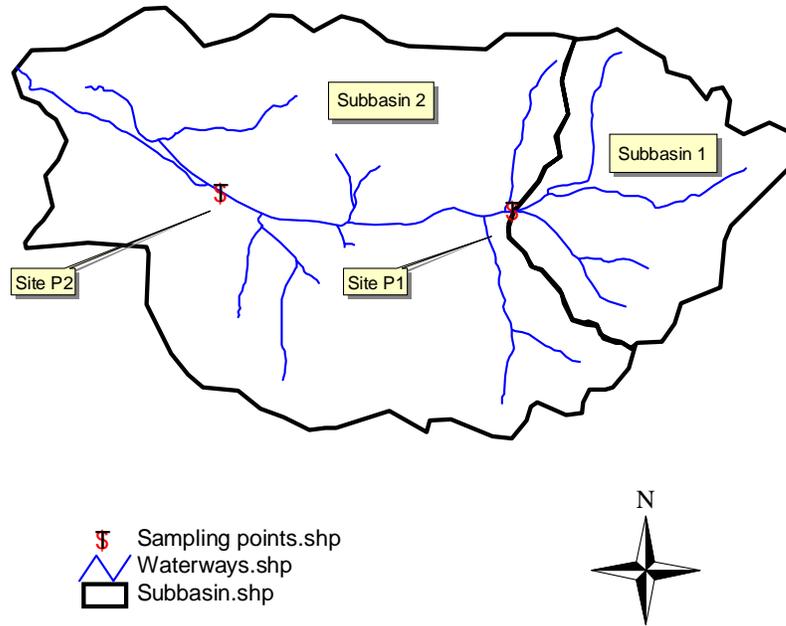
Location of Monitoring Points and Subbasin Boundaries for Beech Creek

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

In recognition of the inherent difficulties associated with imposition of a "no-exceedance" pH criteria on potentially intermittent streams, the KDOW has decided to use the lowest one year average discharge of the most recent 10-year flow record as the flow basis for setting the appropriate TMDL and associated loading reduction. Previous pH TMDLs have used a 3-year recurrence interval of the average flow as the critical flow. However, this flow resulted in a target discharge that frequently was significantly greater than any of the observed flows for the sites as collected over several years. Thus use of a 3-year flow would require an extrapolation of the observed ion vs. flow model, well beyond the upper limit of the observed data. The selection of the 10-year frequency was based on

a consideration of water quality standards (WQSs) (i.e. 7Q10). However, since many of these streams have a 7Q10 of zero, a greater duration was needed. The consensus of the KDOW was to use the 1-year duration. The use of an average annual flow as the basis for determining the TMDL provides a more appropriate mechanism for determining the total annual load, the total annual reduction that would be derived from an annual summation of the daily TMDLs, and the associated daily load reductions for the critical year using historical daily flows.

TMDL for Beech Creek: To develop a TMDL for Beech Creek, there are two possible strategies. Either a cumulative aggregate TMDL may be obtained for the outlet of the watershed, or separate TMDLs, and associated load reductions, may be developed for each individual subbasin. As a result of the availability of data at multiple sampling locations, individual TMDLs were developed for each monitored sampling location. The TMDLs and associated load reductions for each impaired subbasin are shown below.

TMDLs and Associated Load Reductions

Location	Incremental Contributing Area (Hectares)	Incremental Contributing Area (mi^2)	Incremental TMDL @ pH = 6.0 (lbs/day)	Predicted Load (lbs/day)	Required Load Reduction (lbs/day)
Total Watershed	1,393	5.38	0.018	15.457	15.439
Subbasin 1	319	1.23	0.004	2.390	2.386
Subbasin 2	1,074	4.15	0.014	13.067	13.053

Permitting in the Beech Creek Watershed

New Permits: New permits (except for new remining permits) for discharges to streams in the Beech Creek watershed could be allowed anywhere in the watershed contingent upon end-of-pipe pH permit limits in the range of 6.35 to 9.0 standard units. WQSs 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 should not cause or contribute to an existing impairment. Application of agricultural limestone on mine sites results in highly buffered water leaving the site. A buffered solution with nearly equal bicarbonate and carbonic acid components will have a pH of 6.35 (Carew, personal communication, 2004). Discharge of this buffered solution will use up free hydrogen ions in the receiving stream, thus it should not cause or contribute to an existing low pH impairment. New permits having an effluent limit pH of 6.35 to 9.0 will not be assigned a hydrogen ion load as part of a Waste Load Allocation (WLA).

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 remining 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 WQSs (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. 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 WLA. The variance allows an exception to the applicable WQS 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 nonpoint 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. 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.

General KPDES Permit for Coal Mine Discharges: This permit covers all new and existing discharges associated with coal mine runoff. This permit does not authorize discharges that (1) are subject to an existing individual KPDES permit or application, (2) are subject to a promulgated storm water effluent guidelines or standard, (3) the Director has determined to be or may reasonably be expected to be contributed to a violation of a water of a WQS or to the impairment of a 303(d) listed water, or (4) are into a surface water that has been classified as an Exceptional or Outstanding or National Resource Water. A signed copy of a Notice of Intent (NOI) form must be submitted to the Kentucky Division of Water (KPDES Branch) when the initial application is filed with the Division of Mine Permits. However, coverage under this general permit may be denied and submittal of an application for an individual KPDES permit may be required based on a review of the NOI and/or other information.

Antidegradation Policy: Kentucky's Antidegradation Policy was approved by EPA on April 12, 2005. For impaired waters, general permit coverage will not be allowed for one or more of the pollutants commonly associated with coal mining (i.e., sedimentation, solids, pH, metals, alkalinity of acidity). The individual permit process remains the same except new conditions may apply if a Total Maximum Daily Load (TMDL) has been developed and approved.

Distribution of Load: Because there were no point source discharges active during the 2000-2002 monitoring period, the existing hydrogen ion load for the watershed was defined entirely as a nonpoint source load. Because new permits (pH 6.35 to 9.0) should 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 WLA category.

Wasteload and Load Allocation for Each Subbasin in the Beech Creek Watershed

Subbasin	Incremental Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation* (lbs/day)	Load Allocation (lbs/day)
Subbasin 1	0.76	0.004	0.000	0.004
Subbasin 2	2.58	0.014	0.000	0.014

*pH limits for new discharges must be between 6.35 and 9.0

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 (DAML) is charged with performing reclamation to address the impacts from pre-law and bond forfeiture mine sites in accordance with priorities established in SMCRA. SMCRA sets environmental problems as third in priority in the list of abandoned mine land (AML) problem types.

Prior to initiating reclamation activities to improve water quality, a watershed plan should be developed in order to more precisely identify past mine site operations in the watershed. For example, the watershed plan should include a detailed overview of past mine operations, including the location of the mine, the permit number, the type of mining and the status of the mine (e.g. active, bond forfeited, bond released, illegal "wildcat" mining, etc.). Refining historic landuses in the watershed, with a particular focus on mine site operations, will assist with identifying the most appropriate funding source(s) as well as the best management practices needed for remediating the pH impacts.

In addition to historic mine operation inventory, the watershed plan should identify (1) point and nonpoint source controls needed to attain and maintain WQSs, (2) who will be responsible for implementation of controls and measures, (3) an estimate of the load reductions to be achieved, (4) threats to other waters, (5) an estimate of the implementation costs and identify financing sources, (6) a

monitoring plan and adaptive implementation process and (7) a public participation process. The watershed plan should consider non-traditional opportunities and strive for the most cost-effective long-term solutions for restoring the water quality of Beech Creek.

