

Final
pH (H⁺ Ion Mass)
Total Maximum Daily Load (TMDL)
for
Copperas Fork of Cooper Creek Watershed
(McCreary 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

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Frankfort, Kentucky

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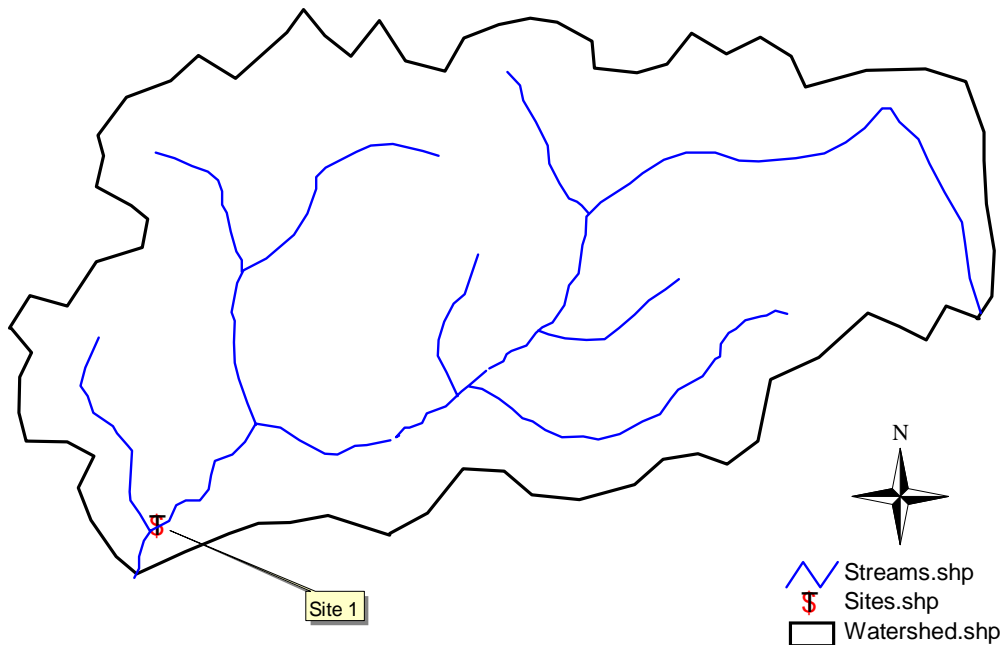
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Copperas Fork of Cooper Creek, Kentucky

Total Maximum Daily Load (TMDL) Fact Sheet

Project Name:	Copperas Fork
Location:	McCreary County, Kentucky
Scope/Size:	Copperas Fork Watershed 2,682 acres (4.19 mi ²) Stream Segment: river mile 0.0 to 3.8
Land Type:	forest, agricultural, barren/spoil
Type of Activity:	acid mine drainage (AMD) caused by abandoned mines
Pollutant(s):	H ⁺ Ion mass, sulfuric acid
TMDL Issues:	nonpoint sources
Water Quality Standard/Target:	pH shall not be less than six (6.0) or more than nine (9.0) and shall not fluctuate more than one and zero tenths (1.0) pH unit over a 24-hour period. This standard is found within regulation 401 KAR 5:031.
Data Sources:	Kentucky Pollutant Discharge Elimination System Permit Historical Sampling Data, Kentucky Division of Water (KDOW) Data Collection
Control Measures:	Kentucky nonpoint source TMDL implementation plan, Kentucky Watershed Framework
Summary:	Copperas 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 1998 and 2002 303(d) lists for TMDL development. The creek segment is characterized by a depressed pH, the result of AMD from abandoned mining sites. In developing the TMDL for Copperas Fork, pH readings were attempted at one location within the watershed. The most recent sampling supports the conclusion that the watershed has unacceptable pH levels.



University of Kentucky Water Sampling Location on Copperas Fork

TMDL Development:

TMDLs in grams H^+ ions per day were computed based on the allowable minimum pH value (6.0) for creeks and streams to meet primary and secondary contact 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 “no-exceedance” pH criteria on potentially intermittent streams, the KDOW has decided to use the lowest one year average discharge of the most recent 10-year flow record as the flow basis for setting the appropriate TMDL and associated loading reduction. Previous pH TMDLs have used a 3-year recurrence interval of the average flow as the critical flow. However, this flow resulted in a target discharge that frequently was significantly greater than any of the observed flows for the sites as collected over several years. Thus use of a 3-year flow would require an extrapolation of the observed ion vs. flow model, well beyond the upper limit of the observed

data. The selection of the 10-year frequency was based on a consideration of water quality standards (WQSs) (i.e. 7Q10). However, since many of these streams have a 7Q10 of zero, a greater duration was needed. The consensus of the KDOW was to use the 1-year duration. Use of an average annual flow as the basis for determining the TMDL also 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 the actual historical daily flows.

**TMDL for
Copperas Fork:**

To develop a TMDL for Copperas Fork, a cumulative TMDL was obtained for the downstream extent of the impaired portion of the watershed. The TMDL and associated load reduction are shown below.

