# **Total Maximum Daily Load (TMDL) Development**

- pH (H<sup>+</sup> Ion Mass) -

For

# **Brier Creek Watershed**

(Muhlenberg County, Kentucky)

Kentucky Department for Environmental Protection

**Division of Water** 

Frankfort, Kentucky

May 2001

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This report has been approved for release:

hon Jack A. Wilson, Director Division of Water

May 3, 2001

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# Kentucky Department for Environmental Protection Division of Water

Frankfort, Kentucky

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# **Brier Creek, Kentucky**

## **TMDL Fact Sheet**

Project Name:	Brier Creek
Location:	Muhlenberg County, Kentucky
Scope/Size:	Brier Creek, watershed 2720 acres (4.25 mi <sup>2</sup> )
Land Type:	Forest, agricultural, barren/spoil
Type of Activity:	Acid Mine Drainage (AMD) caused by Strip/Abandoned Mines
Pollutant(s):	H <sup>+</sup> Ion mass, Sulfuric Acid
TMDL Issues:	Non-point sources
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:	Brier Creek was determined as not supporting the designated use of recreation and aquatic life. Therefore, the creek was placed on the 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 is at peak-flow conditions. Peak flow conditions were chosen as critical because they generated maximum loads and reductions.
TMDL Development:	Total maximum daily loads in pounds $H^+$ ions per day were computed based on the allowable minimum pH value (6.0) for creeks and streams for recreation and aquatic life. The TMDL was done for pounds of ions because the units for pH do not allow for the computation of a quantitatively useful load or reduction amount.

#### Implementation/Remediation

In response to the documented problems in the Brier Creek Watershed, the Kentucky Division of Abandoned Lands developed a remediation project designed to mitigate the pH impairment. Some of the remediation activities are considered experimental. The remediation project included reclamation of approximately 120 acres of barren or poorly vegetated areas affected by past strip mining. The restoration included construction of ditches and PVC coated gabion baskets utilized as velocity reducers and energy dissipators; bale silt checks and silt trap dug-outs 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 reclamation activities focused on only a portion of the area within the watershed that exhibited significant water quality degradation. The total cost of the Brier Creek project was \$913,000 (i.e. \$7,600/acre). For 2000, the total federal allocation for Kentucky AML 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.

The strategy employed in Brier Creek is similar in some respects to a remediation project that is underway on Rock Creek and a tributary, White Oak Creek in McCreary County Kentucky. This 12-acre project is a Clean Water Action Plan project and involves the removal of coal refuse from the banks of Rock Creek, the establishment of vegetative cover on the refuse areas in the watershed, and the application of limestone sand at selected locations to neutralize the effects of AMD. Limestone sand has also been used to neutralize acid mine drainage in West Virginia.



Total TMDL for Brier Creek = 0.424 lbs H+ Ions/day

	In anoma anta l	3-Year	Incremental	3-Year	Incremental
	Incremental Contribution	Incremental	TMDL	Incremental	Reduction
		Flow Rate	@pH=6	Load	Needed
	Area (mi2)	(cfs)	(lbs/day)	(lbs/day)	(lbs/day)
Site 1	0.6048	13.8	0.084	0.158	0.074
Site 2	0.2531	5.8	0.035	0.015	0.000
Site 3	0.9719	22.2	0.133	15.825	15.692
Site 4	0.2070	4.7	0.029	55.570	55.541
Site 5	0.3891	8.9	0.054	63.411	63.357
Site 6	0.6453	14.7	0.089	46.696	46.607

#### 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 their 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, 1991). This report provides the TMDL for Brier Creek.

#### Location

The Brier 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 River.



Figure 1: Location of Brier Creek Watershed

#### Hydrologic Information

Brier Creek, a third order stream, originates in northwest Muhlenberg County and flows west to discharge into the Pond River 13.2 km (8.2 miles) upstream from its confluence with the Green River (Figure 2). The Green River and its tributaries, the Mud River and the Pond River, carry the runoff from the county northward to discharge into the Ohio River.