Practical application of pH TMDLs, especially for AMLs, will normally involve a phased implementation approach with associated monitoring in order to insure that the implemented measures are having the desired effect. That has been the strategy pursued thus far with regard to watersheds in Kentucky. Typical remediation strategies have involved channel restoration, re-vegetation, and the use of agricultural limestone. On sites where applicable, and funding allows, passive treatment systems have been used to treat AMD including open limestone channels, vertical flow systems, limestone dosing, and constructed wetlands.

There are currently no remediation activities underway in the Beech Creek watershed. However, reclamation activities have occurred at other locations within the state where AMD affects water quality. Examples of reclamation projects addressing AMD in western KY are summarized below.

Reclamation Projects Addressing AMD in Western KY

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
Render Creek	McHenry Coop. Agreement	$130,165
	McHenry II	$1,075,340
	Vulcan Mine	$585,359

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. Of the total annual federal budget allocation, AML receives only approximately $700,000 in Appalachian Clean Streams Initiative funds, which are targeted for Priority 3 environmental problems. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the DAML program, 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.

Introduction

Section 303(d) of the Clean Water Act and Environmental Protection Agency's (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 of their water resources (EPA, 1991).

Location

The Beech Creek watershed is entirely contained within Muhlenberg County, in southwestern Kentucky (Figure 1). Muhlenberg County is bounded on the northeast by the Green River, on the east by the Indian Camp Creek, and on the west by the Pond Creek.
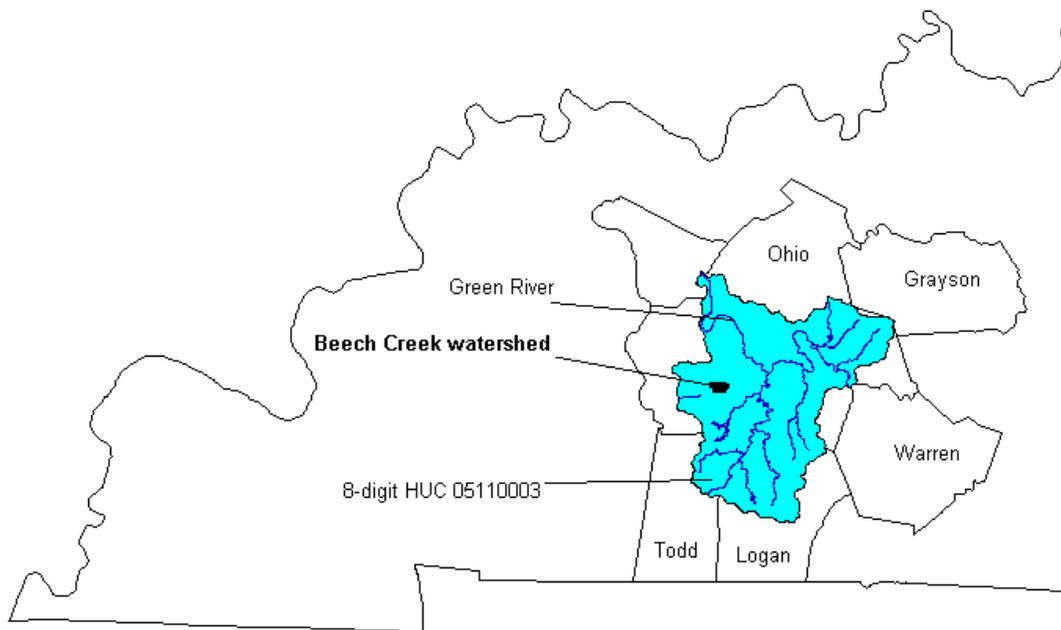
Figure 1. Location of the Beech Creek Watershed

Hydrologic Information

Beech Creek, a third order stream, originates in southeastern Muhlenberg County and flows westward to discharge into Pond Creek at RM 15.5 (Figure 1). Beech Creek's main stem is approximately 3.9 miles long and drains an area of 5.38 sq. miles. The average gradient is 12.8 feet per mile. Elevations for Beech Creek range from 500 ft above mean sea level (msl) in the headwaters to 450 ft above msl at the mouth. Like most of the smaller watersheds, many of the tributary streams are intermittent.

Geologic Information

The Beech Creek 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 (US Department of Agriculture, 1980). The relief of the Pond Creek watershed (Beech Creek watershed is a subbasin of Pond Creek 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.

Land Use Information

Coal, oil, and natural gas are among the natural resources of Muhlenberg County. Coal is the county's most important revenue-producing natural resource and at one time Muhlenberg County was the largest coal-producing county in the United States. In 1973, this county produced over 19 million tons of coal from strip mines and over 5 million tons from underground mines. The Beech Creek watershed contains three main land uses: resource extraction (mining and disturbed land area), forestry and agriculture.

Soils Information

Beech Creek watershed is dominated by nearly level loamy and clayey soils near to the mouth and level to steep loamy soils in the headwaters. Most of the watershed is Udorthents soil, which consists of strip mine spoil containing rock fragments.

Mining and Reclamation History

Mining activities in the Beech Creek Watershed occurred prior to 1977. A list of the various mining permits that have been issued for Beech Creek since 1984 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.

Table 1. Permits in the Beech Creek Watershed

Permit #	Permitted Area (ac)	Associated Company	Date Issued	Date Expired
8890041	223.8	West Ken Coal Corp.	07/17/1987	07/17/1992
8890046	324.7	Pond Creek Coal Co Inc.	01/11/1989	01/11/1994
8890057	57	Crown Energy Corp.	01/19/1990	01/19/1997
8890069	60.5	Pond Creek Coal Co Inc.	06/27/1991	06/27/1996
8890084	5.45	Beech Creek Energy Inc.	11/20/1995	11/20/2000

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 that are permitted but never disturbed by mining or for areas that 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 have 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 post-mining land use. Up to 60 percent of the original bond amount is released at Phase One. An additional 25 percent 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 determined that fraudulent documentation was submitted as part of the remediation process.

Monitoring History

The waters of Beech Creek were monitored as early as 1978 by the Kentucky Division of Water (KDOW) as reported in *The Effects of Coal Mining Activities on the Water Quality of Streams in the Western and Eastern Coalfields of Kentucky,* published in 1981 by the KDOW as part of an agreement with the DAML. Subsequently, the KDOW has continued to monitor the watershed at various sites (see Figure 2). The results recorded at these sites are provided in Table 2.
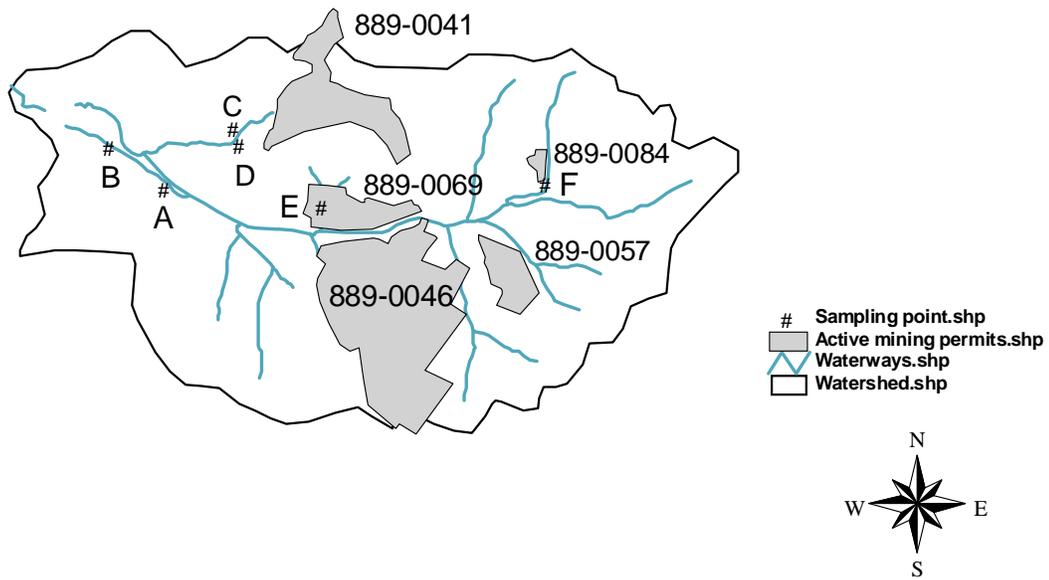
Figure 2. Recent Permits and Historic Sampling Sites in the Beech Creek Watershed

