Final

pH (H^+ Ion Mass)

Total Maximum Daily Load (TMDL)

for

Mussin Branch of Moore Creek Watershed

(Marion County, Kentucky)

Kentucky Department for Environmental Protection

Division of Water

Frankfort, Kentucky

January 2006

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This report has been approved for release:

David W. Morgan, Director

Division of Water

Date 1/13/06

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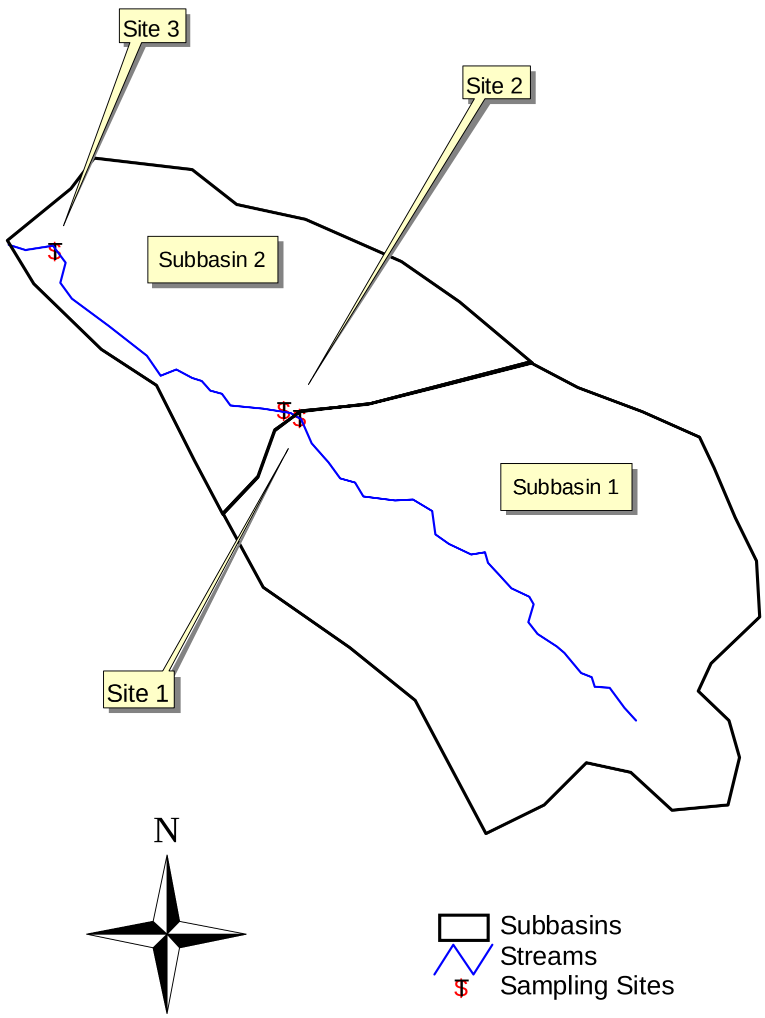
Mussin Branch of Moore Creek

Total Maximum Daily Load (TMDL) Fact Sheet

Project Name:	Mussin Branch of Moore Creek
Location:	Marion County, Kentucky
Scope/Size:	Mussin Branch Watershed 740 acres (1.16 mi^2) Stream Segment: River Mile 0.0 to 1.7
Land Type:	forest, agricultural, barren/spoil
Type of Activity:	acid drainage caused by highway construction
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 Division of Water (KDOW) Data Collection
Control Measures:	Kentucky nonpoint source TMDL implementation plan, Kentucky Watershed Framework
Summary:	Mussin Branch was determined as not supporting the designated uses of primary and secondary contact recreation (swimming and wading) and warm water aquatic habitat (aquatic life). Therefore, the creek was placed on the 2002 and subsequent 303(d) lists for TMDL development. The creek segment is characterized by a depressed pH, the result of leaching of the embankment (fill) material. In developing the TMDL for Mussin Branch, pH readings and corresponding streamflow measurements were made at three different locations within the watershed. The most recent sampling supports the conclusion that Subbasin 1 (Site 2) and Subbasin 2 (Site 3) do not support acceptable pH levels. The watershed is impaired because of low pH at these sites.



Most Recent Sampling Locations on Mussin Branch

TMDL Development:

TMDLs in grams H^+ ions per day were computed based on the allowable minimum pH value of 6.0 for creeks and 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 (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 convenient 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 Mussin Branch:

In developing a TMDL for Mussin Branch, there are two possible strategies. Either a cumulative aggregate TMDL may be obtained for the downstream extent of the impaired portion of the watershed, or separate TMDLs (and associated load reductions) may be developed for each individual subbasin. As a result of the availability of sampling data at multiple sampling points, individual TMDLs were developed for Subbasins 1 and 2. The low pH condition extends to Site 3, which is close to the outlet of Subbasin 2. The TMDLs and associated load reductions for Subbasins 1 and 2 are shown below.