Brier Creek's mainstem is approximately 3.3 km (2.1 miles) long and drains an area of 2720 acres (4.25 sq. miles). The average gradient is 14.3 feet per mile. Elevations for Brier Creek range from 152 m (500 ft) above mean sea level (msl) in the headwaters to 116 km (380 ft) above msl at the mouth. Like most of the smaller watersheds, many of the tributary streams are intermittent.





#### Geologic Information

The Brier 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 (USDA, 1980). The relief of the Brier 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.

#### Landuse 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, the county strip mined over 19 million tons of coal and mined over 5 million tons from the underground. The Brier Creek watershed contains three main landuses: resource extraction (mining and disturbed land area), forest, and agriculture.

#### Soils Information

The Brier Creek watershed is dominated by nearly level loamy and clayey soils near to the mouth and level to steep loamy soils in the headwaters. Nearly 30 percent of the watershed is Udorthents soil, which consists of strip mine spoil.

#### Watershed History

In 1945, the Island Creek Coal Company began seam mining in the Brier Creek watershed. By 1977 the company had ceased all mining activity, making them exempt from reclamation efforts and characterizing the watershed under the jurisdiction of the Abandoned Lands division of the federal government. In 1978 the Kentucky Division of Water's Earlington Field Office conducted studies on several acid mine drainage affected streams in the western coal fields and reported a pH of 3.5 at two sites on Brier Creek (DOW, 1981). In August of 1988 a fish kill was reported downstream of the disturbed area and verified as caused by high iron concentrations and low pH, symptoms of acid mine drainage and pH impairment. In response to this incident and other complaints within the watershed, the Kentucky Division of Abandoned Mines investigated the site and developed a comprehensive remediation for the watershed that was finally approved and funded in 1996. In 1997 the Kentucky Natural Resources and Environmental Protection Cabinet (KNREPC) conducted a year long stream water sampling program to document the pH impairment within Brier Creek watershed and provide a baseline for assessment of the remediation project (see Table 1). Finally, in 1998 Kentucky issued its latest 303(d) list for impaired watersheds, including Brier Creek as a first-level priority under pH impairment. Areas of the watershed disturbed by past mining operations are shown in Figure 3.

Brier Creek Watershed

	Sit	e 1	Sit	e 2	Site 3		Site 3 Site 4		Site 5	
	Flow Rate		Flow Rate		Flow Rate		Flow Rate		Flow Rate	
Date	(gpm)	pН	(gpm)	pН	(gpm)	pН	(gpm)	pН	(gpm)	pН
4/15/97	No flow	No flow	No flow		No flow	No flow	No flow	No flow	No flow	No flow
4/22/97	191	3.2	6.48	2.7	No flow	No flow	No flow	No flow	No flow	No flow
5/6/97	234	2.8	2.2	2.4	1047	3.5	No flow	No flow	No flow	No flow
5/20/97	220	2.7	6.15	2.4	1764	3.8	68	2.8	1148	6.1
6/3/97	1325	2.6	21	2.6	6567	4.6	110	2.8	5152	5.8
7/8/97	190	2.7	2.2	2.3	340	2.9	52	2.7	153	5.5
7/22/97	45	2.9	No flow	No flow	No flow	No flow	45	2.9	10	5.2
8/5/97	13.2	2.9	No flow	No flow	No flow	No flow	No flow	No flow	No flow	No flow
8/19/97	16	2.9	9.7	2.6	82	2.8	6.25	2.8	No flow	No flow
9/2/97	13.2	3	3.3	2.6	33.6	3	3.5	2.9	No flow	No flow
9/16/97	22.3	2.9	No flow	No flow	218	2.8	7.47	2.7	No flow	No flow
10/7/97	11.77	2.9	No flow	No flow	44	2.8	9.5	2.8	No flow	No flow
10/22/97	26	3	No flow	No flow	No flow	No flow	No flow	No flow	No flow	No flow
11/4/97	33.58	3.2	No flow	No flow	64	3	9.6	3.1	No flow	No flow
11/18/97	258	3.1	No flow	No flow	No flow	No flow	No flow	No flow	No flow	No flow
12/2/97	39.75	3.1	No flow	No flow	223	3.3	No flow	No flow	No flow	No flow