TMDL and Associated Load Reduction

Watershed (mi ²)	Critical flow (cfs)	TMDL for a pH of 6.0 (lbs/day)	Predicted load (lbs/day)	Load reduction needed (lbs/day)
4.19	5.10	0.0275	0.3476	0.3201

Permitting in the Copperas Fork Watershed

New Permits:

New permits (except for new reming permits) for discharges to streams in the Copperas Fork watershed could be allowed anywhere in the watershed contingent upon end-of-pipe pH permit limits in the range of 6.35 to 9.0 standard units. WQSs state that the pH value should not be less the 6.0 nor greater than 9.0 for meeting the designated uses of aquatic life and swimming. This range of 6.0 to 9.0 for pH is generally assigned as end-of-pipe effluent limits. However, because a stream impairment exists (low pH), new discharges should not cause or contribute to an existing impairment. Application of agricultural limestone on mine sites results in highly buffered water leaving the site. A buffered solution with nearly equal bicarbonate and carbonic acid components will have a pH of 6.35 (Carew, personal communication, 2004). Discharge of this buffered solution will use up free hydrogen ions in the receiving stream, thus it should not cause or contribute to an existing low pH impairment. New permits having an effluent limit

pH of 6.35 to 9.0 will not be assigned a hydrogen ion load as part of a Waste Load Allocation (WLA).

Remining Permits:

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

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

**General KPDES Permit
for Coal Mine Discharges:**

This permit covers all new and existing discharges associated with coal mine runoff. This permit does not authorize discharges that (1) are subject to an existing individual KPDES permit or application, (2) are subject to a promulgated storm water effluent guidelines or standard, (3) the Director has determined to be or may reasonably be expected to be contributed to a violation of a water of a WQS or to the impairment of a 303(d) listed water, or (4)

are into a surface water that has been classified as an Exceptional or Outstanding or National Resource Water. A signed copy of a Notice of Intent (NOI) form must be submitted to the Kentucky Division of Water (KPDES Branch) when the initial application is filed with the Division of Mine Permits. However, coverage under this general permit may be denied and submittal of an application for an individual KPDES permit may be required based on a review of the NOI and/or other information.

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

Distribution of Load: Because new permits (pH 6.35 to 9.0) should not cause or contribute to the existing impairment and remining permits would be exempt from the TMDL requirements, no load has been provided for the WLA category.

Wasteload and Load Allocation for the Copperas Fork Watershed

Critical Flow (cfs)	TMDL for a pH of 6.0 (lbs/day)	Wasteload Allocation* (lbs/day)	Load Allocation (lbs/day)
5.10	0.0275	0.00	0.0275

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

Implementation/ Remediation Strategy: Remediation of pH-impaired streams as a result of current mining operations is the responsibility of the mine operator. The Kentucky Division of Field Services of the Kentucky Department of Surface Mining Reclamation and Enforcement is responsible for enforcing the Surface Mining Control and Reclamation Act of 1977 (SMCRA). The Kentucky Division of Abandoned Mine Lands (DAML) is charged with performing reclamation to address

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

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

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

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

There are currently no ongoing remediation activities for the Copperas Fork watershed. However, reclamation activities have occurred at other locations within the State where water quality is affected by AMD. Examples of reclamation projects addressing AMD in the Upper Cumberland River watershed are summarized below.

Reclamation Projects Addressing AMD in the Upper Cumberland

Watershed	Project Name	Cost
Back Creek	Pruden-Fonde Reclamation Project	\$840,000
Rock Creek	Rock Creek AMD Abatement Projects	\$1,300,000

For 2000, the total federal Kentucky AML budget allocation was approximately \$17 million. However, the bulk of these funds were used to support Priority 1 (extreme danger of adverse effects to public health, safety, welfare, and property) and Priority 2 (adverse effects to public health, safety, and welfare) projects. Of the total annual federal budget allocation, AML receives only approximately \$700,000 in Appalachian Clean Streams Initiative funds, which are targeted for Priority 3 environmental problems. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the AML program, as well as rearrangement of priorities as established in SMCRA, would be required in order for the AML program to play a significant part in meeting the TMDL implementation requirement associated with pH impaired streams in the state of Kentucky.

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 Copperas Fork watershed is entirely contained within McCreary County, in southeastern Kentucky (Figure 1).

