Final

pH (H^+ Ion Mass)

Total Maximum Daily Load (TMDL)

for

UT of Rolling Fork (at River Mile 94.6) 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

David Morgan, Director

Division of Water

1/13/06

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UT of Rolling Fork (at River Mile 94.6)

Total Maximum Daily Load (TMDL) Fact Sheet

Project Name: UT of Rolling Fork at RM 94.6

Location: Marion County, Kentucky

Scope/Size: UT of Rolling Fork Watershed 848 acres (1.33 mi^2)
Stream Segment: River Mile 0.0 to 0.60

Land Type: forest, agricultural, barren/spoil

Type of Activity: acid drainage caused by highway construction

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

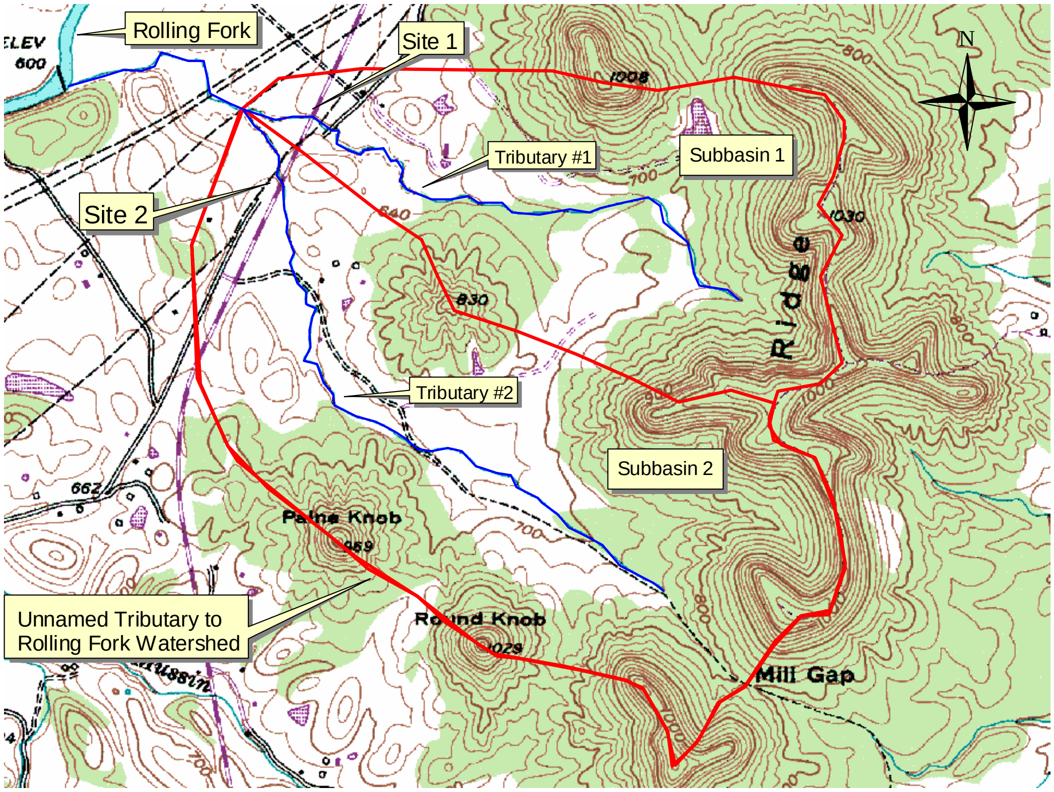
TMDL Issues: nonpoint sources

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
Kentucky Water Resources Research Institute

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

Summary: UT of Rolling Fork 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 Total Maximum Daily Load (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 UT of Rolling Fork, pH readings and corresponding stream flow measurements were made at two different locations within the watershed, corresponding to the two tributaries. The most recent sampling supports the conclusion that Site 2 (sub-watershed for tributary #2) does not support acceptable pH levels. The watershed is impaired because of low pH at this site.



Most Recent Sampling Locations on UT of Rolling Fork

TMDL Development: Total maximum daily loads in grams H^+ ions per day were computed based on the allowable minimum pH value of 6.0 for streams to meet the primary and secondary contact recreation and aquatic life uses. The TMDL was done for grams of ions (subsequently converted to lbs/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 criterion on potentially intermittent streams, the Kentucky Division of Water 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 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 (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: (1) the total annual load; (2) the total annual reduction that would be derived from an annual summation of the daily TMDLs; and (3) the associated daily load reductions for the critical year using historical daily flows.