Table 2. Historic Monitoring Data, KDOW 1983-1995

Point	Date	pH
A	6/22/1993	3.64
	11/01/1993	3.28
	2/22/1994	3.16
	5/17/1994	3.2
	8/09/1994	5.11
	11/01/1994	3.17
	1/31/1995	6.13
B	6/22/1993	2.82
	11/01/1993	3.11
	2/22/1994	4.36
	5/17/1994	3.23
	8/09/1994	3.08
	11/01/1994	3.28
	1/31/1995	4.9
C	12/14/1987	4.7
	4/01/1988	6.94
	5/26/1989	2.65
D	5/01/1983	7.67
	11/01/1983	7.57
	12/01/1983	7.61
	5/01/1984	7.21
	4/01/1984	7.57
	1/01/1984	7.73
	2/01/1984	7.39
	3/01/1984	7.56
E	1/30/1990	5.8
	12/27/1990	6.97
	12/27/1990	6.97
	1/30/1991	5.8
	2/15/1991	6.7
	3/18/1991	5.6
	4/18/1991	5.19
	5/06/1991	5.56
	12/01/1991	6.03
	3/11/1992	4.21
	2/01/1993	5.6
	3/01/1993	5.8
	4/01/1993	6.42
	5/01/1993	5.47
	4/01/1986	6.95
F	1/31/1995	3.05
	4/25/1995	3.0
	6/30/1995	2.71
	7/31/1995	2.63
	9/01/1995	2.71
	9/21/1995	2.85

In 1997, the KDOW conducted an intensive survey of streams in the Western Kentucky Coal Fields, including Beech Creek. The KDOW recorded a pH of 2.7 on July 2, 1997 on Beech Creek at RM 2.6 at the Hwy 1163 bridge (Site P1 in this report). Based on this information and previous information, Beech Creek was assessed as not supporting the designated uses of aquatic life and swimming because of low pH. The source of the pH impairment is acid mine drainage (AMD) from resource extraction.

Problem Definition

The 1998 and subsequent 303(d) list of waters for Kentucky (KDOW, 1998 and 2003) indicate that 3.4 miles of Beech Creek, from the headwaters to the confluence with Pond Creek in Muhlenberg County, do not meet the designated uses of primary and secondary contact recreation and aquatic life. The Beech Creek watershed provides a classic example of impairment caused by AMD. Bituminous coal mine drainage, like that found in the Beech Creek watershed, contains very concentrated sulfuric acid and high concentrations of metals, especially iron, manganese, and aluminum.

AMD can: (1) ruin domestic and industrial water supplies; (2) decimate aquatic life; and (3) cause waters to be unsuitable for swimming and wading. 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 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:

$$4\ FeS_2 + 14\ O_2 + 4\ H_20 + bacteria \rightarrow 4\ Fe + SO_4 + 4\ H_2SO_4 \qquad (1)$$
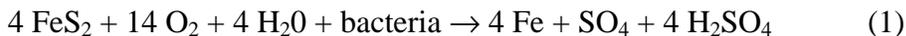
The subsequent oxidation of ferrous iron and acid solution to ferric iron is generally slow. The reaction may be represented as:

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

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:

$$2\ Fe_2(SO_4)_3 + 12\ H_2O \rightarrow 4\ Fe(OH)_3 + 6\ H_2SO_4 \qquad\qquad (3)$$
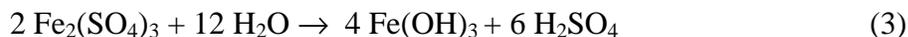
The brownish yellow ferric hydroxide ($Fe(OH)_3$) may remain suspended in the stream even when it is no longer acidic. Although the brownish, yellow staining of the stream-banks and water does not cause the low pH, it does indicate that there has been production of sulfuric acid. The overall stoichiometric relationship is shown in equation (4):

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

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 a pH TMDL is to achieve a pH concentration and associated hydrogen ion load in lbs/day that supports aquatic life and recreation uses. The pH criterion to protect these uses is 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. Water quality criteria have not been specified in terms of a particular frequency of occurrence. As pointed out in the recent NRC TMDL report (2001), "All chemical criteria should be defined in terms of magnitude, frequency, and duration. Each of these three components is pollutant-specific and may vary with season. The frequency component should be expressed in terms of a number of allowed flow excursions in a specified period (return period) and not in terms of the low flow or an absolute "never to be exceeded" limit. Water quality criteria may occasionally be exceeded because of the variability of natural systems and discharges from point and nonpoint sources." Small intermittent streams are especially vulnerable to this variability.

The Technical Support Document for Water Quality-Based Toxic Control (EPA, 1991) states that daily receiving water concentrations (loads) can be ranked from the lowest to the highest without regard to time sequence. In the absence of continuous monitoring, such values can be obtained through continuous simulation or monte-carlo analysis. A probability plot can be constructed from these ranked values, and the frequency of occurrence of any 1-day concentration of interest can be determined. Where the frequency (or probability) of the resulting concentration is greater than the maximum exceedance frequency of the water quality target (e.g. once in 10 years), associated load reductions will be required until the resulting concentration is above the minimum target value (e.g. pH = 6.0). Where the load and the associated target value can be directly related through a flow rate (also referred to as discharge or streamflow), the frequency (or probability) of the associated flow rate (e.g. 365Q10) can be directly related to the frequency (or probability) of the target pH.

In recognition of the inherent difficulties associated with imposition of a "no-exceedance" pH criteria on potentially intermittent streams, the KDOW has decided to use the lowest one year average daily discharge of the most recent 10-year flow record as the flow basis for setting the appropriate TMDL and associated load reduction. Previous pH TMDLs have used a 3-year recurrence interval of the average flow as the critical flow. However, this flow resulted in a target discharge that frequently was significantly greater than any of the observed flows for the sites as collected over several years. Thus use of a 3-year flow would require an extrapolation of the observed ion vs. flow model, well beyond the upper limit of the observed data. The selection of the 10-year frequency was based on a consideration of water quality standards (WQS) (i.e. 7Q10). However, since many of these streams have a 7Q10 of zero, a greater duration was needed. The consensus of the KDOW was to use the 1-year duration. Use of an average daily flow over a one year period as the basis for determining the TMDL provides an appropriate mechanism for determining: (1) the total annual load; (2) the total annual reduction that would be derived from an annual summation of both the daily TMDLs; and (3) the associated daily load reductions for the critical year using the actual historical daily flows. The equivalent total annual load can be determined by simply multiplying the TMDL (derived by using the average daily flow) by 365 days. Likewise, the equivalent total annual load reduction can be obtained by multiplying the average daily load reduction (derived by using the average daily flow over a one year period) by 365 days. Although the 10-year lowest average annual flow (which roughly corresponds to the 365Q10) is typically only exceeded by approximately 20% of the days in the critical year, it still provides for explicit load reductions for approximately 80% of the total annual flow. For actual daily flows less than average flow, incremental load reductions may be accomplished by explicit imposition of a pH standard of 6 units.

Source Assessment

Point Source Loads

During the 2000-2002 sampling period, there were no active permitted point source loads contributing to the existing pH impairment in the watershed.