Table 1. Historic Monitoring Data



Figure 3. Mining Operations and Historic Sampling Sites in Brier Creek Watershed

#### **Problem Definition**

The 1998 303(d) list of waters for Kentucky (Ky. Dept. for Environmental Protection Division of Water, 1998) indicates 4.7 miles of Brier Creek, from the headwaters to the confluence with the Pond River in Muhlenberg County, does not meet its designated use for both contact recreation (swimming) and aquatic life. The Brier Creek watershed provides a classic example of impairment caused by acid mine drainage (AMD). Bituminous coal mine drainage, like that found in the Brier Creek watershed, contains very concentrated sulfuric acid and 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 (primary 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 is deleterious to 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<sub>2</sub>) 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:

$$2 \operatorname{FeS}_2 + 7 \operatorname{O}_2 + 2 \operatorname{H}_2 0 + \operatorname{bacteria} \rightarrow 2 \operatorname{FeSO}_4 + 2 \operatorname{H}_2 \operatorname{SO}_4$$
(1)

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

$$4 \operatorname{Fe}_2 \operatorname{SO}_4 + \operatorname{O}_2 + 2 \operatorname{H}_2 \operatorname{SO}_4 \to 2 \operatorname{Fe}_2 (\operatorname{SO}_4)_3 + 2 \operatorname{H}_2 \operatorname{O}$$
(2)

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

$$\operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3} + 6 \operatorname{H}_{2}\operatorname{O} \rightarrow 2 \operatorname{Fe}(\operatorname{OH})_{3} + 3 \operatorname{H}_{2}\operatorname{SO}_{4}$$
(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):

$$4 \operatorname{FeS}_2 + 15 \operatorname{O}_2 + 14 \operatorname{H}_2\operatorname{O} \longleftrightarrow 8 \operatorname{H}_2\operatorname{SO}_4 + 4 \operatorname{Fe}(\operatorname{OH})_3 \tag{4}$$

Reaction (4) indicates that a net of 4 moles of H+ are liberated for each mole of pyrite (FeS<sub>2</sub>) 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 load in lbs/day) that allows for the sustainability of aquatic life and swimming uses in these stream reaches. The chronic pH criterion to protect Warm Water Aquatic Habitat Use in Kentucky requires that the pH be maintained between 6 and 9 (Title 401, Kentucky Administrative Regulations, Chapter 5:031). For a watershed impacted by AMD, the focus will be on meeting the lower criteria. In the case of violations caused by non-point sources on small intermittent streams, such standards must be evaluated on the basis of an appropriate critical exceedance frequency as opposed to a critical period or flow (e.g. 7Q10). For pH violations on such stream, the Kentucky Division of Water has determined that a one day average 3-year exceedance frequency be used for setting the appropriate TMDL and associated loading reduction.

The Technical Support Document for Water Quality-Based Toxic Control (USEPA, 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 occurrence frequency of any 1-day concentration of interest can now be determined. Where the resultant frequency exceeds that of the stated target value (e.g. 3 years) associated load reductions will be required until the resultant concentration satisfies the stated target value and its associated exceedance frequency. As in the case of this study, where the load and the resultant target indicator (i.e. pH) can be directly related through discharge (flow rate), the exceedance frequency of the target value (e.g. pH).

#### Source Assessment

#### Point Source Loads

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

#### Non-Point Source Loads

In August of 1988 a fish kill was reported downstream of the disturbed area and verified as caused by high iron concentrations and low pH, symptoms of acid mine drainage and

pH impairment. In response to this incident and other complaints within the watershed, the Kentucky Division of Abandoned Mines investigated the site and determined that the cause of the major source of the problem was due to runoff from mine spoils associated with previous deep mine activities. In 1997 the Kentucky Natural Resources Environmental Protection Cabinet (KNREPC) conducted a year long stream water sampling program to document the pH impairment within Brier Creek watershed. The location of the monitoring sites is shown in Figure 3. A summary of the historic pH readings at these sites is shown in Table 1.