TMDL for UT of Rolling Fork:

In developing a TMDL for UT of Rolling Fork, 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, an individual TMDL was developed for Subbasin 2. The TMDL and associated load reductions for Subbasin 2 are shown below.

Summary of Flow Rate and TMDL for Subbasin 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)
2	0.79	0.334	0.0018	0.0031	0.0013

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 as reflected in the above table. The table given below splits the TMDL (which is based on meeting the minimum WQS 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 Subbasin 2.

Wasteload and Load Allocation for Subbasin 2

	Incremental Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation (lbs/day)	Load Allocation (lbs/day)
Subbasin 2	0.334	0.0018	0.0009	0.0009

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 UT of Rolling Fork, 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 second 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 the UT of Rolling Fork, 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 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 controls to reduce pollution from both point and nonpoint sources and restore and maintain the quality of their water resources (EPA, 1991).

Location

The UT of Rolling Fork watershed is entirely contained within Marion County, in central Kentucky (Figure 1).

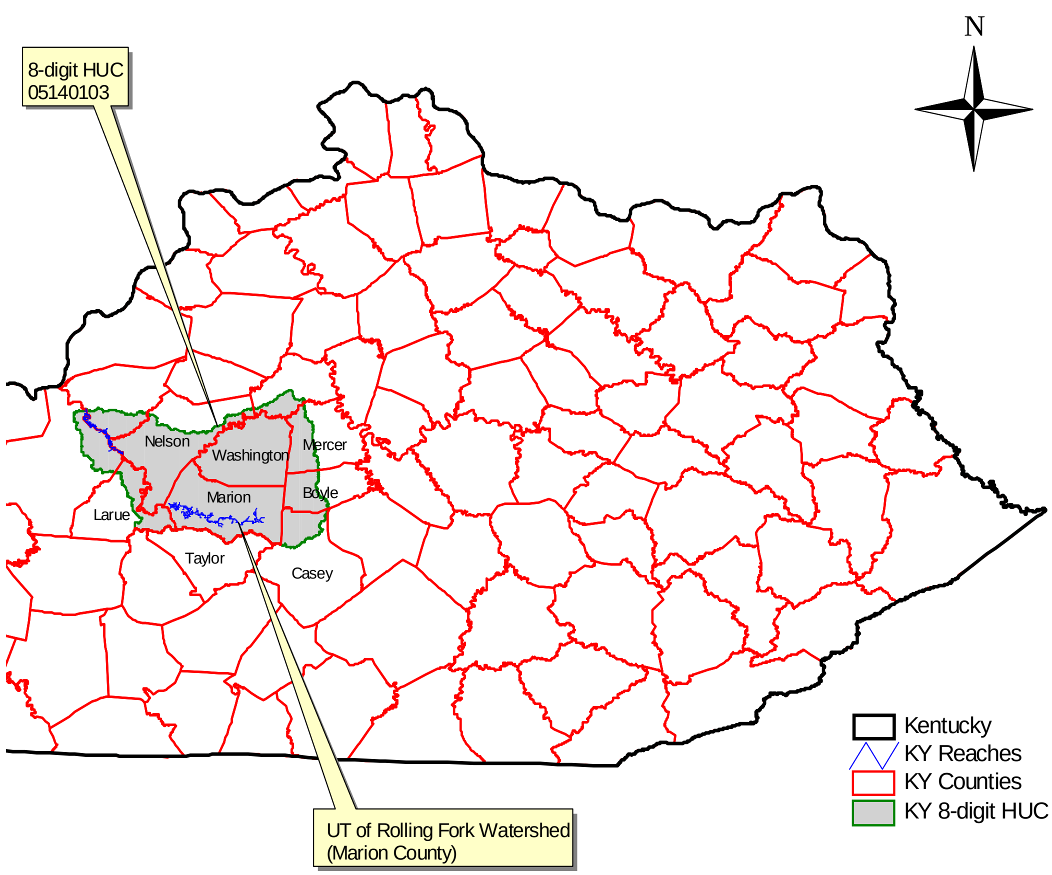


Figure 1. Location of the UT of Rolling Fork Watershed

Hydrologic Information

The unnamed tributary (UT) of Rolling Rock originates in Marion County and flows west to discharge into the Rolling Fork. The Rolling Fork River drains the 8-digit USGS HUC watershed 05140103 as shown in Figure 1.