Nonpoint Source Loads

In order to provide a more recent characterization of the pH levels in the watershed, KDOW personnel collected additional pH and streamflow data at a number of sites in the watershed (Figure 3), including Sites P1 (at River Mile 2.6) and P2 (at River Mile 1.2). A summary of the results obtained from these sites is shown in Table 3. Table 3 indicates that low pH values were observed in Subbasins 1 and 2, in effect the entire watershed. The Tracy Farmer Center for the Environment received funding through an EPA Water Quality Cooperative Grant to develop the TMDL.
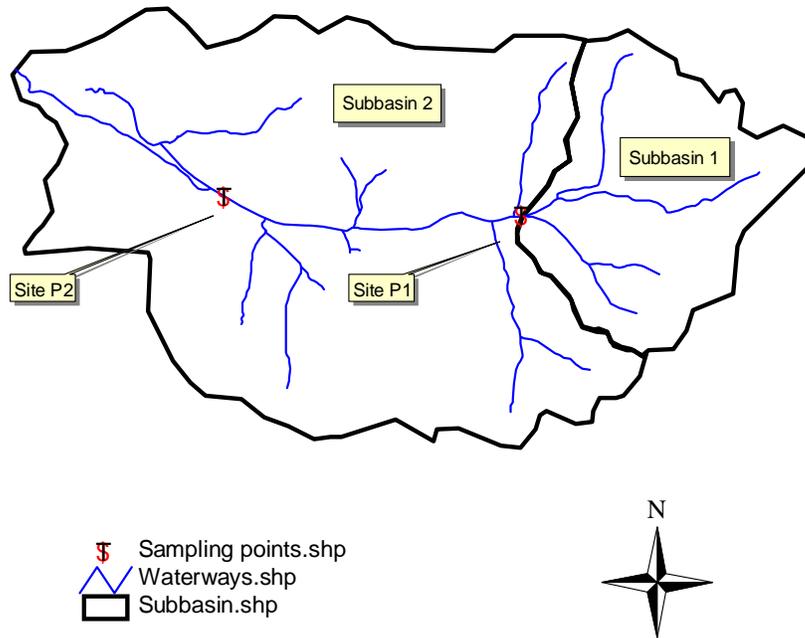
Figure 3. KDOW Sampling Sites

Table 3. KDOW Sample Results, 2000-2002

Date	Site P1 (River Mile 2.6) 37° 10' 27" / 87° 03' 37"		Site P2 (River Mile 1.2) 37° 10' 30" / 87° 05' 08"	
	Flow (cfs)	pH	Flow (cfs)	pH
10/24/2000	0.01	2.74	0.03	2.6
11/7/2000	0.06	3.12	0.18	2.89
11/9/2000	0.44	3.49	1.9	3.06
3/27/2000	0.46	3.15	0.94	3.31
4/20/2001	0.02	3.3	0.53	3.19
8/13/2001	0.01	2.94	0.13	2.85
8/22/2001	0.0	-----	0.1	2.93
1/9/2002	0.15	3.58	0.51	4.5

TMDL Development

Theory

The TMDL is a term used to describe the maximum amount of a pollutant a stream can assimilate without violating WQSs and includes a MOS. The units of a load measurement are mass of pollutant per unit time (mg/hr, lbs/day). In the case of pH, there is no direct associated mass unit (pH is measured in Standard Units).

TMDLs are comprised of the sum of individual wasteload allocations (WLAs) for point sources and load allocations (LAs) from both nonpoint sources and natural background for a given watershed. The sum of these components cannot result in exceedance of WQS for that location of the stream. In addition, the TMDL must include a MOS, which is either implicit or explicit, that accounts for the uncertainty in the relationship between pollutant loads and the quality of the receiving water body. Conceptually, this definition is denoted by the equation:

$$TMDL = Sum\ (WLAs) + Sum\ (LAs) + MOS \qquad (9)$$

Margin of Safety

The 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 (EPA, 1991):

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.

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:

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

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 (Snoeyink and Jenkins, 1980):

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

Alternatively, the ionic strength of a given source of water may be related to the measured specific conductance (SC) through the following relationship (Snoeyink and Jenkins, 1980):

$$\mu = (1.6 * 10^{-5}) * SC \tag{8}$$

Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Figure 4 (Snoeyink and Jenkins, 1980).
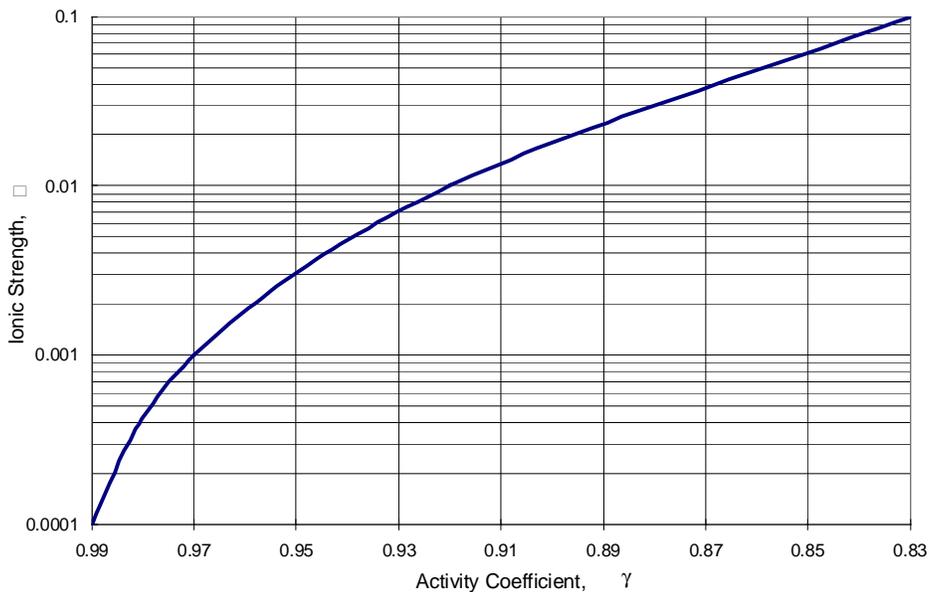

Figure 4. Activity Coefficients of H+ as a Function of Ionic Strength
(Snoeyink and Jenkins, 1980)

In the absence of actual measured values of TDS or specific conductivity, an estimate of the upper limit of the ionic strength may be obtained from an evaluation of historic values of TDS or specific conductivity collected in the area. For example, an evaluation of over 1,600 measurements of specific conductivity obtained from streams in the western Kentucky coalfields (Grubb and Ryder, 1972; KDOW, 1981; and US Geological Survey [USGS], 1983) revealed a range of values from 45 μ ohms/cm to 5920 μ ohms/cm. Use of an upper limit of 6000 μ ohms/cm yields an ionic strength of 0.096 or approximately 0.10. Use of a value of ionic strength of 0.10 yields an activity coefficient of approximately 0.83.

For the Beech Creek watershed, specific conductance values were observed to vary from 1650-1900 μ ohms/cm, which yields ionic strength values of 0.026 to 0.030 respectively. Application of Figure 4 for the observed ionic strengths in Beech Creek yields activity coefficients of 0.885 to 0.880.

The atomic weight of hydrogen is one gram per mole. Thus, 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.