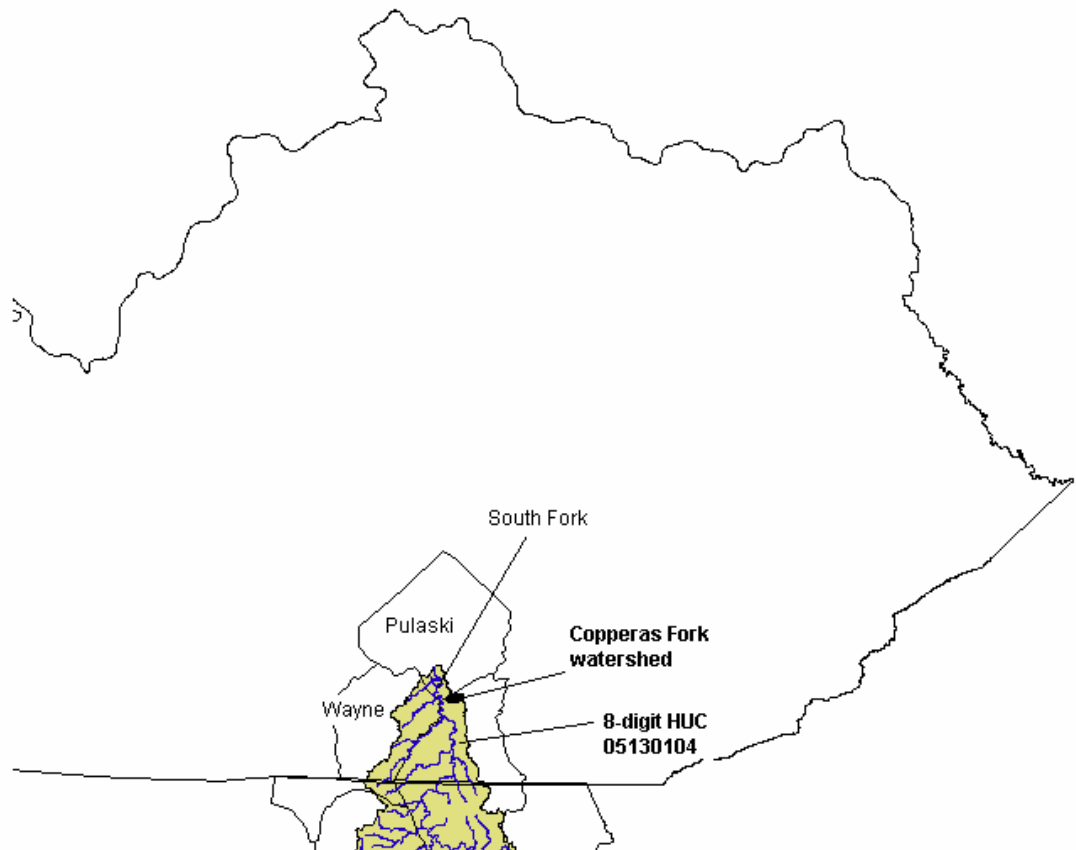


Figure 1. Location of the Copperas Fork Watershed

Hydrologic Information

Copperas Fork, a third order stream, originates in northwestern McCreary County and flows southwest to discharge into Cooper Creek, approximately 2.5 miles upstream from the confluence with South Fork Cumberland River. Copperas Fork's mainstem is approximately 4.36 miles long and drains an area of 2,682 acres (4.19 mi²). The average gradient is 92 feet per mile. Elevations for Copperas Fork range from 1200 feet above mean sea level (msl) in the headwaters to 800 feet above msl at the most downstream point near its confluence with Cooper Creek.

Geologic Information

The Copperas Fork watershed is in the northwestern part of McCreary County, entirely within the Daniel Boone National Forest. The watershed lies in the Mountain and Eastern Coal Fields physiographic region, which is a part of the Cumberland Plateau section of the Appalachian Plateaus Province. This physiographic region is underlain by sedimentary rocks that dip gently to the southeast at about 40 to 60 feet per mile. Formations of limestone, calcareous shale, sandstone, and shale can be found in different parts of the watershed. In western and northern parts of the County, which includes the Copperas Fork watershed, a mantle of silty material covers broad ridgetops (US Department of Agriculture, 1964). The relief of the Copperas Fork watershed ranges from sloping to moderately steep.

Landuse Information

The area can be described as a complex forest that has an abundance of tree species. Because shrubs, herbs, and forbs are numerous and in great variety, this area is of great interest to naturalists. Production of timber products provides a major source of income and employment for the people in McCreary County. About 210,000 acres of the county is woodland, and about 24,000 acres of this is in the Daniel Boone Forest and is administered by the Forest Services. Farming is also an important occupation in the county.

Soils Information

Soils in Copperas Fork watershed are dominated by sandstone and shale and are steep.

Mining and Reclamation History

No pre-law mining permits were found for the Copperas Fork watershed. No records of reclamation projects were discovered in The Kentucky Division of Abandoned Mine Lands (DAML) archives. Mining permits in Kentucky are classified on the basis of whether the original permit was issued prior to May 3, 1978 (pre-law permit), after January 18, 1983 (post-Kentucky primacy) or between these dates (interim period). An explanation of the permit numbering system is provided in Appendix A.

Monitoring History

In 1997, the Kentucky Division of Water (KDOW) conducted an intensive survey to determine the bodies of water in Kentucky to be placed on the 303(d) List of Waters for TMDL Development. Physical and habitat assessments conducted during this survey indicated that Copperas Fork failed to support warm water aquatic habitat (aquatic life) and recreation (swimming) uses because of low pH from resource extraction activities.

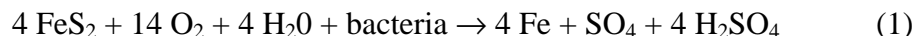
Problem Definition

The 1998 and 2002 303(d) Lists of waters for Kentucky (KDOW, 1998 and 2003) indicate that 3.8 miles of Copperas Fork, from the upstream mile point 3.8 to downstream mile point 0.0 in McCreary County, do not meet the designated uses of primary and secondary contact recreation (swimming and wading) and aquatic life. The Copperas Fork watershed provides a classic example of impairment caused by acid mine drainage (AMD). Bituminous coal mine drainage, like that found in the Copperas watershed, generally contains very concentrated sulfuric acid and may contain high concentrations of metals, especially iron, manganese, and aluminum.

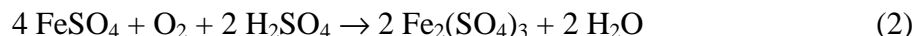
AMD can: (1) ruin domestic and industrial water supplies; (2) decimate aquatic life; and (3) cause waters to be unsuitable for swimming and wading (primary and secondary contact recreation). In addition to these problems, a depressed pH interferes with the natural stream self-purification processes. At low pH levels, the iron associated with AMD is soluble. However, in downstream reaches where the pH begins to improve, most of the ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$] is hydrolyzed to essentially insoluble iron hydroxide [$\text{Fe}(\text{OH})_3$]. The stream bottom can become covered with a sterile orange or yellow-brown iron hydroxide deposit that impacts benthic algae, invertebrates, and fish.