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 indicated in Figure 4. A summary of the results obtained from these sites is shown in Table 2. Both data sets (Tables 1 and 2) indicate significant pH degradation in the watershed and serve as a basis for the establishment of a TMDL.

# **Brier Creek Watershed**



Figure 4. Sampling Sites monitored by Murray State Personnel

1/17/99

1/24/99

1/31/99

1.9

3.1

1.9

2.5

2.6

2.9

	Site 1		Sit	Site 2		Site 3	
	Flow Rate		Flow Rate	Flow Rate			
Date	(cfs)	pН	(cfs)	pН	(cfs)	pН	
10/7/98	17.0	6.6	0.5	7.4	25.0	5.6	
10/16/98	0.5	5.4	No flow	No flow	1.0	2.9	
10/25/98	0.5	4.3	No flow	No flow	3.0	1.0	
11/8/98	0.5	6.0	No flow	No flow	3.0	3.2	
11/13/98	0.7	5.1	No flow	No flow	3.0	3.2	
11/24/98	0.7	4.7	No flow	No flow	13.0	2.9	
12/13/98	18.0	5.7	0.6	6.0	30.0	4.1	
12/18/98	0.8	5.1	No flow	No flow	3.0	3.3	
12/26/98	5.5	5.3	0.5	5.8	5.0	4.6	
1/17/99	0.8	6.3	0.8	6.2	5.0	4.1	
1/24/99	12.5	6.3	0.7	6.7	46.0	5.7	
1/31/99	22.0	6.0	120.0	6.4	80.0	6.0	
	Sit	e 4	Sit	e 5	Sit	e 6	
	Flow Rate		Flow Rate		Flow Rate		
Date	(cfs)	pН	(cfs)	pН	(cfs)	pН	
10/7/98	7.3	3.1	295.0	3.5	440.0	4.7	
10/16/98	1.0	2.8	2.0	2.9	20.0	2.9	
10/25/98	3.1	0.6	2.0	0.8	32.0	0.6	
11/8/98	1.0	2.8	2.0	2.8	20.0	2.6	
11/13/98	1.9	3.1	4.0	3.3	0.8	3.3	
11/24/98	1.0	2.5	2.0	2.6	0.9	2.6	
12/13/98	1.9	2.6	40.0	3.1	0.9	3.0	
12/18/98	1.0	2.9	40.0	3.1	0.9	3.0	
12/26/98	1.0	2.9	2.0	3.5	440.0	3.8	

4.0

113.0

203.0

3.3

3.9

4.6

440.0

13.0

440.0

3.4

4.1

5.4

Table 2.	Murray	State	Sample	Results
----------	--------	-------	--------	---------

#### **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:

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

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

$$[\mathrm{H}^+] = \{\mathrm{H}^+\}/\gamma \tag{6}$$

The activity coefficient  $\gamma$  is dependent on the ionic strength  $\mu$  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, 1980):

$$\mu = (2.5 * 10^{-5}) * \text{TDS}$$
(8)

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 5) with an associated conservative probability of exceedence of 95% (Snoeyink, 1980).



Figure 5: Distribution Function of TDS Concentration for Terrestrial Waters

(Snoeyink, 1980)

Use of Figure 5 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 8 yields an ionic strength of 0.0225. Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Figure 6 (Snoeyink, 1980). Use of an ionic strength of 0.0225 yields an activity coefficient of 0.89.



Figure 6: Activity Coefficients of H+ as a Function of Ionic Strength (Snoeyink, 1980)

The atomic weight of hydrogen is 1 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 Example Calculation

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

- Average discharge (Q) = 70.0 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 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

 $(0.000001 \text{ moles/liter})^{*}(1 \text{ gram/mole})^{*}(11 \text{ iter}/0.035314667 \text{ ft}^{3}) = 0.0000283168 \text{ g/ft}^{3}$ 

The goal is to achieve a loading rate in terms of g/day, or lbs/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:

 $(0.0000283168 \text{ g/ft}^3)*(70.0 \text{ ft}^3/\text{s})*(86400\text{s}/1\text{day}) = 171.26 \text{ g/day}, \text{ or } 0.38 \text{ lbs/day}$ 

Assuming an activity correction factor of 0.89, the final load is 192.43 g/day, or 0.424 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 a Q = 70.0 cfs, the load reduction needed to attain a pH of 6.0 if the observed pH is 5.0 is 3.82 lbs/day. For an observed pH of 4.0 the reduction needed is 42.0 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 (see Figure 6). This figure thus provides a basis for establishing the maximum ion load for a given discharge.