Because pH and equivalent hydrogen ion load can be related as a function of flow (or flow rate) and ionic strength, a functional relationship can be developed between flow and the associated ion loading for a given pH value. By specifying a minimum pH value (e.g. 6) and an associated minimum activity correction factor (e.g. 0.87), an envelope of maximum hydrogen ion loads (that could still yield a pH of 6) may be obtained as a function of flow rate (see the upper $TMDL_x$ curve in Figure 5). In using the proposed methodology, the MOS may be incorporated explicitly through the properties of water chemistry that determine the relationship between pH and hydrogen ion concentration. In an electrically neutral solution, 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. To develop a TMDL for an impaired stream, the most conservative approach would be to assume an activity coefficient of 1.0, which would yield the lowest value for the TMDL for a given range of activity coefficients (see lower $TMDL_1$ curve in Figure 5). The difference between the maximum $TMDL_x$ (based on the observed activity coefficient) and the minimum $TMDL_1$ (based on an activity coefficient of 1.0) would thus provide a margin of safety (MOS) in setting the TMDL for the stream, as well as for calculating the associated load reduction. Thus, in developing a TMDL for the Beech Creek watershed, the TMDL for each subbasin will be established assuming an activity coefficient of 1.0, while the observed load will be determined using an activity coefficient of 0.88, thus providing for an upper limit representing a MOS of approximately 12 percent. Even though this MOS can be deemed as an explicit MOS, for this TMDL it will be expressed as an implicit MOS because a conservative assumption has been used in the model to determine the value of the TMDL.
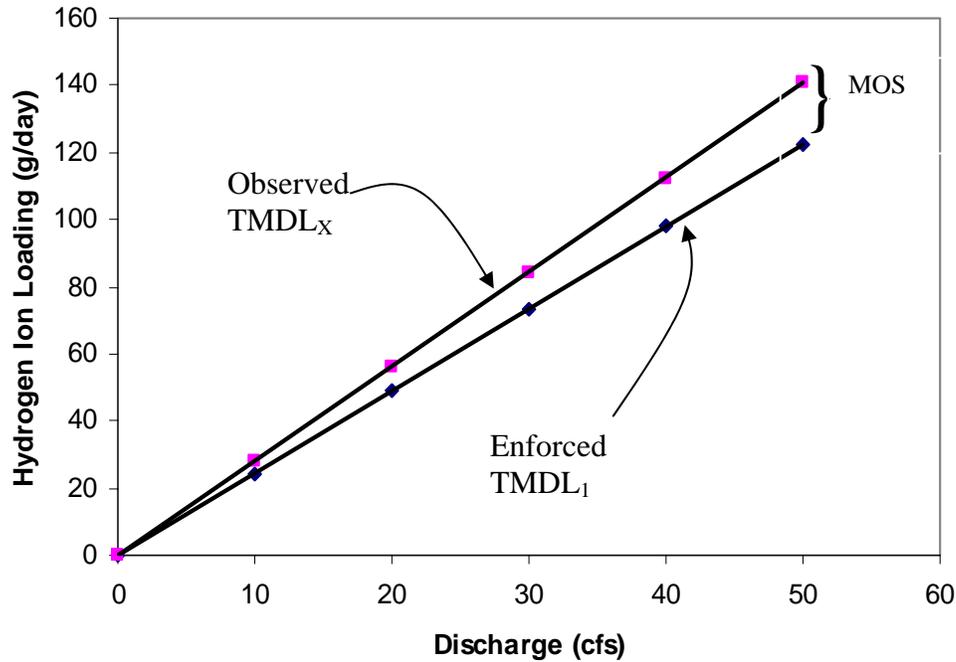
Figure 5. Relation between Discharge and Maximum Ion Load for a pH of 6.0

Hydrogen Loading Example Calculation

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

- Critical discharge (Q) = 3.34 cfs (cumulative)
- Measured pH = 6.0

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

$$pH = -\log \{H^+\} \tag{17}$$

The resulting moles of hydrogen is 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, or lbs/day. If the amount of hydrogen ions 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:

$(0.0000283168 \text{ g/ft}^3)*(3.34 \text{ ft}^3/\text{s})*(86400\text{s}/1\text{day}) = 8.17$ g/day, or 0.018 lbs/day

Assuming an activity correction factor of 0.88, the final load is 9.28 g/day, or 0.020 lbs/day:

8.17 g/day / 0.88 = 9.28 g/day, or 0.020 lbs/day

Thus, by using an activity coefficient of 1.0 instead of 0.88 to determine the TMDL, a MOS of approximately 12 percent is realized.

Critical Flow and TMDL Determination

Because hydrogen ion loading values can be directly related to flow (Figure 5), the associated allowable ion loading can be directly related to the flow. In order to find the lowest 10-year average annual flow rate for the Beech Creek watershed, a regional hydrologic frequency analysis was used. Regional analysis can be used to develop an inductive model using data collected at streamflow gaging stations that are located in the same hydrologic region as the watershed of interest. For this study, the following USGS gaging stations were selected: 03320500, 03384000, 03383000, and 03321350. The data from these gages were used to estimate the lowest average annual flows of the most recent 10 years (see Table 4). These flows were then regressed with watershed area to produce Figure 6. Using Figure 6, the lowest 10-year mean annual discharge for a given watershed area can be determined.

Table 4. Lowest 10-year Mean Annual Flow Rates (cfs) for Stations in Regional Analysis

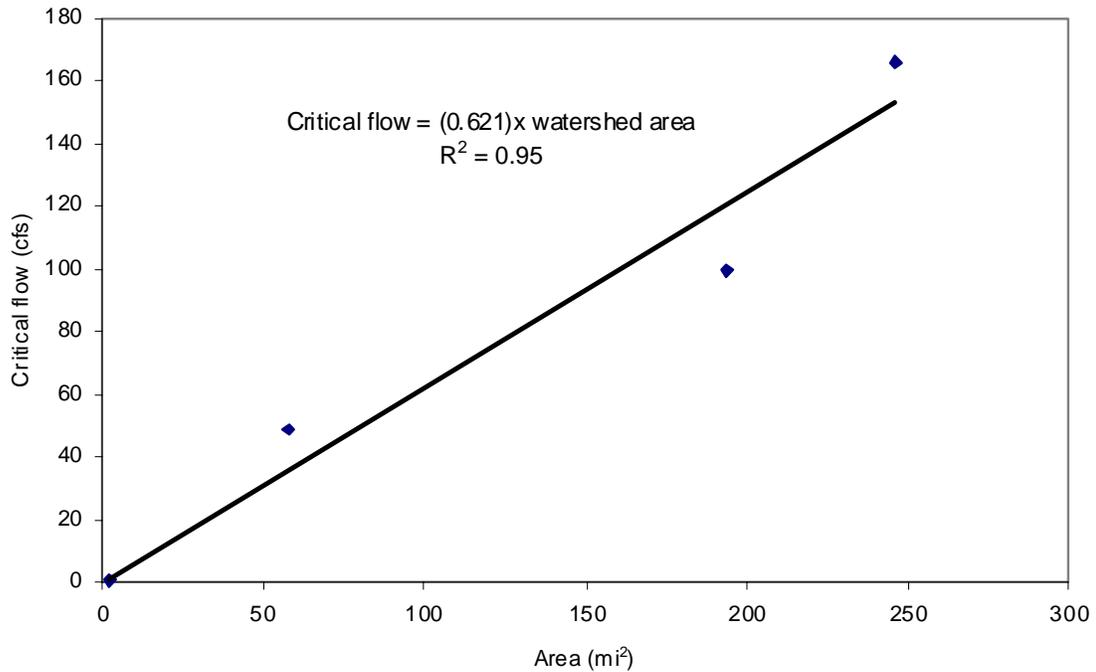|	USGS Gaging Station Numbers			
Station	3384000	3321350	3320500	3383000
Area (mi^2)	2.10	58.20	194.00	255.00
Flow (cfs)	0.69	49.10	99.70	166.00

Figure 6. Relation Between Drainage Area and the Critical TMDL Flow

Application of Figure 6 for the Beech Creek watershed yields a TMDL critical average annual discharge of 3.34 cfs, assuming a watershed area of 5.38 mi^2 (0.621 x 5.38 = 3.34). Application of a critical discharge (the lowest 10-year mean annual flow) of 3.34 cfs with the lower $TMDL_1$ curve in Figure 5 yields a TMDL of 0.018 lbs/day of hydrogen ions (see Hydrogen Loading Example Calculation on page 13). The lowest 10-year mean annual flows for each individual subbasin are obtained using a simple mass balance technique. For a mass balance to be obtained, the flow at the outlet must equal the summation of the incremental flows at each subbasin. Therefore, the calculated outlet flow is distributed throughout the watershed based on subbasin area. This process gives the larger subbasins a larger incremental flow; likewise, it gives the smaller subbasins a lesser flow. These incremental flows can be used in conjunction with Figure 5 to obtain incremental TMDL values for each subbasin. See Table 5 for the results.