The UT of Rolling Fork is actually made up of unnamed tributaries, tributary #1 and #2 as shown in Figure 2. These tributaries join together west of U.S. Highway 68/State Highway 55, and ultimately discharge into Rolling Fork as shown in Figure 2. Tributary #1 is approximately 1.28 miles long (average gradient of 93 feet per mile) and drains an area of 339 acres (0.53 mi^2). Tributary #2 is approximately 1.49 miles long (average gradient of 80 feet per mile) and drains an area of 509 acres (0.79 mi^2). Elevations for both the tributaries range from 740 feet above mean sea level (msl) in the headwaters to 620 feet at the most downstream point near the confluence of the two tributaries.

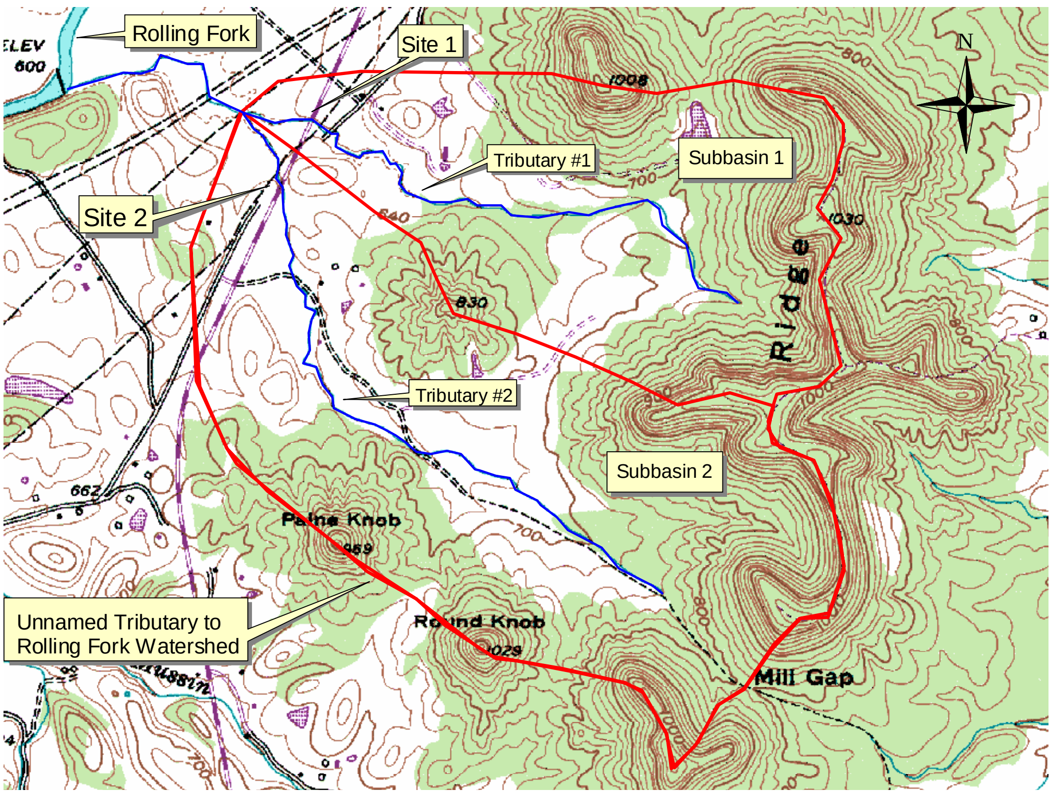


Figure 2. Sampling Sites Monitored in the UT of Rolling Fork Watershed

Geologic Information

Marion County has diverse topography. The UT of Rolling Fork 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 UT of Rolling Fork 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. Southern Marion County, the location of the UT of Rolling Fork watershed, is very hilly and 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 (USDA, 1986).

Soils Information

Soils in the UT of Rolling Fork 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 this area are deep and have a very strong acid or strongly acidic, loamy subsoil (USDA, 1986).