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

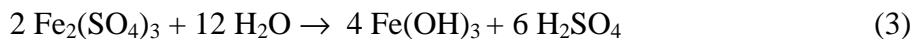
In the process of mining, the iron sulfide (FeS_2) is uncovered and exposed to the oxidizing action of oxygen in the air (O_2), water, and sulfur-oxidizing bacteria. The end products of the reaction are as follows:



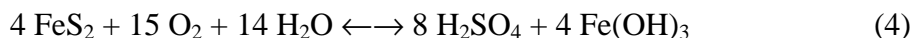
The subsequent oxidation of ferrous iron and acid solution to ferric iron is generally slow. The reaction may be represented as:



As the ferric acid solution is further diluted and neutralized in a receiving stream and the pH rises, the ferric iron [Fe^{3+} or $\text{Fe}_2(\text{SO}_4)_3$] hydrolyses and ferric hydroxide [$\text{Fe}(\text{OH})_3$] may precipitate according to the reaction:



The brownish yellow ferric hydroxide ($\text{Fe}(\text{OH})_3$) 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):



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

Target Identification

The endpoint or goal of a pH TMDL is to achieve a pH concentration and associated hydrogen ion load in lbs/day that supports aquatic life and recreation uses. The pH criterion to protect these uses is in the range of 6.0 to 9.0 (Title 401, Kentucky Administrative Regulations, Chapter 5:031). For a watershed impacted by AMD, the focus will be on meeting the lower criterion. Water quality criteria have not been specified in terms of a particular frequency of occurrence. As pointed out in the recent NRC TMDL report (2001), "All chemical criteria should be defined in terms of magnitude, frequency, and duration. Each of these three components is pollutant-specific and may vary with season. The frequency component should be expressed in terms of a number of allowed flow excursions in a specified period (return period) and not in terms of the low flow or an absolute "never to be exceeded" limit. Water quality criteria may occasionally be exceeded because of the variability of natural systems and discharges from point and nonpoint sources." Small intermittent streams are especially vulnerable to this variability.

The Technical Support Document for Water Quality-Based Toxic Control (EPA, 1991b) 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 have used a 3-year recurrence interval of the average flow as the critical flow. However, this flow resulted in a target discharge that frequently was significantly greater than any of the observed flows for the sites as collected over several years. Thus use of a 3-year flow would require an extrapolation of the observed ion vs. flow model, well beyond the upper limit of the observed data. The selection of the 10-year frequency was based on a consideration of water quality standards (WQSs) (i.e. 7Q10). However, since many of these streams have a 7Q10 of zero, a greater duration was needed. The consensus of the KDOW was to use the 1-year duration. 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

In order to provide a more recent characterization of the pH levels in the watershed, the University of Kentucky conducted additional water quality sampling of Copperas Fork during the summer of 2002 at the site indicated in Figure 2. A summary of the recent results obtained from this site is shown in Table 1 and indicates continued pH degradation in the streamflow discharging from the watershed.

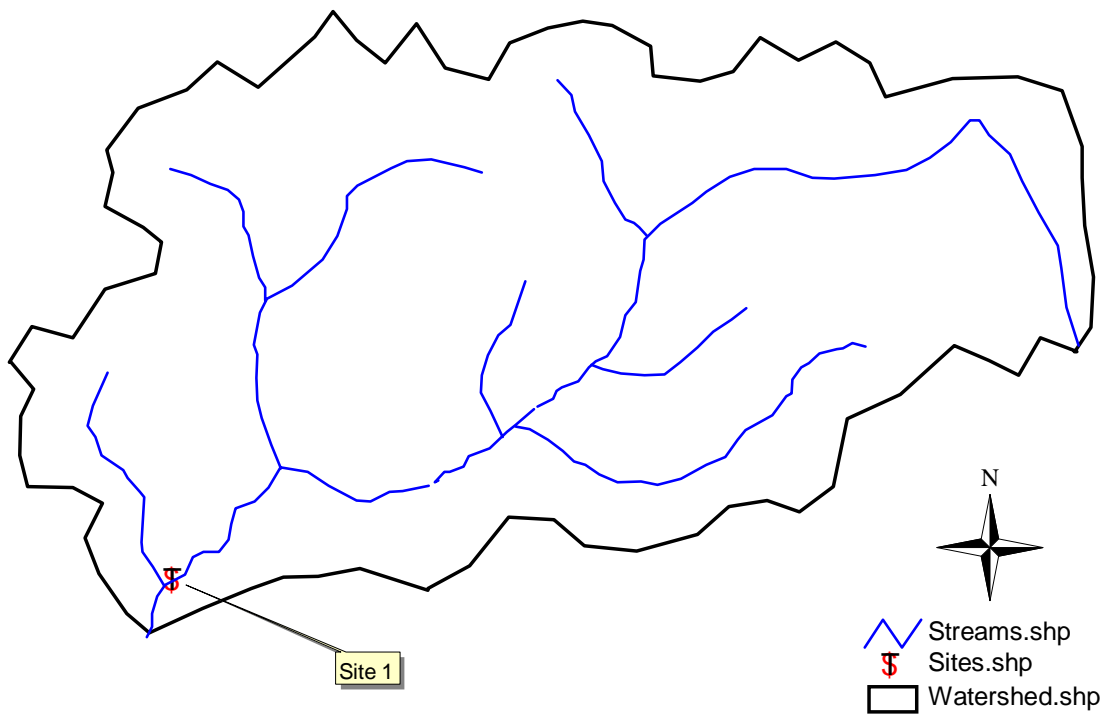


Figure 2. Sampling Site Monitored by the University of Kentucky

Table 1. University of Kentucky Water Sample Results, 2002

Date	Site 1	
	Flow rate (cfs)	pH
3/1/2002	2.78	5.8
3/6/2002	3.08	5.6
3/13/2002	4.86	5.2
3/15/2002	3.92	4.8
3/25/2002	7.81	4.8
3/29/2002	6.37	4.9
4/2/2002	18.25	4.9
4/18/2002	15.02	5.1
4/30/2002	4.34	4.7

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 it includes a MOS. The units of a load measurement are mass of pollutant per unit time (i.e. mg/hr, lbs/day). In the case of pH there is no 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 may not 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:

$$\{\text{H}_3\text{O}^+\} = 10^{-\text{pH}} \text{ or more commonly } \{\text{H}^+\} = 10^{-\text{pH}} \quad (5)$$

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

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

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):

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

Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Figure 3 (Snoeyink and Jenkins, 1980).