Table 5. Critical Flow and Corresponding TMDLs for the Beech Creek Watershed

Location	Area (mi^2)	Incremental Flow Rate (cfs)	Incremental TMDL (g/day)	Incremental TMDL (lbs/day)
Total Watershed	5.38	3.34	8.17	0.018
Subbasin 1	1.23	0.76	1.86	0.004
Subbasin 2	4.15	2.58	6.31	0.014

Hydrogen Ion Loading Model

There were no permitted point sources in this watershed during the 2000-2002 monitoring period that contributed to the existing pH impairment. As a result, the wasteload allocations for the Beech Creek watershed are assumed to be zero. Therefore, the entire hydrogen ion load can be attributed to abandoned mine land (AML) nonpoint sources.

Based on a physical inspection of the watershed, it is hypothesized that the lowering of the pH in the stream is directly related to the oxidation of sulfur that occurs as runoff flows over the spoil areas associated with previous mining activities in the basin. Using the most recent monitoring data, inductive models were developed for each monitoring site that relate total hydrogen ion loading to flow. The models developed for Subbasins 1 and 2 are shown in Figures 7 and 8 and were developed using a conservative estimate of 0.88 for the associated ion activity coefficient based on an upper limit of measured specific conductance values for Beech Creek of 1900 μ ohms/cm. As can be seen from the figures, the total load increases as a function of flow, illustrating the significant relationship between low pH and nonpoint sources. The developed relationships may be used to predict total ion loading to a stream on the basis of flow.
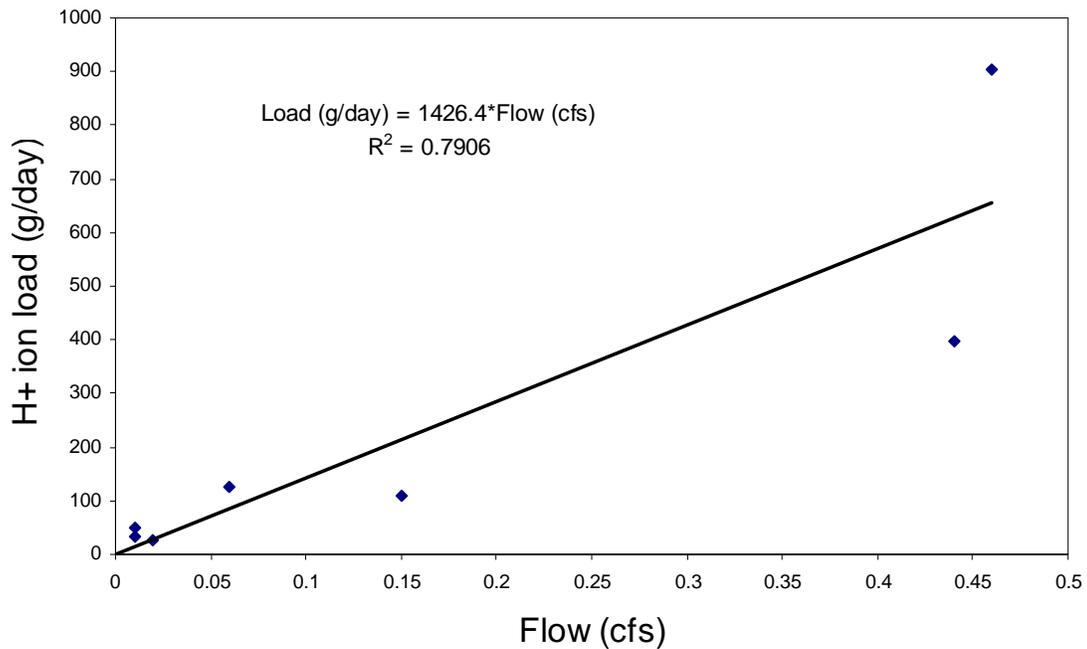

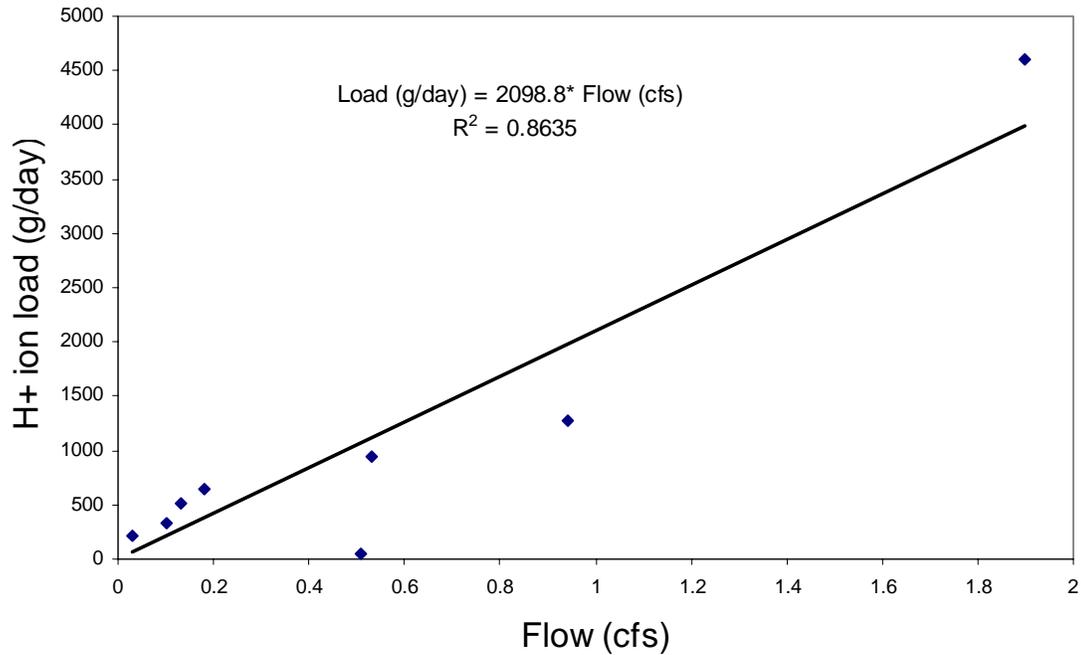Figure 7. Relation Between Flow and Ion Load for Site P1

Figure 8. Relation Between Flow and Ion Load for Site P2

Predicted Load

The predicted hydrogen ion loads for each site may be obtained using the critical flow from Table 5 and the associated load relationships (Figures 7 and 8). Application of this approach yields the predicted loads for each subbasin as shown in Table 6. For example, for Subbasin 1, use of the critical flow of 0.76 cfs with the fitted line in Figure 7 yields a load of 2.390 lbs/day (1426.4 x 0.76 = 1084 g/day or 2.39 lbs/day). It should be noted that for Subbasin 2, the monitoring data for use in developing Figure 8 was collected at a point upstream from the outlet of the watershed.   It is assumed that the loading relationship is proportional to the watershed area.   Since the critical discharge was determined based on the area of Subbasin 2 (to the outlet of the watershed), and since the area-flow relationship in Figure 6 is linear, the predicted load at the outlet of Subbasin 2 should be equivalent to the load obtained at monitoring Site P2 as adjusted to reflect a larger area. Also, note that for an independent tributary, the incremental load is equal to the cumulative load for that tributary. On the other hand, a subbasin that has flows entering from adjacent or upstream subbasins requires a mass balance application to find the incremental load. For example, the incremental load for Subbasin 2 is determined by subtracting the cumulative load for Subbasin 1 from the cumulative load for Subbasin 2 (15.457 – 2.390 = 13.067).