Monitoring History

The Kentucky Division of Water (KDOW) first monitored the waters of the UT of Rolling Fork in 2000 at Site 2. The results of the sample analysis are shown in Table 1. This data prompted the 2002 303(d) listing of the UT of Rolling Fork as being impaired for the swimming, wading, and aquatic life uses because of low pH. The UK Water Resources Research Institute (UKWRRI) and KDOW collected additional data at Sites 1 and 2 in the summer and fall of 2004. Sampling results shown in Table 2, suggest that tributary #2 continues to be impaired due to low pH.

Table 1. KDOW Sampling Results for
UT of Rolling Fork Branch Watershed, 2000

Date	**Tributary #2 (Upstream)**		**Tributary #2 (Downstream)**	
	Flow rate (cfs)	**pH**	**Flow rate (cfs)**	**pH**
10/4/2000	-	5.60	-	4.80
10/16/2000	-	5.40	-	No data

Table 2. KDOW and UKWRRI Sampling Results, 2004

Date	Tributary #1 (Downstream)		Tributary #2 (Downstream)	
	Flow rate (cfs)	pH	Flow rate (cfs)	pH
7/14/2004	-	7.06	0.119	6.09
8/2/2004	-	7.63	0.364	6.38
8/6/2004	-	6.83	2.044	6.22
8/26/2004	0.133	6.44	0.113	6.72
8/30/2004	0.238	6.42	0.173	6.56
10/13/2004	0.490	6.73	0.780	6.06
10/20/2004	0.350	6.34	0.430	5.90
10/29/2004	0.500	6.58	0.470	6.25
11/11/2004	0.120	6.79	0.170	6.51
11/15/2004	0.280	6.06	0.390	5.87

Problem Definition

The 2002 and draft 2004 303(d) lists of waters for Kentucky (KYDOW; 2002 and 2004) indicate that 0.6 miles of UT of Rolling Fork, Marion County, do not meet the designated uses for primary and secondary contact recreation and warm water aquatic habitat use (aquatic life). The UT of Rolling Fork watershed is an example of impairment due to the leaching of 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 the two tributaries to Rolling Fork 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 630 feet, and the stream channel runs at about 620 feet at the highway crossing. This is a vertical elevation difference of 10 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 drop from the upstream side to the downstream side of the culvert on U.S. Highway 68/State Highway 55. This drop 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.

In this leaching process, 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 (equation. 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 and 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 (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. 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 UKWRRI and the KDOW collected pH and stream flow data for UT of Rolling Fork to assess the water quality in the stream. This most recent data was collected from July 2004 through November 2004 at the downstream end of the two tributaries as indicated in Table 2 and Figure 2. This recent sampling shows that the southern tributary (Site #2) had pH readings below 6.0, indicating that there is impairment because of low pH. The UKWRRI used the data in Tables 2 to develop the TMDL. A separate TMDL was developed for the impaired Subbasin 2 (tributary #2) 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 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:

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

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 (USEPA, 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):

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

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 3 (Snoeyink and Jenkins, 1980).