Figure 7. Relationship between discharge and maximum ion loading for a pH of 6

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 will be developed for each of the subbasins identified in Figure 4. Attainment of the individual load reductions should then 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. Using the most recent monitoring data, inductive models were developed at each monitoring site that relate total hydrogen ion loading to streamflow. These models are shown in Figures 8-13. It is recognized that the use of multiple sampling points within the basin provides a better way to isolate those sections of the basin that are contributing the major loads to the stream. However, with a limited sampling budget, the use of multiple points comes at the expense of more accurate models at any one location. This impact is further complicated by the elimination of outliers for the various data sets. Such impacts are reflected to varying degrees in each of the functions. For example, the loading function for site 2 is largely defined by one single point. However, due to the limited observed loading associated with this basin, this function has minimal impact on the overall TMDL. Loading functions for sites 3 and 5 are also heavily influenced by single observations, however, in each case the observed point is consistent with the rest of the data and the general functional trend demonstrated in the other functions.

As can be seen from the figures, the total load increases as a function of flow, illustrating the significant relationship between the pH degradation and non-point sources. The developed relationships may be used to predict total ion loading to a stream on the basis of streamflow.



Brier Creek Site 1

Figure 8. Flow vs. Ion Loading and pH for Site 1



Brier Creek Site 2





Brier Creek Site 3

Figure 10. Flow vs. Ion Loading and pH for Site 3

22

Brier Creek Site 4



Figure 11. Flow vs. Ion Loading and pH for Site 4



Brier Creek Site 5

Figure 12. Flow vs. Ion Loading and pH for Site 5





Figure 13. Flow vs. Ion Loading and pH for Site 6

#### **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 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 wasteload 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), either implicitly or explicitly, 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:

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

#### Wasteload Allocations

There are no permitted point sources in this watershed. As a result, the wasteload allocations for the Brier Creek Watershed are assumed to be zero.

#### Load Allocations

Load allocations for the Brier Creek Watershed are assumed to be directly related to acid mine drainage as a result of water leaching from abandoned mines. The total load allocation for Brier Creek is assumed to be an explicit function of the average daily flow in the stream and an associated pH standard of 6 units. Predicted daily loads for each subbasin within the watershed can be obtained using the inductive loading models shown in Figures 8-13.

#### 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. In an electrically neutral solution (such as all natural systems), the activity coefficient ( $\gamma$  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 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. In addition, 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

Because maximum hydrogen ion loading values can be directly related to discharge via Figure 8, the associated allowable ion loading exceedence frequency (i.e. 3 years) can be directly related to the frequency of the discharge. In order to find the 3-year average daily discharge for Sugar Creek watershed a regional frequency analysis was used. Regional analysis can be used to develop an inductive model using data that has been 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 is used to predict probabilistic discharges based on a 2-year, 5-year, and a 10-year return interval using a Log-Normal probability distribution (see Table 3). These discharges were then normalized by dividing each flow by the 2-year streamflow to produce Figure 9 and regressed with watershed area to produce Figures 14 and 15. Using these two figures, the daily mean discharge for a given frequency and watershed area can be readily determined.

	USGS Gaging Station Numbers								
	3384000	3384000 3321350 3320500 3383000							
Area (mi <sup>2</sup> )	2.10	58.20	194.00	255.00					
Q(2)	98.97	2210.70	4901.80	3675.18					
Q(5)	166.27	2904.86	7450.74	5843.54					
Q(10)	218.13	3349.21	9279.11	7445.91					

Table 3. Return Interval Flow Rates (cfs) for Stations in Regional Analysis

Application of Figures 14 and 15 for the Brier Creek watershed yields a three-year peak average daily discharge of 70 cfs assuming a watershed area of 3.07 mi<sup>2</sup>. Three-year average daily discharges for each individual subbasin can now be obtained using a simply 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 6 to obtain incremental TMDL's. The following table shows a summary of the results.