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Table 6. Predicted Hydrogen Ion Loads for Each Subbasin

Subbasin	Cumulative Flow Rate (cfs)	Cumulative Load (g/day)	Cumulative Load (lbs/day)	Incremental Load (lbs/day)
1	0.76	1,084	2.390	2.390
2	3.34	7,010	15.457	13.067

Load Reduction Allocation

Once a TMDL is developed for a watershed, the needed load reductions can be determined. One way to accomplish this objective is through the use of unit load reductions applied to different land uses within the watershed. The impacts of such reductions in meeting the WQS 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 3. Attainment of the reductions in the load from each subbasin should then meet the TMDL requirement for the complete watershed. Translation of the incremental TMDLs in Table 5 into associated daily load reductions for each subbasin may be accomplished by subtracting the incremental TMDLs from the incremental predicted loads for each subbasin (Table 6). For Subbasin 1, this calculation is 15.457 – 0.018 = 15.439. This approach allocates the total load reduction for Beech Creek (defined at Site P2) between each of the contributing subbasins 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 7.

Table 7. TMDL Summary and Reductions Needed for the Beech Creek Watershed

Location	Incremental Contributing Area (Hectares)	Incremental Contributing Area (mi^2)	Incremental TMDL @ pH = 6.0 (lbs/day)	Predicted Load (lbs/day)	Required Load Reduction (lbs/day)
Total Watershed	1,393	5.38	0.018	15.457	15.439
Subbasin 1	319	1.23	0.004	2.390	2.386
Subbasin 2	1,074	4.15	0.014	13.067	13.053

Permitting

New Permits

All of the streams in the watershed are considered to be impaired for low pH based on the available data. New permits (except for new remining permits) for discharges to streams in the Beech Creek watershed could be allowed contingent upon end-of-pipe pH limits in the range of 6.35 to 9.0 standard units. WQSs state that the pH value should not be less than 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 should not cause or contribute to an existing impairment. Application of agricultural limestone on mine sites results in highly buffered water leaving the site. A buffered solution with nearly equal bicarbonate and carbonic acid components will have a pH of 6.35 (Carew, personal communication, 2004). Discharge of this buffered solution will use up free hydrogen ions in the receiving stream, thus it should not cause or contribute to an existing low-pH impairment. New permits having an effluent limit pH of 6.35 to 9.0 will not be assigned a hydrogen ion load as part of a WLA.

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 WQSs (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 WQS 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.

General KPDES Permit for Coal Mine Discharges

This permit covers all new and existing discharges associated with coal mine runoff. This permit does not authorize discharges that (1) are subject to an existing individual KPDES permit or application, (2) are subject to a promulgated storm water effluent guidelines or standard, (3) the Director has determined to be or may reasonably be expected to be contributed to a violation of a water of a WQS or to the impairment of a 303(d) listed water, or (4) are into a surface water that has been classified as an Exceptional or Outstanding or National Resource Water. A signed copy of a Notice of Intent (NOI) form must be submitted to the Kentucky Division of Water (KPDES Branch) when the initial application is filed with the Division of Mine Permits. However, coverage under this general permit may be denied and submittal of an application for an individual KPDES permit may be required based on a review of the NOI and/or other information.

Antidegradation Policy

Kentucky's Antidegradation Policy was approved by EPA on April 12, 2005. For impaired waters, general permit coverage will not be allowed for one or more of the pollutants commonly associated with coal mining (i.e., sedimentation, solids, pH, metals, alkalinity of acidity). The individual permit process remains the same except new conditions may apply if a Total Maximum Daily Load (TMDL) has been developed and approved.

Distribution of Load

Because there were no point source discharges in the watershed that contributed to the existing low pH impairment during the monitoring period, the entire load was defined as nonpoint source load. Because new permits (pH 6.35 to 9.0) and remining permits would be exempt from the TMDL requirements, no load has been provided for the WLA category (Table 8).

Table 8. Wasteload and Load Allocation for Each Subbasin

Subbasin	Incremental Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation* (lbs/day)	Load Allocation (lbs/day)
Subbasin 1	0.76	0.004	0.000	0.004
Subbasin 2	2.58	0.014	0.000	0.014

*pH limits for new discharges must be between 6.35 and 9.0

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 (DAML), also a part of DSMRE, is charged with performing reclamation to address the impacts from pre-law and bond forfeiture mine sites in accordance with priorities established in SMCRA. SMCRA sets environmental problems as third in priority in the list of AML problem types.

Prior to initiating reclamation activities to improve water quality, a watershed plan should be developed in order to more precisely identify past mine site operations in the watershed. For example, the watershed plan should include a detailed overview of past mine operations, including the location of the mine, the permit number, the type of mining and the status of the mine (e.g. active, bond forfeited, bond released, illegal "wildcat" mining, etc.). Refining historic landuses in the watershed, with a particular focus on mine site operations, will assist with identifying the most appropriate funding source(s) as well as the best management practices needed for remediating the pH impacts.

In addition to historic mine operation inventory, the watershed plan should identify (1) point and nonpoint source controls needed to attain and maintain WQSs, (2) who will be responsible for implementation of controls and measures, (3) an estimate of the load reductions to be achieved, (4) threats to other waters, (5) an estimate of the implementation costs and identify financing sources, (6) a monitoring plan and adaptive implementation process and (7) a public participation process. The watershed plan should consider non-traditional opportunities and strive for the most cost-effective long-term solutions for restoring the water quality of Beech Creek.

Practical application of pH TMDLs, especially for AMLs, will normally involve a phased implementation approach with associated monitoring in order to insure that the implemented measures are having the desired effect. Typical remediation strategies have involved channel restoration, re-vegetation, and the use of agricultural limestone.

There are currently no remediation activities underway in the Beech Creek watershed. However, reclamation activities have occurred at other locations within the state where AMD affects water quality. Examples of reclamation projects addressing AMD in western KY are summarized in Table 9

Table 9. Reclamation Projects Addressing AMD in Western Kentucky

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
Render Creek	McHenry Coop. Agreement	$130,165
	McHenry II	$1,075,340
	Vulcan Mine	$585,359

For 2000, the total federal 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. Of the total annual federal budget allocation, AML receives only approximately $700,000 in Appalachian Clean Streams Initiative funds, which are targeted for Priority 3 environmental problems. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the DAML 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.