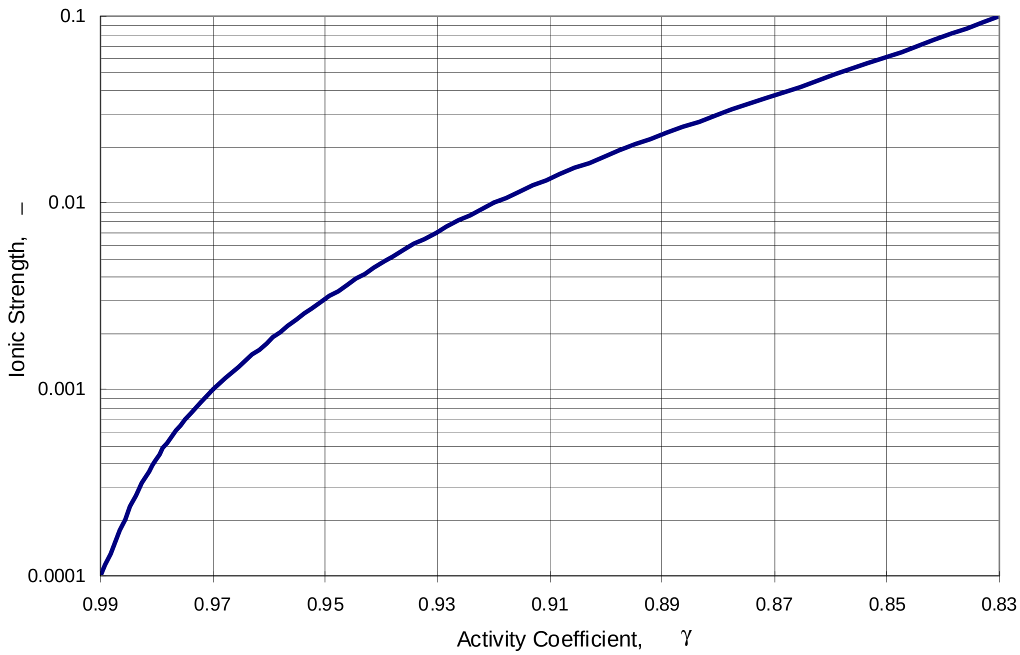


Figure 3. Activity Coefficients of H+ as a Function of Ionic Strength
(Snoeyink and Jenkins, 1980)

For the UT of Rolling Fork watershed, specific conductance values were observed to vary from 106 to 550 (μ mho/cm), which yields ionic strength values from 0.0017 to 0.0088 respectively. Application of Figure 3 for the observed ionic strengths in UT of Rolling Fork watershed yields activity coefficients of 0.96 to approximately 0.92.

The atomic weight of hydrogen is 1 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 flow rate and ionic strength, a functional relationship can be developed between flow rate 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. 0.92), 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 4). In using the proposed methodology, the MOS may be incorporated explicitly through 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, which suggests there is no quantitative difference between activity and molar concentration. In the case of leaching 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 4). 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 provides 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 UT of Rolling Fork watershed, the TMDL for the impaired Subbasin 2 (tributary #2) will be established assuming an activity coefficient of 1.0, while the observed load will be determined using an activity coefficient of 0.92, providing for an upper limit of a MOS of approximately 8 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.

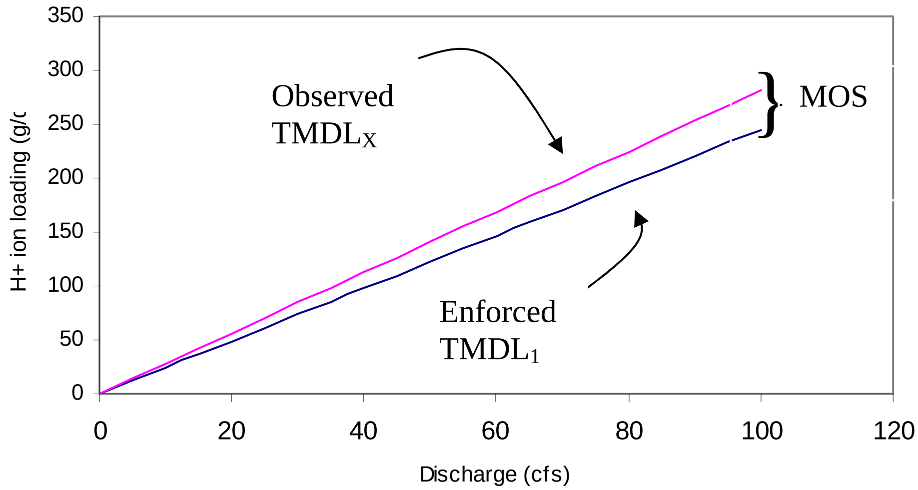


Figure 4. Relation Between Flow (Discharge) and Maximum Ion Load for a pH of 6.0

Hydrogen Loading Example Calculation

In order to demonstrate the hydrogen loading conversion procedure, use the following data for Site 2 of tributary #2 to Rolling Fork:

- Critical discharge (Q) = 0.334 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 g/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)*(0.334 ft^3/s)*(86400s/1day) = 0.82 g/day, or 0.0018 lbs/day

Assuming an activity correction factor of 0.92, the maximum load would be 0.89 g/day, or 0.002 lbs/day:

0.82 g/day / 0.92 = 0.89 g/day, or 0.002 lbs/day

Therefore, by using an activity coefficient of 1.0 instead of 0.92 to develop the TMDL values, a MOS of approximately 8% would be realized.