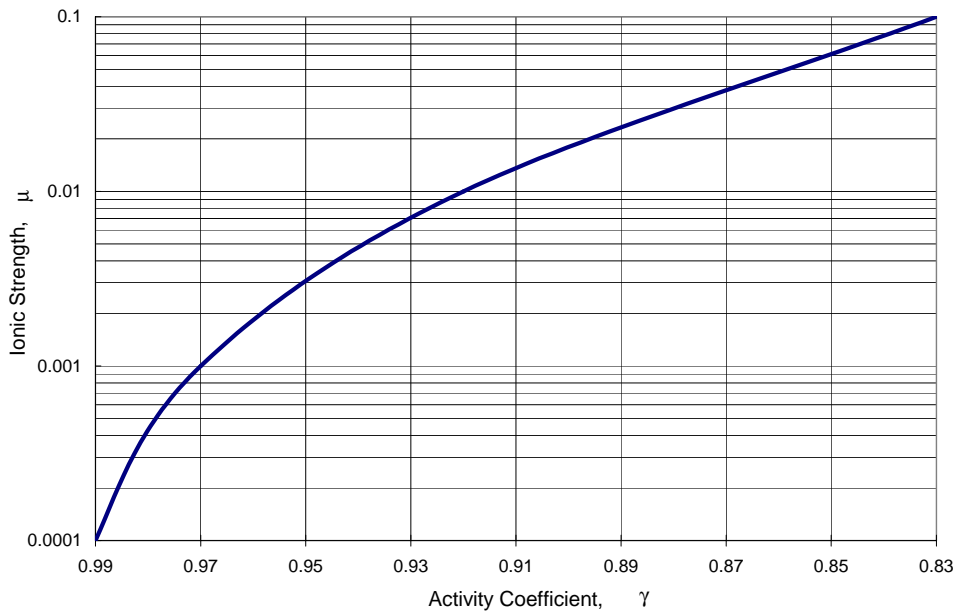


Figure 3. Activity Coefficients of H+ as a Function of Ionic Strength

In the absence of actual measured values of TDS or specific conductance, an estimate of the upper limit of the ionic strength may be obtained from an evaluation of historic values of TDS or specific conductance collected in the area. For example, an evaluation of over 268 measurements of specific conductance obtained from streams in three eastern Kentucky counties namely McCreary, Whitley, and Pulaski revealed a range of values from 2 to 3200 μ ohms/cm. Use of an upper limit of 3200 μ ohms/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 Copperas Fork watershed, specific conductance values were observed to vary from 170 to 3200 μ ohms/cm, which yields ionic strength values from 0.003 to 0.05 respectively. Application of Figure 3 for the observed ionic strengths in Copperas Fork Creek yields activity coefficients of 0.95 to 0.86.

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 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 (e.g. 6) and an associated minimum activity correction factor (e.g. 0.86), 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 4). 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 AMD there obviously exists the possibility of additional ions in the water column that may affect the relationship between the measured activity and the associated ion load. To develop a TMDL for an impaired stream, the most conservative approach would be to assume an activity coefficient of 1.0, which would yield the lowest value for the TMDL for a given range of activity coefficients (see lower TMDL₁ curve in Figure 4). The difference between the maximum TMDL_x (based on the observed activity coefficient) and the minimum TMDL₁ (based on an activity coefficient of 1.0) would provide an explicit 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 Copperas Fork watershed, the TMDL will be established assuming an activity coefficient of 1.0, while the observed load will be determined using an activity coefficient of 0.86, providing for an upper limit for an explicit MOS of approximately 14 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.

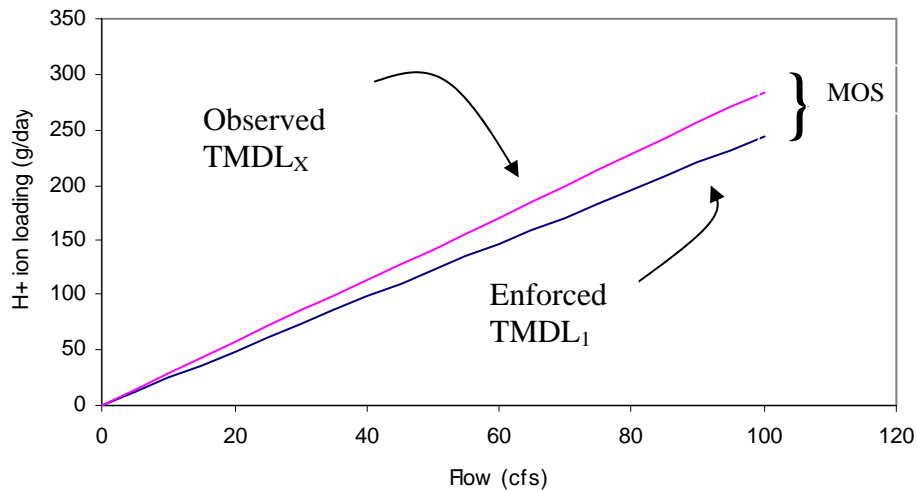


Figure 4. Relationship Between Discharge and Maximum Ion Loading for a pH of 6.0

Hydrogen Loading Example Calculation

In order to demonstrate the hydrogen loading conversion procedure, use the following data for Copperas Fork:

- Critical discharge (Q) = 5.10 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

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

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

$$(0.0000283168 \text{ g/ft}^3) * (5.10 \text{ ft}^3/\text{s}) * (86400 \text{ s}/1 \text{ day}) = 12.46 \text{ g/day, or } 0.0275 \text{ lbs/day}$$

Assuming an activity correction factor of 0.86, the maximum load is 14.48 g/day, or 0.032 lbs/day:

$$12.46 \text{ g/day} / 0.86 = 14.49 \text{ g/day, or } 0.0319 \text{ lbs/day}$$

Thus, by using an activity coefficient of 1.0 instead of 0.86, a MOS of approximately 14 percent is assumed.

Critical Flow and TMDL Determination

Because maximum hydrogen ion loading values can be directly related to flow via Figure 4, the associated allowable ion loading can be directly related to the flow. In order to find the lowest 10-year average annual discharge for the Copperas Fork watershed, a regional hydrologic frequency analysis was used. Regional analysis can be used to develop an inductive model using data collected at streamflow gaging stations that are located in the same hydrologic region as the watershed of interest. For this study, the following US Geological Survey (USGS) gaging stations were selected: 03400500, 03402000, and 03304500. The data from these gages were used to estimate the lowest average annual flows of the most recent 10 years (see Table 2). Since there were no gaging stations that had a contributing drainage area comparable to the watershed under study and for which data was available for the last 10 years, historic data (1950-1960) were used in developing the regional flow-area curve. These discharges were then regressed with watershed area to produce Figure 5. Using this figure, the lowest 10-year mean annual discharge for a given watershed area can be readily determined.

Table 2. Flow Rates (cfs) for Stations in Regional Analysis

	USGS Gaging Station Numbers		
Station	03304500	03402000	03400500
Area (mi ²)	2.14	60.6	82.3
Q (cfs)	1.02	78.9	96.2

Regional Flow Analysis

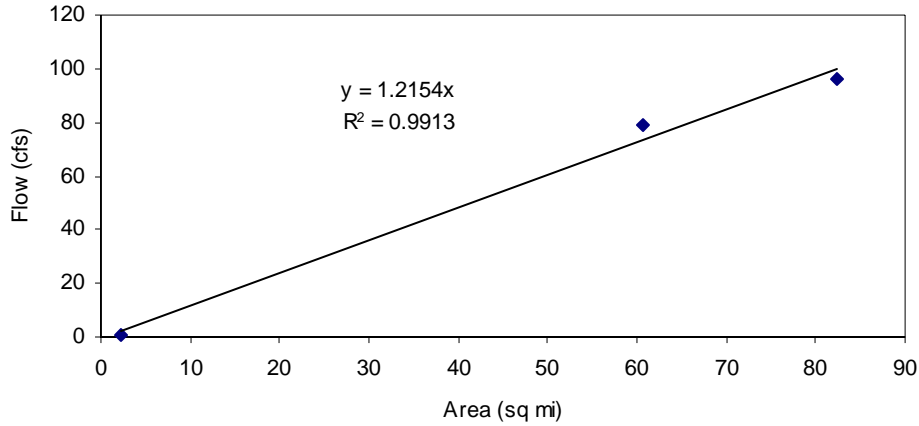


Figure 5. Relationship Between Basin Area and the Critical TMDL Flow

Application of Figure 5 for the Copperas Fork watershed yields a TMDL critical average annual discharge of 5.10 cfs using an upstream watershed area of 4.19 mi² (1.2154 x 4.19 = 5.10). Application of a critical discharge of 5.10 cfs with the lower TMDL₁ curve in Figure 4 yields a TMDL of 0.0275 lbs/day (see Hydrogen Loading Example Calculation on page 10) as shown in Table 3.

Table 3. Critical Flow and Corresponding TMDL for Copperas Fork Watershed

Watershed Area (mi ²)	Critical Q (cfs)	TMDL (lbs/day)
4.19	5.10	0.0275

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 separate TMDL is developed for the entire Copperas Fork 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 spoil areas associated with previous mining activities in the basin. Using the most recent monitoring data, an inductive model was developed at monitoring Site 1 that

relates total hydrogen ion loading to flow. This model is shown in Figure 6 and is derived from the data in Table 1. In developing this model, a conservative value of 0.86 was assumed for the activity coefficient based on the upper limit of measured specific conductance values of 3200 μ ohms/cm. This model will be used in conjunction with the plot of the minimum TMDL₁ curve shown in Figure 4. As discussed previously, this curve was developed assuming an activity coefficient of 1.0, thus providing for an upper limit for a MOS for the TMDL of approximately 14 percent.