Subbasin	Area (mi <sup>2</sup> )	Incremental Q (cfs)	Incremental TMDL (lbs/day)
Total	3.0712	70.09	0.424
1	0.6048	13.80	0.084
2	0.2531	5.78	0.035
3	0.9719	22.18	0.133
4	0.2070	4.72	0.029
5	0.3891	8.88	0.054
6	0.6453	14.73	0.089

Table 4. 3-Year Incremental Flow and Corresponding TMDL



**Regional Analysis** 

Figure 14. Relationship between return interval and normalized flow



Regional Analysis: Q(2) vs. Area

Figure 15. Relationship between basin area and 2-year flow

#### Predicted Load

The predicted 3-year frequency hydrogen ion loads for each site may be obtained using the 3-year frequency discharges from Table 3 along with the associated load relationships shown in Figures 8-13. Application of this approach yields the predicted 3-year frequency loads for each site as shown in Table 5.

Subbasin	Cumulative Q	Cumulative	Incremental
	(cfs)	Load (lbs/day)	Load (lbs/day)
1	13.80	0.158	0.158
2	5.78	0.015	0.015
3	41.76	15.998	15.825
4	4.72	55.570	55.570
5	55.36	134.979	63.411
6	70.09	181.675	46.696

Table 5. 3-Year Incremental, Predicted Ion Loads (lbs/day)

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 subbasins requires a mass balance application to find the incremental load. For example, the incremental load at subbasin 5 is found by subtracting the cumulative load at subbasins 3 and 4 from the cumulative load at subbasin 5. A similar approach is used to calculate all of the remaining incremental loads.

#### Load Reduction Allocation

Translation of the TMDL in Table 4 (obtained for a 3-year exceedance frequency) 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 allocatse the total load reduction for Brier Creek (site 6) between each of the contributing sites in the watershed, so that the entire watershed is rehabilitatesd and the pH is improved throughout the stream network. Application of this approach yields the values in Table 6.

	Total TM	Total TMDL for Brier Creek = 0.424 lbs H+ Ions/day						
	T	3-Year	Incremental	3-Year	Incremental			
	Contributing	Incremental	TMDL	Incremental	Reduction			
	Area (mi2)	Flow Rate	@pH=6	Load	Needed			
		(cfs)	(lbs/day)	(lbs/day)	(lbs/day)			
Site 1	0.6048	13.8	0.084	0.158	0.074			
Site 2	0.2531	5.8	0.035	0.015	0.000			
Site 3	0.9719	22.2	0.133	15.825	15.692			
Site 4	0.2070	4.7	0.029	55.570	55.541			
Site 5	0.3891	8.9	0.054	63.411	63.357			
Site 6	0.6453	14.7	0.089	46.696	46.607			

Table 6.	TMDL	Summarv	and	Allocations	for	Brier	Creek
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#### Implementation/Remediation

In response to the documented problems in the Brier Creek Watershed, the Kentucky Division of Abandoned Lands developed a remediation project designed to mitigate the pH impairment. Some of the remediation activities are considered experimental. The remediation project included reclamation of approximately 120 acres of barren or poorly vegetated areas affected by past strip mining. The restoration included construction of ditches and PVC coated gabion baskets utilized as velocity reducers and energy dissipators; bale silt checks and silt trap dug-outs 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 reclamation activities focused on only a portion of the area within the watershed that exhibited significant water quality degradation. The total cost of the Brier Creek project was \$913,000 (i.e. \$7,600/acre). For 2000, the total federal allocation for Kentucky AML 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.