Critical Flow and TMDL Determination

Because maximum hydrogen ion loading values can be directly related to flow rate, 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 UT of Rolling Fork 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 stream flow gauging stations located in the same hydrologic region as the watershed of interest. For this study, the following two USGS gauging 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). Historic data (1954-1964) were used in developing the regional flow-area curve because no gauging stations had contributing drainage areas comparable to the subbasins in this watershed. These flows were then regressed with watershed area to produce Figure 5. Using this figure, the lowest 10 year mean annual flow 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 Gauging Station Numbers	
Station	03304500	03309500
Area (mi^2)	2.14	5.34
Q (cfs)	1.02	2.21

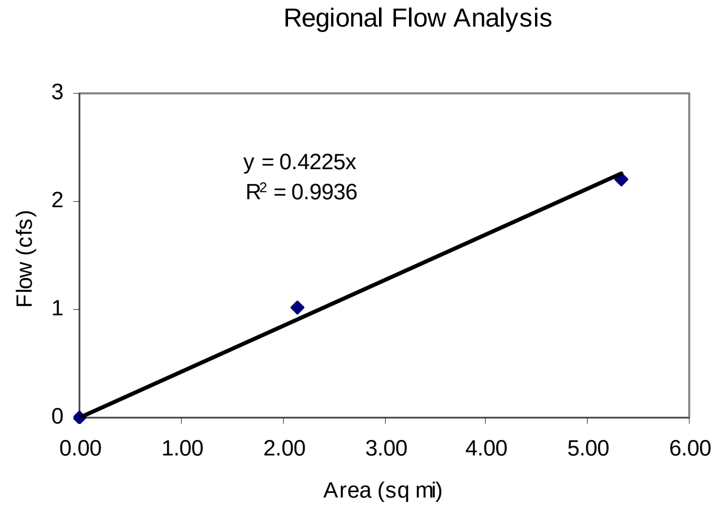


Figure 5. Relation Between Basin Area and the Critical TMDL Flow

Application of Figure 5 for the UT of Rolling Fork 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, 0.4225 x 0.79 = 0.334). Application of this critical flow (the lowest 10-year mean annual flow) with the lower $TMDL_1$ curve in Figure 4 yields a TMDL for Subbasin 2 (see Hydrogen Loading Example Calculation on page 10). These results are summarized in Table 4.

Table 4. Flow and Corresponding TMDL for Subbasin 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)
2	0.79	0.79	0.334	0.334	0.0018	0.0018

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 Subbasin 2 in the UT to Rolling Fork 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 exposed embankment. Using the most recent monitoring data, an inductive model was developed at monitoring Site 2 that relates total hydrogen ion loading to flow. This model is shown in Figure 6 and is derived from the data in Table 2. This model is developed by utilizing data points that were within a feasible range of the critical flow for the impaired subbasin in the watershed. In developing the inductive regression model for defining the current load, a conservative value of 0.92 was assumed for the activity coefficient based on the upper limit of measured specific conductance values of 550 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 8 percent.

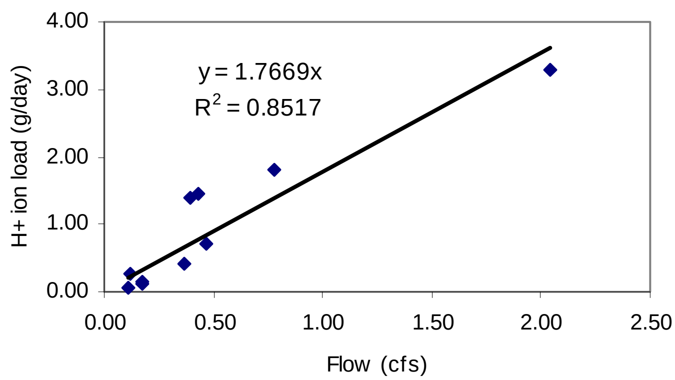


Figure 6. Relation Between Flow and Ion Load for Site 2

The best trend line, through the monitoring data (Figure 6), yields the estimated current hydrogen ion loading for different flow values of critical discharge. The trend line is based on a regression analysis of the observed field data collected at Site 2. The trend line is developed over the expected flow domain of the critical discharge for the impaired subbasin. Once the trend line is 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 4. The difference between the critical loading and the TMDL will be the reduction needed for the subbasin.