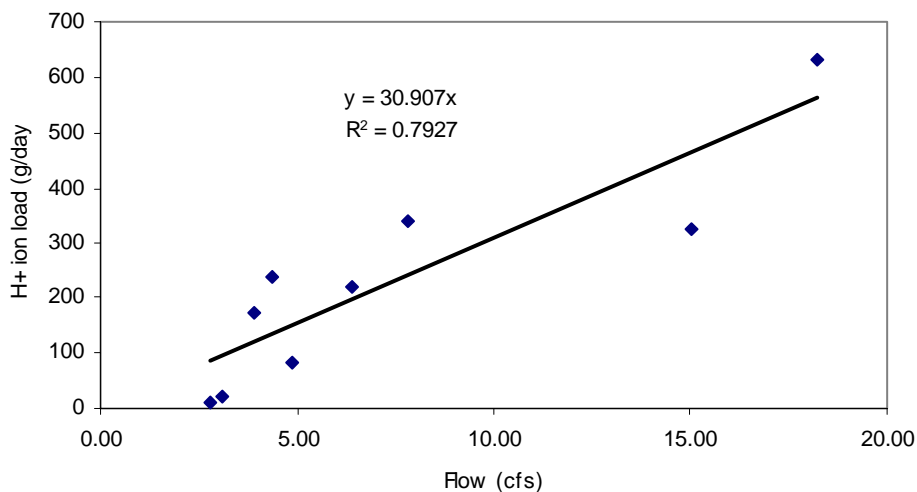


Figure 6. Relationship Between Flow and Ion Load for Site 1

The best trend line through the monitoring data (Figure 6) yields the projected hydrogen ion loading for different flow values. This trend line is based on a regression analysis of the observed field data collected for Site 1. Using the critical flow for the watershed, a projected hydrogen ion loading can be obtained. The lower TMDL curve in Figure 4 can then be used to obtain the TMDL corresponding to the critical flow calculated for the watershed. The difference of the critical loading and the TMDL will be the load reduction required. Note that the TMDL curves in Figure 4 are based on a pH of 6.0.

Predicted Load

The predicted hydrogen ion load for the watershed may be obtained using the critical discharge from Table 3 and the associated load relationship shown in Figure 6. However, in this case, since the monitoring data for use in developing Figure 6 was collected at a point upstream from the outlet of the watershed, the loading relationship is assumed to be proportional to the watershed area. Since the critical discharge was determined based on the total watershed area and the area-flow relationship in Figure 6 is linear, the predicted load at the outlet of the watershed should be equivalent to the load obtained at monitoring Site 1 as adjusted to reflect a larger area. Thus, use of a critical flow of 5.10 cfs (based on the total watershed area) with the fitted line in Figure 6 (based on the data from monitoring Site 1) yields a predicted load of 157.63 g/day ($30.907 \times 5.10 = 157.63$) or 0.348 lbs/day, which is greater than the associated TMDL of 0.0275 lbs/day.

Table 4. Predicted Ion Load for Copperas Fork Watershed

Watershed Area (mi ²)	Critical Flow (cfs)	Predicted load (gm/day)	Predicted load (lbs/day)
4.19	5.10	157.63	0.3476

Load Reduction Allocation

Once a TMDL is developed for a watershed, the needed load reductions can be determined. One way to accomplish this objective is through the use of unit load reductions applied to different land uses within the watershed. The impacts of such reductions in meeting the WQS can then be verified through mathematical simulation. Alternatively, separate TMDLs and associated load reductions can be developed for individual subbasins within the watershed. In the current study, a TMDL and associated load reduction were developed for the entire Copperas Fork watershed.

Translation of the TMDL in Table 3 into an associated daily load reduction for the watershed may be accomplished by subtracting the incremental TMDL from the predicted load for the watershed (Table 4). Application of this approach yields the values in Table 5 ($0.3476 - 0.0275 = 0.3201$).

Table 5. TMDL Summary and Reduction Needed for Copperas Fork Watershed

Watershed Area (mi ²)	Critical Flow (cfs)	TMDL for a pH of 6.0 (lbs/day)	Predicted load (lbs/day)	Load reduction needed (lbs/day)
4.19	5.10	0.0275	0.3476	0.3201

Permitting

New Permits

New permits (except for new remining permits) for discharges to Copperas Fork could be allowed contingent upon end-of-pipe pH limits in the range of 6.35 to 9.0 standard units. WQSs state that the pH value should not be less than 6.0 nor greater than 9.0 for meeting the designated uses of aquatic life and swimming. This range of 6.0 to 9.0 for pH is generally assigned as end-of-pipe effluent limits. However, because a stream impairment exists (low pH), new discharges should not cause or contribute to an existing impairment. Application of agricultural limestone on mine sites results in highly buffered water leaving the site. A buffered solution with nearly equal bicarbonate and carbonic acid components will have a pH of 6.35 (Carew, personal communication, 2004). Discharge of this buffered solution will use up free hydrogen ions in the receiving stream, thus it should not cause or contribute to an existing low-pH impairment. New permits having an effluent limit pH of 6.35 to 9.0 will not be assigned a hydrogen ion load as part of a WLA.

Remining Permits

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

The eventual reclamation of the remining site should result in a reduction of the nonpoint source ion load of the subbasin. The reclamation should also result in an improved stream condition (increased pH) because a previously disturbed and unreclaimed area will be reclaimed. Follow-up, in-stream monitoring would need to be done at the subbasin outfall to determine the effect of reclamation activities following remining on the overall ion load coming from the subbasin.

General KPDES Permit for Coal Mine Discharges

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

Antidegradation Policy

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

Distribution of Load

Because new permits (pH 6.35 to 9.0) would not contribute to an existing impairment and reming permits would be exempt from the TMDL requirements, no load has been provided for the WLA category (Table 6).

Table 6. Wasteload and Load Allocation for the Copperas Fork Watershed

Critical Flow (cfs)	TMDL for a pH of 6.0 (lbs/day)	Wasteload Allocation* (lbs/day)	Load Allocation (lbs/day)
5.10	0.0275	0.00	0.0275

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

Implementation/Remediation Strategy

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

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

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

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

There are currently no remediation activities underway in the Copperas Fork watershed. However, reclamation activities have occurred at other locations within the state where AMD affects water quality. Examples of reclamation projects addressing AMD in the Upper Cumberland River watershed are summarized in Table 7.