Load Reduction Strategy Using Limestone Sand

Recent studies in West Virginia (Clayton, et. al., 1998) and Kentucky (Carew, 1998) have demonstrated that limestone sand can be used as an effective agent for restoring the pH in acidified streams.   For streams with a pH < 6, $CaCO_3$ may be used to neutralize free hydrogen ions based on the following relationship:

$$CaCO_3 + 2H^+ \rightarrow H_2CO_3 + Ca^{2+} \qquad (11)$$
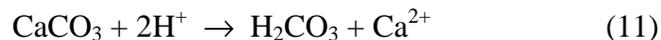
Thus, the theoretical total mass of $CaCO_3$ required to neutralize 1 gm of H^+ ions can be obtained by dividing the molecular weight of $CaCO_3$ (100) by the molecular weight of 2 hydrogen atoms (2) to yield:

$$\text{Required mass of limestone} = 50*\text{Mass of Hydrogen Ions} \qquad (12)$$

Or, in terms of a required annual load:

Annual required mass of limestone = 18,250*Mass of Hydrogen Ions (g/day)   (13)

In practice, however, this value will only represent a lower bound of the required mass as a result of two issues: 1) not all the limestone added to a stream will be readily available as soluble $CaCO_3$, and 2) an increasing fraction of the $CaCO_3$ mass will be required to neutralize other metal ions (e.g. Fe, Al, Mn) that will also most likely be present in the acid mine drainage, especially in the case of streams with pH $<$ 4.5 (Snoeyink and Jenkins, 1980).

One way to deal with the first limitation, is to simply add more limestone to the stream. Recent studies in both West Virginia and Kentucky have found that application rates of 2 to 4 times the theoretical limestone requirement have been found to be effective in restoring AMD streams.   The most effective way to deal with the second limitation is to determine the additional amount of limestone that must be added to neutralize both the hydrogen ions and the additional ions that might be present. One way to approximate this quantity is by calculating the total acidity in the water column (as expressed directly as $CaCO_3$).

Total acidity is normally defined as a measure of the concentration of acids (both weak and strong) that react with a strong base. Acidity may be determined analytically by titrating a water sample with a standard solution of a strong base (e.g. NaOH) to an electrometrically observed end point pH of 8.3. (For waters associated with acid mine drainage it is important that any ferric salts present must first be oxidized prior to the determination of the total acidity).   The required mass of NaOH required to raise the sample pH to 8.3 can then be expressed directly in terms of $CaCO_3$ as follows:

$$\text{Acidity, as mg } CaCO_3 = \frac{50,000*(\text{mL of NaOH})*(\text{Normality of NaOH})}{\text{Weight of sample used (mg)}} \quad (14)$$

In general, a relationship between pH (or the associated mass of free hydrogen ions), and the total acidity can be readily developed for a given stream using measured values of pH and acidity (Clayton, et. al, 1998).   Using measured streamflow data, an additional relationship between the required hydrogen ion reduction (required to raise the pH up to 8.3) and the corresponding load of $CaCO_3$ (required to neutralize both the hydrogen ions and other free ions) can also be determined such as the one shown in Figure 9. In this particular case, Figure 9 was constructed from an analysis of data from five separate watersheds in the western Kentucky Coal Fields, and thus provides a regional curve for application to similar watersheds in the area.   A similar curve could be developed for application to watersheds in other areas using regional data for that area. Alternatively, a site-specific curve could be developed for an individual watershed using measured values of flow, pH, specific conductance, and total acidity.
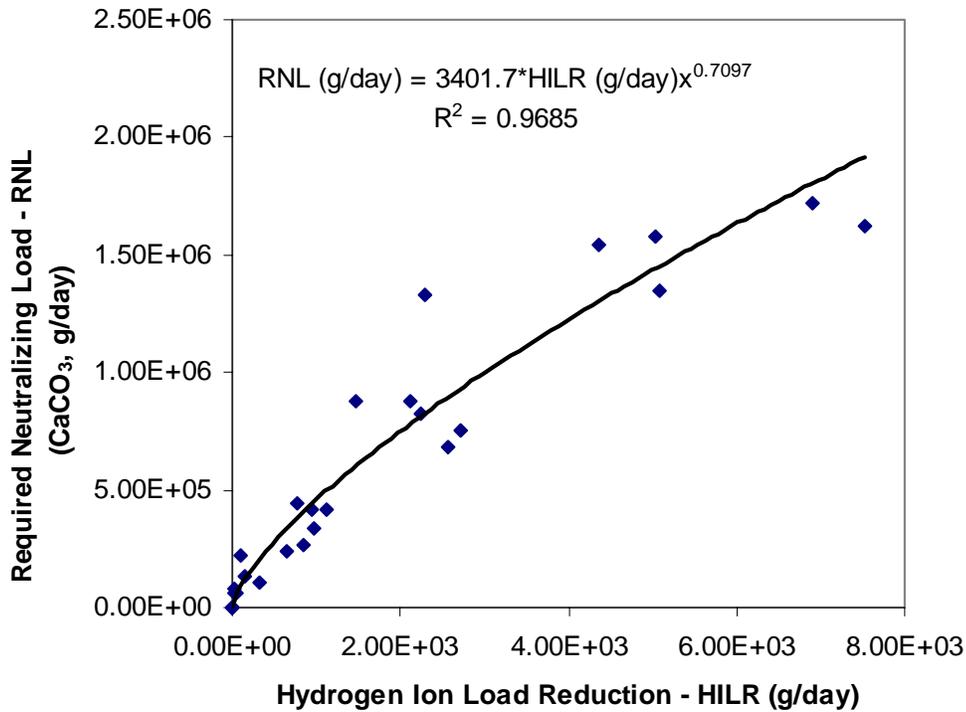
$$RNL\ (g/day) = 3401.7 * HILR\ (g/day)x^{0.7097}$$

$$R^2 = 0.9685$$

Figure 9. $CaCO_3$ Loading vs. the Required Hydrogen Ion Reduction

For the case of Beech Creek, site-specific stream acidity data were not collected as part of the overall sampling effort. As a result, the required $CaCO_3$ loading was determined using the regional curve. It should be recognized that the loading values produced by application of Figure 9 should theoretically increase the pH to 8.3 (based on the definition of total acidity), although pragmatically the achieved value will likely be less. As a result, Figure 9 is likely to provide a conservative estimate of the $CaCO_3$ loading required initially for a particular stream. Subsequent applications of limestone can be further refined through follow-up monitoring.

Application of Figure 9, using the required hydrogen ion load reduction values shown in Table 7, yields the corresponding values of $CaCO_3$ loadings shown in Table 10. For Subbasin 1, the calculation is: 3401.7 x $(1,082)^{0.7097}$ = 484,269. A corresponding approximation of the annual loading required can be obtained by simply multiplying the daily values by 365. Based on the work of Clayton, et. al., (1998), it is recommended that the values in Table 10 be multiplied by a factor of 2 to 4 in order to provide a conservative estimate of the initial loading.

Table 10. CaCO$_3$ Loadings for Beech Creek

Location	Required Reduction (lbs/day)	Required Reduction (g/day)	CaCO$_3$ Loading (g/day)	CaCO$_3$ Loading (lbs/day)	CaCO$_3$ Loading (tons/yr)
Subbasin 1	2.386	1,082	484,269	1,068	195
Subbasin 2	13.053	5,920	1,617,755	3,567	651
Total	15.439	7,002	1,822,427	4,018	733

Public Participation

This TMDL was placed on 30-day public notice and made available for review and comment from Nov. 16 through Dec. 16, 2005. The public notice was prepared and published as an advertisement in the Leader-News, a newspaper with wide circulation in Muhlenberg County. A press release was also distributed to newspapers statewide. In addition, the press release was submitted to approximately 275 persons via a Kentucky Nonpoint Source electronic mailing distribution list.

The TMDL was made available on KDOWs website at www.water.ky.gov/sw/tmdl, and hard copies could be requested by contacting the KDOW. The public was given the opportunity to review the TMDL and submit comments to KDOW in writing prior to the close of the public comment period. At the end of the public comment period, all written comments received became part of KDOWs administrative record. KDOW considered all comments received by the public prior to finalization of this TMDL and subsequent submission to EPA Region 4 for final review and approval.

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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