The strategy employed in Brier Creek is similar in some respects to a remediation project that is underway on Rock Creek and a tributary, White Oak Creek in McCreary County Kentucky. This 12-acre project is a Clean Water Action Plan project and involves the removal of coal refuse from the banks of Rock Creek, the establishment of vegetative cover on the refuse areas in the watershed, and the application of limestone sand at selected locations to neutralize the effects of AMD. Limestone sand has also been used to neutralize acid mine drainage in West Virginia.

#### **LITERATURE CITED**

- EPA, Clean Water Act, Section 303(d), 40 CFR Part 130, 1991.
- EPA, Compendium of Tools for Watershed Assessment and TMDL Development, EPA 841-B-97-006, May 1997.
- EPA, Report of the Federal Advisory Committee on the Total Maximum Daily Load (TMDL) Program, EPA 100-R-98-006, The National Advisory Council for Environmental Policy and Technology (NACEPT), July 1998.
- EPA, *Technical Support Document for Water Quality-based Toxics Control*, EPA 505/2-90-001, March 1991.
- Sawyer, Clair N., Perry L. McCarty and Gene F. Parkin, *Chemistry for Environmental Engineering*, McGraw-Hill, Inc., New York, NY, 4<sup>th</sup> Ed., 1994, pp. 107-112.
- USGS, Technique for Estimating Magnitude and Frequency of Floods in Kentucky, 1985.

## INDEX OF TMDL SUBMITTAL DOCUMENTATION

## 303(d) LIST INFORMATION

State	Kentucky			
Name of 303(d) listed waterbody	Brier Creek (Muhlenberg County)			
Segment as identified from 303(d) list	River Mile 0.0 to 4.7			
City/County	Muhlenberg County			
Watershed(s)/8-digit cataloging unit code	05110006			
3-digit EPA reach file number	135			
Length (mi) or area (acres) of impairment	4.7 miles			
Water quality standards being violated	pH<6.0			
Water use classification	Recreation and Aquatic Life			
Pollutant of concern	pH from acid mine drainage			
Location description of waterbody	Located in Western Kentucky			
Sources of impairment	Acid mine drainage (AMD) caused by			
	strip/abandoned mines			
PUBLIC NOTIFICATION INFORMATIO	N			
Form of public notification				
Beginning/ending dates of public notice	March 6, 2000 / April 6, 2000			
Notice mentioned TMDL proposal	X yesno			
Comments received from public	None Received			
Responsiveness summary prepared	Not Applicable			

#### INDEX OF TMDL SUBMITTAL DOCUMENTATION (cont.)

## TMDL INFORMATION

Critical Conditions	high flowlow flow			
	X other: max load at high, min pH at low			
Seasonality	X_Annual_Summer/Winter_Monthly			
TMDL development tool(s)	Water quality model(s)			
	X_Mass balance equations			
	X Other: Intensive synoptic survey			
Supporting Models/Documents	Technical Support Document for Water			
	Quality-based Toxics Control, Compendium			
	of Tools for Watershed Assessment and			
	TMDL Development			

## TOTAL MAXIMUM DAILY LOADS

#### Total TMDL for Brier Creek = 0.424 lbs H+ Ions/day

	Incromontal	3-Year	Incremental	3-Year	Incremental
	Contributing	Incremental	TMDL	Incremental	Reduction
	Area (mi2)	Flow Rate	@pH=6	Load	Needed
	Area (mi2)	(cfs)	(lbs/day)	(lbs/day)	(lbs/day)
Site 1	0.6048	13.8	0.084	0.158	0.074
Site 2	0.2531	5.8	0.035	0.015	0.000
Site 3	0.9719	22.2	0.133	15.825	15.692
Site 4	0.2070	4.7	0.029	55.570	55.541
Site 5	0.3891	8.9	0.054	63.411	63.357
Site 6	0.6453	14.7	0.089	46.696	46.607

#### Loadings Wasteld

Wasteload Allocation

There are no point sources in this watershed

Load Allocation

Distibuted among six subbasins according to the above chart

Margin of Safety \_\_Explicit X\_Implicit

None	
Adjustment factor for ion activity ( $\gamma$ =0.5)	
(conservative assumptions used)	_