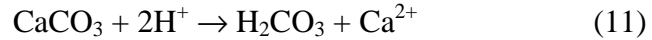
Table 7. Reclamation Projects Addressing AMD in the Upper Cumberland Watershed

Watershed	Project Name	Cost
Back Creek	Pruden-Fonde Reclamation Project	\$840,000
Rock Creek	Rock Creek AMD Abatement Projects	\$1,300,000

For 2000, the total federal Kentucky AML budget allocation was approximately \$17 million. However, the bulk of these funds were used to support Priority 1 (extreme danger of adverse effects to public health, safety, welfare, and property) and Priority 2 (adverse effects to public health, safety, and welfare) projects. Of the total annual federal budget allocation, AML receives only approximately \$700,000 in Appalachian Clean Streams Initiative funds, which are targeted for Priority 3 environmental problems. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the AML program, as well as a rearrangement of priorities as established in SMCRA, would be required in order for the AML program to play a significant part in meeting the TMDL implementation requirement associated with pH impaired streams in the state of Kentucky.

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, CaCO₃ may be used to neutralize free hydrogen ions based on the following relationship:



Thus, the theoretical total mass of CaCO₃ required to neutralize 1 gm of H⁺ ions can be obtained by dividing the molecular weight of CaCO₃ (100) by the molecular weight of 2 hydrogen atoms (2) to yield:

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

Or, in terms of a required annual load:

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

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 CaCO₃, and 2) an increasing fraction of the CaCO₃ mass will be required to neutralize other metal ions (e.g. Fe, Al, Mn) that will also most likely be present in the AMD, 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 CaCO₃).

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 AMD 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 CaCO₃ 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 CaCO₃ (required to neutralize both the hydrogen ions and other free ions) can also be determined such as the one shown in Figure 7. In this particular case, Figure 7 was constructed from an analysis of data from five separate watersheds in the eastern 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.

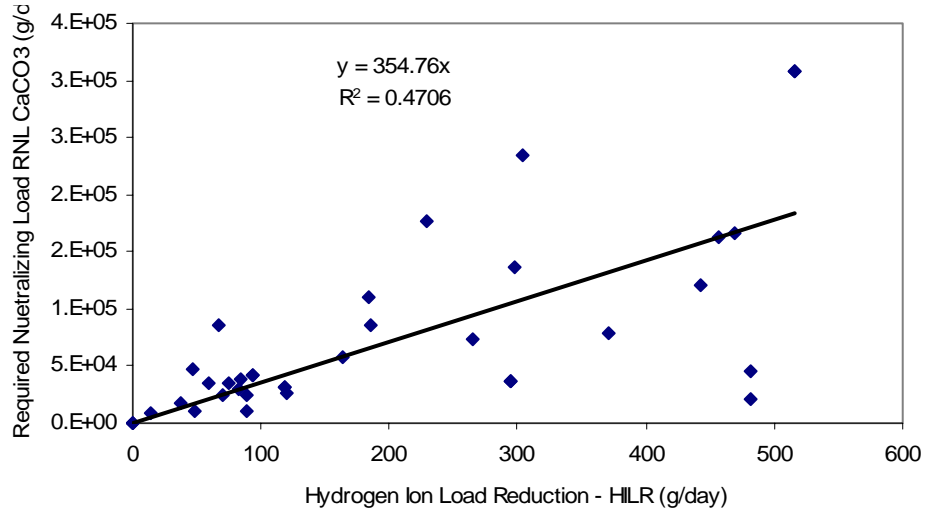


Figure 7. CaCO₃ Loading vs. Required Hydrogen Ion Reduction

For the case of Copperas Fork, site-specific stream acidity data were not collected as part of the overall sampling effort. As a result, the required CaCO₃ 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 CaCO₃ loading required initially for a particular stream. Subsequent applications of limestone can be further refined through follow-up monitoring.

Application of Figure 7 using the required hydrogen ion load reduction values shown in Table 5 yields the corresponding values of CaCO₃ loadings shown in Table 8 ($354.76 \times 145.17 = 51,501$). 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 in order to provide a conservative estimate of the initial loading. Loading values for subsequent years can be modified by an analysis of pH values obtained from subsequent field monitoring.

Table 8. CaCO₃ Loading for Copperas Fork Watershed

Required reduction (lbs/day)	Required reduction (g/day)	CaCO ₃ loading (g/day)	CaCO ₃ loading (lbs/day)	CaCO ₃ loading (tons/yr)
0.3201	145.17	51,501	114	21

Public Participation

This TMDL was placed on 30-day public notice and made available for review and comment from Nov. 15 through Dec. 16, 2005. The public notice was prepared and published as an advertisement in the News Journal and the McCreary County Record, newspapers with wide circulation in Whitley and McCreary Counties, respectively. A press release was also distributed to newspapers statewide. In addition, the press release was submitted to approximately 275 persons via a Kentucky Nonpoint Source electronic mailing distribution list.

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

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APPENDIX A: MINING PERMITS NUMBERING SYSTEM

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

XXX-XXXX Permit issues after May 3, 1978. The first three numbers indicate the location of the mine by county and the timing of the original permit issuance.

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

If 200 have been added to the county number, the permit was originally issued prior to May 3, 1978, and carried through into the interim program.

If 400 has been added to the county number the permit was issued prior to the Permanent Program and was to remain active after January 18, 1983.

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

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

COAL

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

NON-COAL

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