Summary of Flow Rate and TMDL for each Subbasin in the Mussin Branch Watershed

Subbasin	Upstream contributing area (mi^2)	Incremental critical flow (cfs)	Incremental TMDL for a pH of 6.0 (lbs/day)	Predicted incremental load (lbs/day)	Load Reduction needed (lbs/day)
1	0.7609	0.3215	0.0017	0.0177	0.0160
2	0.3953	0.1670	0.0009	0.0000	0.0000
Total Watershed	1.1600	0.4901	0.0026	0.0177	0.0160

Distribution of Load: Because there were no observed point source discharges during the study period, the existing hydrogen ion load for the watershed was defined entirely as a nonpoint source load and that is what is reflected in the above table. The table given below splits the TMDL (which is based on meeting the minimum water quality standard value for pH of 6.0) evenly between the Waste Load Allocation (WLA) and the Load Allocation (LA) as a means of defining a conservative approach for each subbasin in the watershed.

Wasteload and Load Allocation for Each Subbasin in the Mussin Branch Watershed

	Incremental Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation (lbs/day)	Load Allocation (lbs/day)
Subbasin 1	0.3215	0.0017	0.00085	0.00085
Subbasin 2	0.1670	0.0009	0.00045	0.00045

Implementation/ Remediation Strategy: Remediation of pH-impaired streams, as a result of leaching from the pyritic fill material used in highway construction, is the responsibility of the entity that owns and maintains the highway. In the case of Mussin Branch, the cause of impairment is the fill material that was used in the construction process of the upgrading/relocation of U.S. Highway 68/Kentucky Highway 55 just south of Lebanon in Marion County. The remediation of this stream is thus the responsibility of the Kentucky Transportation Cabinet that owns and maintains these highways. This is the first TMDL to be developed for a stream impaired by highway construction related activities and will be used in the future as guidelines for any other similar impairment in streams. Permanent mitigation measures may involve sealing the pyritic fill material in the road embankments from surface water infiltration with lime and topsoil. For Mussin Branch, remediation needs to be done on the embankment and possibly the exposed road cuts on either side of the embankment. Before the permanent mitigation is implemented, the stream can be treated with limestone to bring the stream to acceptable limits of pH (6.0 – 9.0).

Introduction

Section 303(d) of the Clean Water Act and the 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 Mussin Branch watershed is entirely contained within Marion County, in central Kentucky (Figure 1).

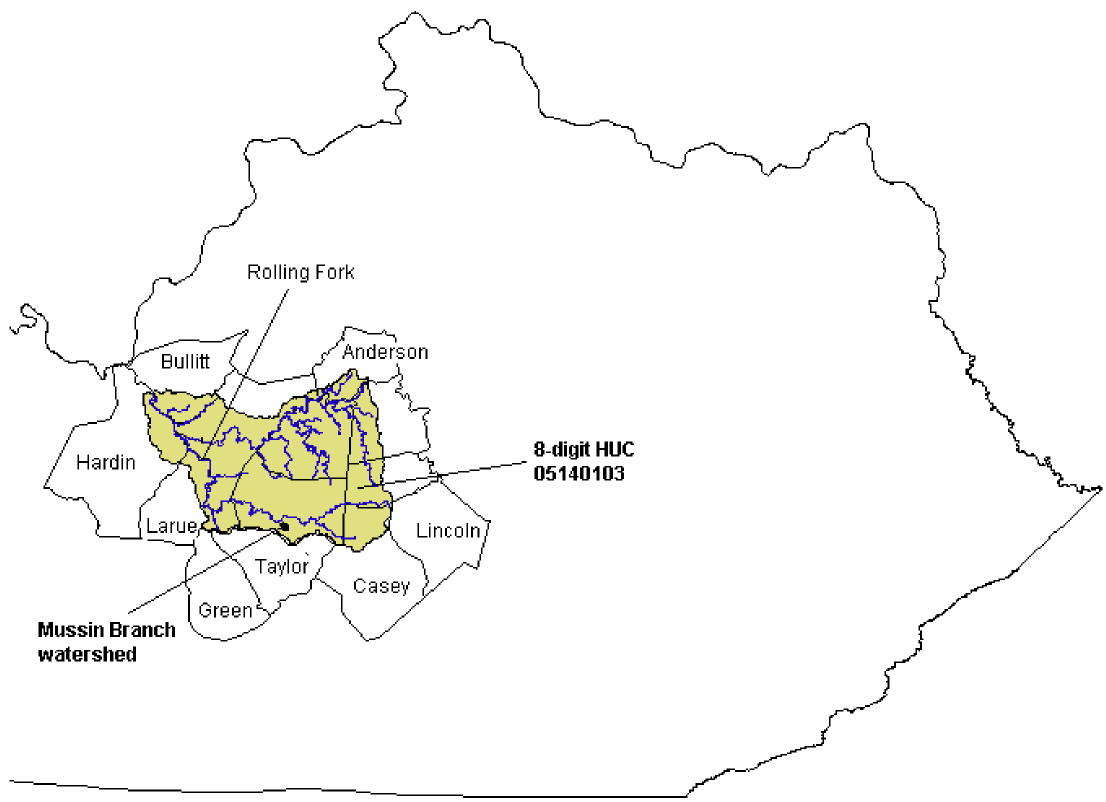


Figure 1. Location of the Mussin Branch Watershed

Hydrologic Information

Mussin Branch, a first order stream, originates in southern Marion County and flows northwest to discharge into Moore Creek, which in turn discharges into Rolling Fork. Mussin Branch's mainstem is approximately 1.95 miles long and drains an area of 740 acres (1.16 mi^2). The average gradient is 0.0175 feet per foot. Elevations for Mussin Branch range from 800 feet above mean sea level (msl) in the headwaters to 620 feet above msl at the most downstream point near its confluence with Moore Creek.