Predicted Load

The predicted hydrogen ion loads for the impaired subbasin may be obtained using the critical flow from Table 4 along with the associated load relation shown in Figure 6. Application of this approach yields a predicted load of 0.59 gm/day (1.7669 X 0.334 = 0.59) or 0.0013 lbs/day for Subbasin 2. Note, however, this is less than the highest observed load of 1.40 gm/day (0.0031 lbs/day) for Site 2 (corresponding to a pH of 5.87 on November 15, 2004). Since the corresponding flow rate (0.39 cfs) for this observed load is close to the critical flow rate (0.334 cfs), the actual observed load (i.e. 0.0031 lbs/day) was used instead in setting the predicted load for the critical discharges (see Table 5). This provides an additional factor of safety to the analysis and insures that the predicted load for the associated critical discharge is more accurately reflective of the actual conditions.

Table 5. Predicted Cumulative Ion Load for Subbasin 2

Sub basin	Cumulative Flow (cfs)	Incremental Flow (cfs)	Predicted load (g/day) Cumulative	Predicted load (lbs/day) Cumulative	Predicted load (lbs/day) Incremental
2	0.334	0.334	1.40	0.0031	0.0031

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 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. For this TMDL, the hydrogen ion load is 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 2 (Figure 2).

Translation of the incremental TMDL in Table 4 into associated daily load reduction for Site 2 may be accomplished by subtracting the incremental TMDL from the incremental predicted loads for the site (Table 5). Application of this approach yields the load reduction values in Table 6.

Table 6. TMDL Summary and Reduction Needed for Subbasin 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)
2	0.79	0.334	0.0018	0.0031	0.0013

Load 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 UT of Rolling Fork watershed is assumed to be zero.

Load Allocations

Loads associated with nonpoint sources for the UT of Rolling Fork 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 the UT to Rolling Fork is assumed to be an explicit function of the average daily flow in the stream and an associated pH standard of 6.

Distribution of Load

The table given below splits the TMDL (which is based on meeting the minimum WQS value for pH of 6.0) evenly between the Waste Load Allocation and the Load Allocation for Subbasin 2 as a means of defining a conservative approach toward any new highway construction permits in the watershed.

Table 7. Wasteload and Load Allocation for Subbasin 2

	Incremental Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs/day)	Wasteload Allocation (lbs/day)	Load Allocation (lbs/day)
Subbasin 2	0.334	0.0018	0.0009	0.0009

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 UT of Rolling Fork, 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 and Kentucky (Clayton, et. al., 1998 and 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 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 developed, as shown in Figure 7. In this particular case, Figure 7 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 UT of Rolling Fork, 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 7 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 7 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.

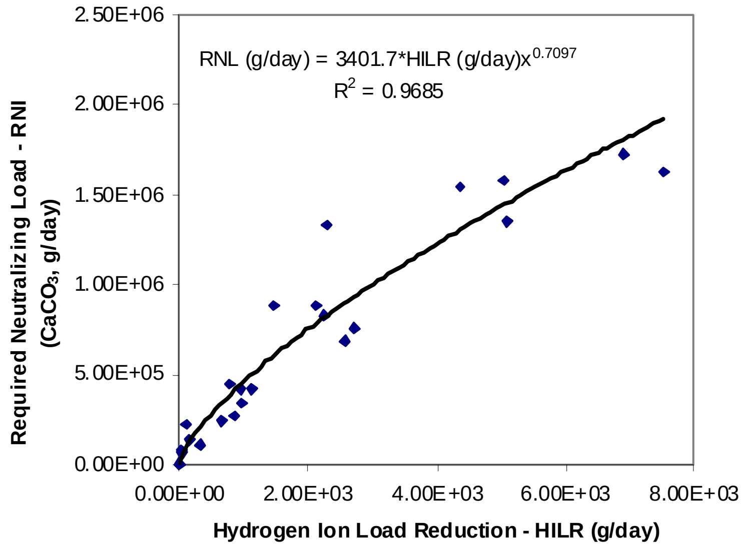


Figure 7. Relation Between $CaCO_3$ Loading vs Required Hydrogen Ion Reduction

Application of Figure 7 using the required hydrogen ion load reduction values shown in Table 6 yields the corresponding values of $CaCO_3$ loadings shown in Table 8 [(3401.7) x $(0.59)^{0.7097}$ = 2339]. 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.

Table 8. $CaCO_3$ Loading for UT of Rolling Fork

	Required reduction (lbs/day)	Required reduction (g/day)	$CaCO_3$ loading (g/day)	$CaCO_3$ loading (lbs/day)	$CaCO_3$ loading (tons/yr)
Subbasin 2	0.0013	0.5900	2339	5.1571	1.0

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.

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