Geologic Information

Marion County has a diverse topography. The Mussin Branch watershed is in the south-central part of Marion County, which lies within the Knobs and Eastern Pennyroyal Physiographic regions. These regions are drained by Rolling Fork and are dissected by many small streams and creeks. Large quantities of sand and gravel are on the valley floor along Rolling Fork. Sand and gravel are used locally for road base and as aggregate for farm and county roads. The relief of the Mussin Branch watershed ranges from sloping to moderately steep to very steep.

Landuse Information

During the last two centuries, much of Marion County has been cleared or converted to farmland. The northern and central parts are used mainly for cultivated crops, hay, or pasture. The southern part, where Mussin Branch watershed is located, is very hilly and is used mainly as second-growth hardwood forest. Farm products are the main source of income in the county. The main farm products are row crops, pasture and hay crops, livestock, and livestock products (US Department of Agriculture, 1986).

Soils Information

Soils in Mussin Branch watershed are dominated by moderate quantities of limestone and large quantities of sand and gravel. Rock strata are limestone interbedded with thin layers of siltstone and calcareous shale. The sloping to moderately steep soils that formed in these areas are deep and have a very strong acid or strongly acidic, loamy subsoil (US Department of Agriculture, 1986).

Monitoring History

The Kentucky Division of Water (KDOW) first monitored the waters of Mussin Branch in 2000 at the locations shown in Figure 2. The results of this sample analysis are shown in Table 1. This data prompted the 2002 303(d) listing of the entire stream for failing to support warm water aquatic habitat (aquatic life) and recreation (swimming) due to low pH.

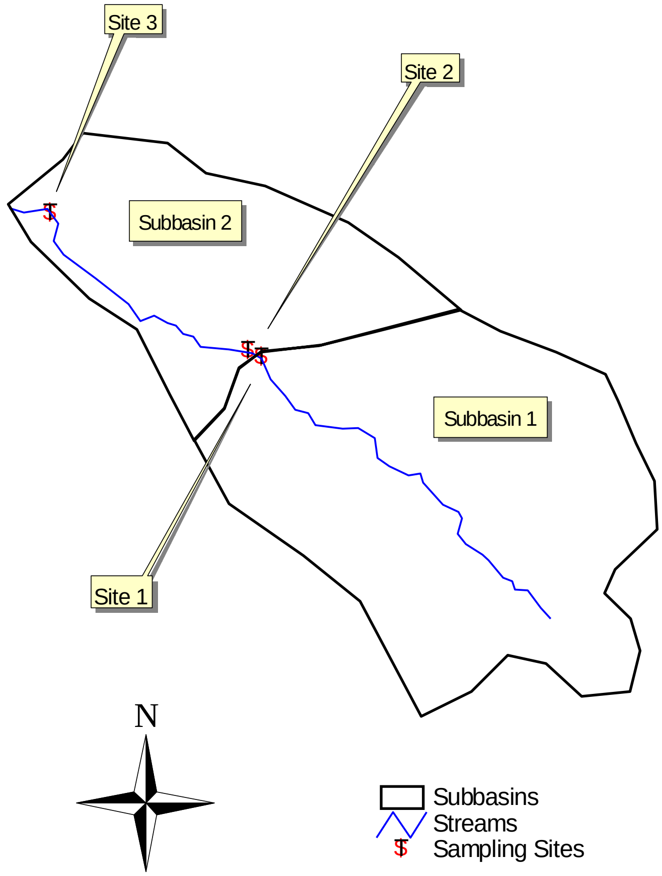


Figure 2. Recent Sampling Sites Monitored in the Mussin Branch Watershed

Table 1. KDOW Sampling Results for Mussin Branch, 2000

	Site 1		Site 2		Site 3	
Date	Flow rate (cfs)	PH	Flow rate (cfs)	pH	Flow rate (cfs)	pH
10/04/00	---	6.60	---	2.70	---	4.30
10/16/00	---	7.0	---	2.90	---	4.80

The observed impairment appears to be the result of leaching from fill material that was used in the construction process of upgrading/relocating U.S. Highway 68 just south of Lebanon in Marion County. The road relocation and new fill are located between sampling Sites 1 and 2. As can be seen from Table 1, the stream shows significant impairment downstream of the road cut at Site 2, then shows some improvement further downstream at Site 3. No impairment was observed upstream of the road cut at Site 1.

In the summer of 2002, staff associated with the Kentucky Water Resources Research Institute (KWRRI) at the University of Kentucky collected additional data from the same sampling locations as the KDOW. The results of this sampling are shown in Table 2. As can be seen from the Table 2, the same general trend was observed, although the pH values had shown some improvement from 2000 to 2002.

Table 2. KWRRI Sampling Results for Mussin Branch, 2002

	Site 1		**Site 2**		**Site 3**	
Date	Flow rate (cfs)	PH	Flow rate (cfs)	pH	Flow rate (cfs)	pH
2/16/2002	---	7.12	---	5.55	1.13	7.15
3/8/2002	0.0344	6.90	---	6.70	0.08	7.20
3/17/2002	0.0844	5.60	1.87	4.20	3.30	5.10
3/23/2002	0.1240	6.50	1.07	5.00	3.34	5.60
3/30/2002	0.0675	6.40	0.33	5.30	0.88	5.60
4/28/2002	---	6.00		4.60	---	5.00
5/2/2002	0.2625	6.80	14.10	5.90	18.14	5.50
5/4/2002	0.0554	6.30	0.98	4.40	2.35	5.40
5/6/2002	0.1050	6.50	0.83	5.20	1.63	5.90
5/22/2002	0.0594	7.05	0.57	4.59	0.94	6.87

Problem Definition

The 2002-303(d) list of waters for Kentucky (KDOW, 2003) indicates that 1.7 miles of Mussin Branch, from the upstream mile point 1.7 to downstream mile point 0.0 in Marion County, do not meet the designated uses of primary and secondary contact recreation (swimming and wading) and aquatic life. The Mussin Branch watershed provides an example of impairment as a result of leaching from the pyritic fill material used in highway construction. Highway excavation exposes the pyritic shale material, which allows leaching of the sulfides in the form of sulfuric acid. Pyrite is the most common iron disulfide (FeS_2) mineral in rock and is frequently found in association with coal and shale deposits. Analysis of water quality data collected in several streams affected by highway construction indicate that a combination of low pH and alkalinity along with increased toxic metal concentrations, resulting from leaching of sulfides, can contribute to toxic conditions for fish (Yew and Makowski, 1989). In addition, a depressed pH interferes with the natural stream self-purification processes.

The upgraded highway crosses Mussin Branch at a fairly constant grade and does not dip at the stream. From the topographic map, it appears that the highway runs at an elevation of approximately 690-695 feet, and the stream channel runs at about 650 feet at the highway crossing. This is a vertical elevation difference of 40-45 feet, which is a fairly high embankment, and the embankment is fairly long. The fill material used for the embankment is broken shale and the shale is exposed on nearly the entire embankment. Data collected indicates that the pH takes a dramatic drop from the upstream side to the downstream side of the culvert on U.S. Highway 68/State Highway 55. The stream on the upstream side of the culvert runs clear (see Figure 3), but on the downstream side is bright orange and the stream bottom cannot be seen (see Figure 4). Water leaches through the embankment and into the culvert staining the culvert apron orange, whereas the pool of water immediately below the culvert and the stream channel for the considerable distance downstream is rendered bright orange. This condition appears to be the result of leaching of the embankment (fill) material, which is exposed on both the upstream and downstream sides of the embankment. Figures 3 and 4 show sampling Sites 1 and 2 respectively indicating the impairment on the downstream side of the highway caused by the leaching through the exposed embankment.

Figure 3. Sampling Site #1 – Upstream of the Highway

Figure 4. Sampling Site #2 – Downstream of the Highway

In the process of leaching from pyritic shale material exposed during highway construction, the iron disulfide (FeS_2) is exposed to the oxidizing action of oxygen in the air (O_2), water, and sulfur-oxidizing bacteria. The end products of the reaction are as follows:

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

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

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

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

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

The brownish yellow ferric hydroxide ($Fe(OH)_3$) may remain suspended in the stream even when it is no longer acidic. Although the brownish, yellow staining of the 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):

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

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 leaching of the embankment (fill) material, 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 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 has 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 (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

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

Nonpoint Source Loads

The KDOW collected pH and stream flow data for Mussin Branch to assess the water quality in the stream. This data was collected in October 2000 at three different sites on the stream as indicated in Table 1 and Figure 2. In order to provide a more recent characterization of the pH levels in the watershed, personnel contracted by the KWRRI collected additional pH and streamflow values from these sites. These results are given in Table 2. The most recent sampling shows that Sites 1 and 2 continue to have pH readings below 6.0, indicating that there is continued impairment due to low pH. The KWRRI used the data in Tables 1 and 2 to develop the TMDL for Mussin Branch. A separate TMDL was developed for each subbasin as part of this study.

TMDL Development

Theory

The TMDL is a term used to describe the maximum amount of a pollutant a stream can assimilate without violating water quality standards (WQSs) and includes a MOS. The units of load measurement are mass of pollutant per unit time (i.e. 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) for both nonpoint sources and natural background levels for a given watershed. The sum of these components cannot result in exceedance of WQSs for that watershed. In addition, the TMDL must include a MOS, which is either implicit or explicit, that accounts for the uncertainty in the relation between pollutant loads and the quality of the receiving water body. Conceptually, this definition is denoted by the equation:

$$\text{TMDL} = \text{Sum (WLAs)} + \text{Sum (LAs)} + \text{MOS} \quad (9)$$

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:

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

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.

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

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):

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

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):

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

Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Figure 5 (Snoeyink and Jenkins, 1980).

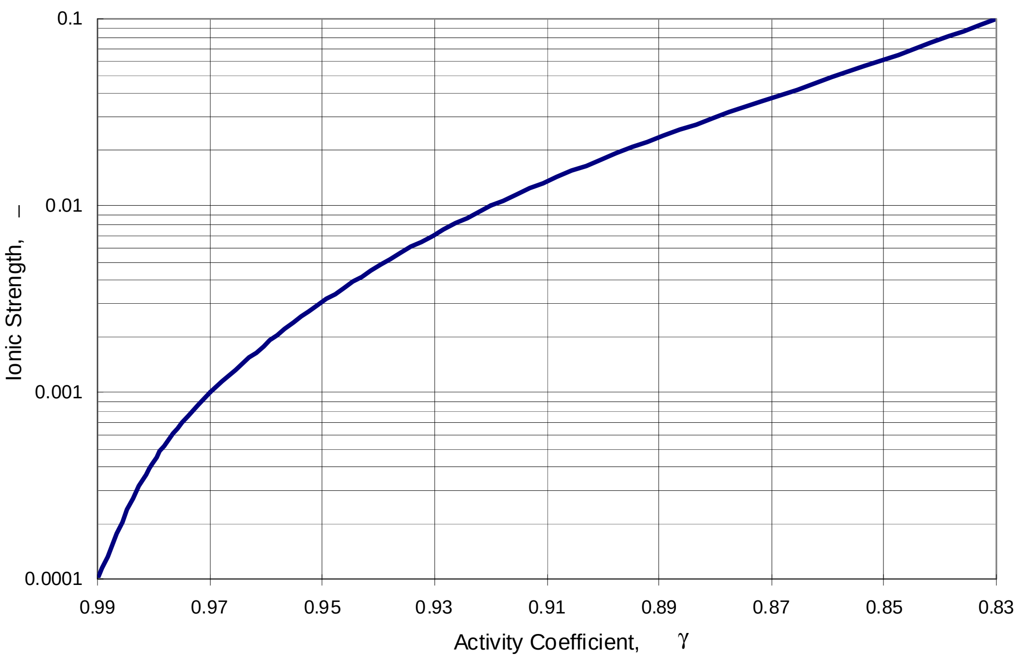


Figure 5. Activity Coefficients of H+ as a Function of Ionic Strength
(Snoeyink and Jenkins, 1980)

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 268 measurements of specific conductivity obtained from streams in three eastern Kentucky counties namely McCreary, Whitley, and Pulaski revealed a range of values from 2 to 3200 μ ohm/cm. Use of an upper limit of 3200 μ ohm/cm yields an ionic strength of 0.0512 or approximately 0.05. Use of a value of ionic strength of 0.05 yields an activity coefficient of approximately 0.86.

For the Mussin Branch watershed, specific conductivity values were observed to vary from 113 to 479 μ ohm/cm, which yields ionic strength values from 0.0018 to 0.0077 respectively. Application of Figure 5 for the observed ionic strengths in Mussin Branch yields activity coefficients of 0.96 to approximately 0.93.

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 g/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.

Because pH and the equivalent hydrogen ion load can be related as a function of discharge 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 (6.0) and an associated minimum activity correction factor (e.g. 0.93), an envelope of maximum hydrogen ion loads that could still yield a pH of 6 may be obtained as a function of discharge (see the upper $TMDL_x$ curve in Figure 6). 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 equation 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 leaching from the pyritic fill material used in highway construction, 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 6). 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. In developing a TMDL for the Mussin Branch watershed, the TMDL for each of the Subbasins 1 and 2 will be established assuming an activity coefficient of 1.0, while the observed load will be determined using an activity coefficient of 0.93, providing for an upper limit of a MOS of approximately 7 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 to determine the value of the TMDL.

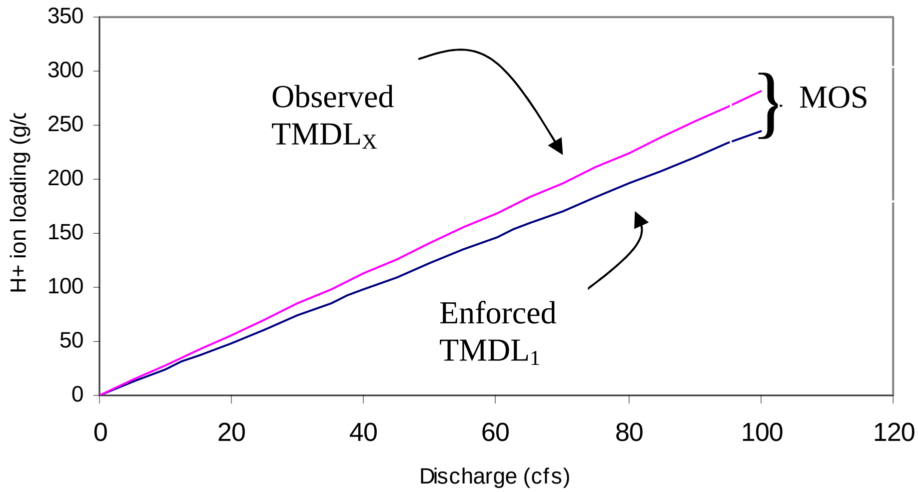


Figure 6. Relation Between Discharge and Maximum Ion Load for a pH of 6.0

Hydrogen Loading Example Calculation

In order to demonstrate the hydrogen loading conversion procedure, use the following data for Site 3 (Subbasin 2) of Mussin Branch:

- Critical discharge (Q) = 0.4901 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:

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

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

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

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

The goal is to achieve a loading rate in terms of g/day, 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 g/ft^3)*(0.4901 ft^3/s)*(86400s/1day) = 1.20 g/day, or 0.0026 lbs/day

Assuming an activity correction factor of 0.93, the maximum load would be 1.29 g/day, or 0.0028 lbs/day:

1.20 g/day / 0.93 = 1.29 g/day, or 0.0028 lbs/day

Therefore, by using an activity coefficient of 1.0 instead of 0.93 to develop the TMDL values, a MOS of approximately 7 percent is assumed.

Critical Flow and TMDL Determination

Because maximum hydrogen ion loading values can be directly related to flow rate using Figures 5 and 6, the associated allowable ion loading exceedance frequency can be directly related to the frequency of the flow. In order to find the lowest 10-year average annual discharge for the Mussin Branch watershed, a regional hydrologic 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 US Geological Survey (USGS) gaging stations were selected: USGS 03304500 McGills Creek near McKinney, Lincoln County, KY, and USGS 03309500 McDougal Creek near Hodgenville, Larue County, KY. The data from these gages were used to estimate the lowest average annual flows of the most recent 10 years (see Table 3). Because there were no gaging stations that had a contributing drainage area comparable to the subbasins in this watershed under study and for which data was available for the last 10 years, historic data (1954-1964) were used in developing the regional flow-area curve. These discharges were then regressed with watershed area to produce Figure 7. Using this figure, the lowest 10 year mean annual discharge for a given watershed area can be readily determined.

Table 3. Lowest 10-year Mean Annual Flow Rates (cfs) for Stations in Regional Analysis

	USGS Gaging Station Numbers	
Station	03304500	03309500
Area (mi^2)	2.14	5.34
Q (cfs)	1.02	2.21

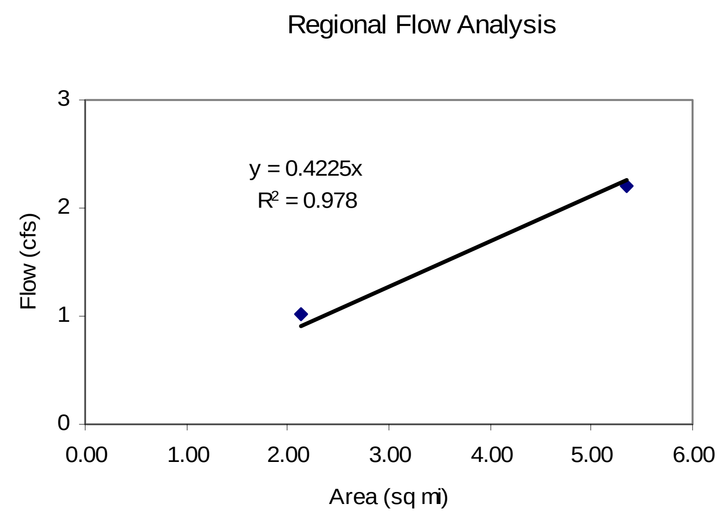


Figure 7. Relation Between Basin Area and the Critical TMDL Flow

Application of Figure 7 for the Mussin Branch watershed yields a TMDL critical average annual flow for all the subbasins in this watershed for which a TMDL will be developed For Subbasin 2, this is calculated as 0.4225 x 1.1600 = 0.4901. Application of these critical flows (the lowest 10-year mean annual flow) with the lower $TMDL_1$ curve in Figure 6 yields a TMDL for Subbasins 1 and 2 (see Hydrogen Loading Example Calculation on page 12). The incremental TMDL is calculated by subtracting the cumulative TMDL of directly contributing subbasins from the cumulative TMDL for the subbasin of interest. Subbasin 1 is a direct contributor to Subbasin 2 so the incremental TMDL for Subbasin 2 is calculated as: 0.0026 – 0.0017 = 0.0009. These results are summarized in Table 4.

Table 4. Flow and Corresponding TMDL for Subbasins 1 and 2

Sub-basin	Cumulative Area (mi^2)	Incremental Area (mi^2)	Cumulative Q (cfs)	Incremental Q (cfs)	Cumulative TMDL (lbs/day)	Incremental TMDL (lbs/day)
1	0.7609	0.7609	0.3215	0.3215	0.0017	0.0017
2	1.1600	0.3953	0.4901	0.1670	0.0026	0.0009

Hydrogen Ion Loading Model

Once a TMDL is developed for a watershed, the associated load reduction must be spatially allocated. One way to accomplish this objective is through unit load reductions as associated with different land uses within the watershed. The impacts of such reductions on the associated 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, a TMDL is developed for individual subbasins in the Mussin Creek watershed.

Based on a physical inspection of the watershed, it is hypothesized that the lowering of the pH in the stream is directly related to oxidation of sulfur that occurs as runoff flows over the exposed embankment. Using the most recent monitoring data, inductive models were developed at monitoring Sites 2 and 3 that relate total hydrogen ion loading to flow. These models are shown in Figures 8 and 9 and are derived from the data in Tables 1 and 2. These models were developed by utilizing data points that were within a feasible range of the critical flow for each of the subbasins in the watershed. In developing these models for defining the current load, a conservative value of 0.93 was assumed for the activity coefficient based on the upper limit of measured specific conductance values of 479 μ ohms/cm. As discussed previously, the lower enforced TMDL curve was developed assuming an activity coefficient of 1.0, thus providing for an upper limit for a MOS for the TMDL of approximately 7 percent.

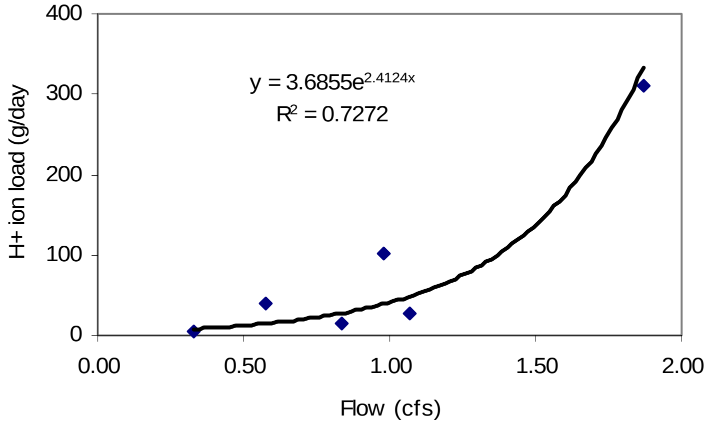


Figure 8. Relation Between Flow and Ion Load for Site 2

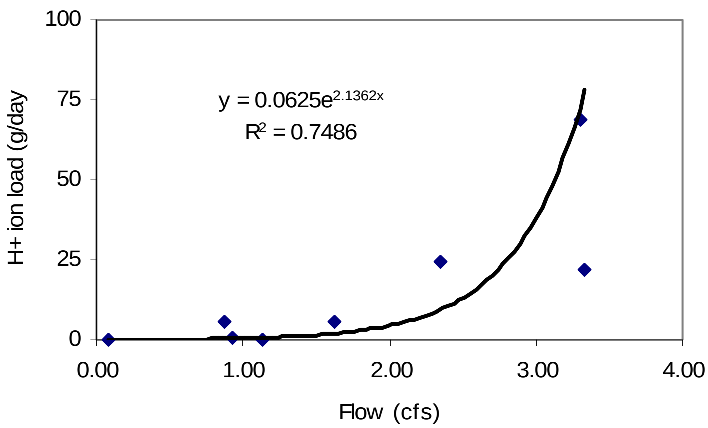


Figure 9. Relation Between Flow and Ion Load for Site 3

The best trend lines through the monitoring data (Figures 8 and 9) yield the projected hydrogen ion loading for different flow values. The trend lines are based on a regression analysis of the observed field data collected at Sites 2 and 3. In each case, the trend lines are developed over the expected flow domain of the critical discharge for each subbasin. Once the trend lines are developed, projected hydrogen ion loadings can be determined for an associated critical discharge. The associated TMDL has earlier been computed using the lower TMDL curve in Figure 6. The difference between the critical loading and the TMDL will be the reduction needed for each subbasin.

Predicted Load

The predicted hydrogen ion loads for each subbasin may be obtained using the critical flow from Table 4 along with the associated load relation shown in Figures 8 and 9. The calculation for Subbasin 2 is: $0.0625e^{(2.1362)x(0.4901)} = 0.1781$. Application of this approach yields the predicted loads for each subbasin as shown in Table 4. 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 flow entering from upstream subbasins (Subbasin 2) requires a mass balance application to find the incremental load (.0004 – 0.01770 = -.0317 = 0).

Table 5. Predicted Cumulative Ion Load for Subbasins 1 and 2

Sub basin	Cumulative Flow (cfs)	Incremental Flow (cfs)	Predicted load (gm/day) Cumulative	Predicted load (lbs/day) Cumulative	Predicted load (lbs/day) Incremental
1	0.3215	0.3215	8.000	0.01770	0.0177
2	0.4901	0.1670	0.1781	0.0004	0.0000

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. For this TMDL, the hydrogen ion load is assumed to be entirely associated with water leaching from the pyritic fill material used in highway construction. Also, separate TMDLs (and associated load reductions) can be developed for individual subbasins within the watershed. In the current study, a separate TMDL and associated load reduction was developed for Subbasin 1 and a cumulative TMDL and associated load reduction was developed for Subbasin 2 (Figure 2).

Translation of the incremental TMDL in Table 4 into associated daily load reduction for Sites 2 and 3 may be accomplished by subtracting the incremental TMDL from the incremental predicted loads for these sites (Table 5). For Subbasin 2 the calculation is:

0.0000 – 0.0009 = -0.0009 = 0. Application of this approach yields the load reduction values in Table 6.

Table 6. TMDL Summary and Reduction Needed for Subbasins 1 and 2

Subbasin	Upstream contributing area (mi^2)	Incremental critical flow (cfs)	Incremental TMDL for a pH of 6.0 (lbs/day)	Predicted incremental load (lbs/day)	Load Reduction needed (lbs/day)
1	0.7609	0.3215	0.0017	0.0177	0.0160
2	0.3953	0.1670	0.0009	0.0000	0.0000
Total Watershed	1.1600	0.4901	0.0026	0.0177	0.0160

Allocations

Wasteload Allocations

There are no known permitted point sources in this watershed that contribute to the existing pH impairment. As a result, the current wasteload allocation for the Mussin Branch Watershed is assumed to be zero.

Load Allocations

Loads associated with nonpoint sources for the Mussin Branch watershed are assumed to be directly related to water leaching from the pyritic fill material used in highway construction. The total load from nonpoint sources for Mussin Branch is assumed to be an explicit function of the average daily flow in the stream and an associated pH standard of 6. Such loads can be obtained using a relationship that relates flow and hydrogen ion loading (g/day) and can be developed inductively using the observed date in Table 1 and 2.

Distribution of Load

The table given below splits the TMDL (which is based on meeting the minimum water quality standard value for pH of 6.0) evenly between the WLA and the LA for each subbasin as a means of defining a conservative approach toward any new highway construction permits in the watershed.

Table 7. Wasteload and Load Allocations for Each Subbasin

	Incremental Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation (lbs/day)	Load Allocation (lbs/day)
Subbasin 1	0.3215	0.0017	0.00085	0.00085
Subbasin 2	0.1670	0.0009	0.00045	0.00045

Implementation/Remediation Strategy

Practical application of pH TMDLs, especially those developed as a result of highway construction/relocation projects, will normally involve a phased implementation approach with associated monitoring in order to insure that the implemented measures are having the desired effect. Permanent mitigation measures may involve sealing the pyritic fill material in the road embankments from surface water infiltration with lime and topsoil. For Mussin Branch, remediation needs to be done on the embankment and possibly the exposed road cuts on either side of the embankment. Until permanent mitigation measures are implemented, the stream can be treated with limestone to reduce the load.

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:

$$\text{Annual required mass of limestone} = 18{,}250 * \text{Mass of Hydrogen Ions (g/day)} \qquad (13)$$

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 drainage from the fill material, 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 developed, as shown in Figure 10. In this particular case, Figure 10 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.

For the case of Mussin Branch, 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 10 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 10 is likely to provide a conservative estimate of the initial required $CaCO_3$ loading for a particular stream. Subsequent applications of additional limestone can be further refined through follow-up monitoring.

Application of Figure 10 using the required hydrogen ion load reduction values shown in Table 6 yields the corresponding values of $CaCO_3$ loadings shown in Table 8. For Subbasin 1, the calculation is: (3401.7) x $(7.25)^{0.7097}$ = 13,876. 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 8 be multiplied by a factor of 2 to 4 in order to provide a conservative estimate of the initial loading.

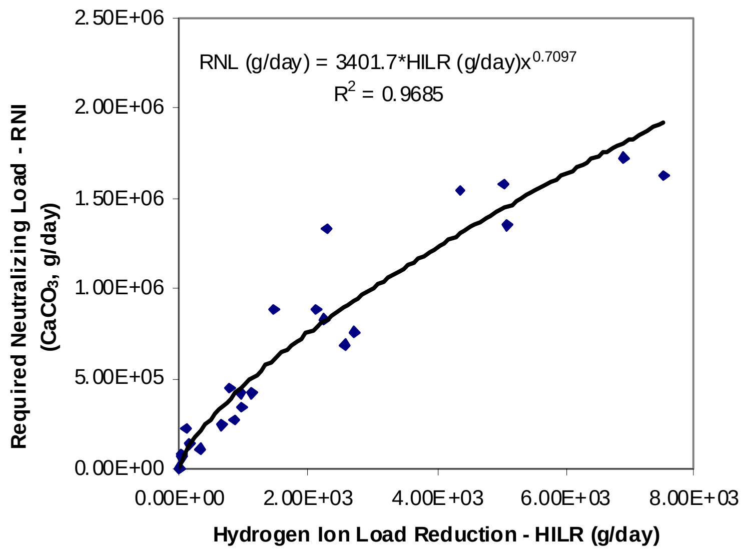


Figure 10. Relation Between $CaCO_3$ Loading and the Required Hydrogen Ion Reduction

Table 8. $CaCO_3$ Loadings for Mussin Branch

	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	0.0160	7.25	13,876	30	6
Subbasin 2	0.0000	0.00	0	0	0

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 Lebanon Enterprise, a newspaper with wide circulation in Marion 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.

LITERATURE CITED

Carew, M, (1998*) Rock Creek Reclamation Project, Kentucky Department for Surface Mining Reclamation and Enforcement*, Kentucky Division of Abandoned Mine Lands, 12 pp.

Clayton, J.L., Dannaway, E.S., Menendez, R., Rauch, H.W., Renton, J.J., Sherlock, S.M. and Zurbuch, P.E. (1998). "Application of limestone to restore fish communities in acidified streams". *North American Journal of Fisheries Management*, 18: 347-360.

Environmental Protection Agency, (1981) *Clean Water Act*, Section 303(d), 40 CFR Part 130, 1991b.

Environmental Protection Agency, (1991) *Technical Support Document for Water Quality-based Toxics Control*, EPA 505/2-90-001, March 1991.

Kentucky Administrative Regulations, (2002) Title 401, Chapter 5:031

Kentucky Division of Water, (1981) *The Effects of Coal Mining Activities on the Water Quality of Streams in the Western and Eastern Coalfields of Kentucky*, Department for Environmental Protection, Kentucky Natural Resources and Environmental Protection Cabinet.

Kentucky Division of Water, (2003). 2002 *303(d) List of Waters for Kentucky*, Department for Environmental Protection, Frankfort, KY.

Snoeyink, V.L., and Jenkins, D., (1980) *Water Chemistry*, Wiley, Inc, New York, NY, 1980, pp. 77-78.

US Department of Agriculture, Soil Survey of Marion County, Kentucky, 1986

Yew, C.P., and Makowski, P.B. 1989, "Water Quality Monitoring of Highway Construction," Preceedings of the 1989 National Conference on Hydraulics Engineering, ASCE, New York, pp. 157-162.