

Methodology for pH Total Maximum Daily Loads: Application to Beech Creek Watershed

Lindell Ormsbee, P.E., M.ASCE¹; Amin Elshorbagy, M.ASCE²; and Emily Zechman³

Abstract: This paper presents a methodology for developing total maximum daily loads (TMDLs) for pH impaired streams that characterizes the pH impact in terms of an associated hydrogen ion load. Because pH and an equivalent 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., 6.0) and an associated ion activity correction factor, an envelope of ion loads may be obtained as a function of discharge. By identifying a critical discharge for a given watershed, the hydrogen ion load and associated TMDL can be obtained. Determination of the associated ion load reduction can further be accomplished by developing functional relationships between measured discharges and measured ion loads for a given watershed. Finally, the required mass loading of an associated neutralizing agent (e.g., CaCO₃) can be determined by constructing a functional relationship between the neutralizing agent and the required hydrogen ion reduction. The proposed approach has been applied to several watersheds in the state of Kentucky and was recently approved by EPA Region IV as an acceptable protocol for pH TMDLs. An application of the methodology is presented for the Beech Creek watershed, which is located in Muhlenberg County, Kentucky.

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Introduction

Section 303(d) of the Clean Water Act (33 U.S.C. 1313) requires 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).

Beginning in 1997, the state of Kentucky launched a comprehensive watershed management initiative in support of TMDL development efforts for the 303(d) listed water bodies in the state. Because of significant mining operations in both eastern and western Kentucky, many streams fail to meet their designated use for aquatic life and primary recreational contact as measured by pH as a result of acid mine drainage. After an extensive literature

and programmatic search failed to reveal any established protocol for the development of TMDLs for pH impaired streams, the Kentucky Division of Water (KYDOW) contracted with the University of Kentucky to develop such a protocol. The developed protocol, which was recently approved by Region IV of EPA, presents a methodology for developing pH TMDLs that characterizes the pH impairment in terms of an associated hydrogen ion load.

Acid Mine Drainage

Acid mine drainage (AMD) can (1) ruin domestic and industrial water supplies, (2) decimate aquatic life, and (3) cause waters to be unsuitable for swimming (primary contact recreation). In addition to these problems, a depressed pH interferes with the natural stream self-purification processes. At low pH levels, the iron associated with AMD is soluble. However, in downstream reaches where the pH begins to improve, most of the ferric sulfate [Fe₂(SO₄)₃] is hydrolyzed to essentially insoluble iron hydroxide [Fe(OH)₃]. The stream bottom can become covered with a sterile orange or yellow-brown iron hydroxide deposit that is deleterious to benthic algae, invertebrates, and fish.

The sulfuric acid in AMD is formed by the oxidation of sulfur contained in the coal and/or the rock or clay found above and below the coal seams. Most of the sulfur in the unexposed coal is found in a pyritic form as iron pyrite and marcasite (both having the chemical composition FeS₂). In the process of mining, the iron sulfide (FeS₂) is uncovered and exposed to the oxidizing action of oxygen in the air (O₂), 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



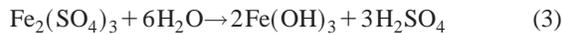
¹Interim Director, Tracy Farmer Center for the Environment, Univ. of Kentucky, Lexington, KY 40506-0281. E-mail: lormsbee@engr.uky.edu

²P.Eng., Assistant Professor, Dept. of Civil and Geological Engineering, Univ. of Saskatchewan, Saskatoon SK, Canada S7N 5A9. E-mail: elshorbagy@engr.usask.ca

³P.Eng., Research Associate, Dept. of Civil Engineering, North Carolina State Univ., Raleigh, NC 27695-7908. E-mail: emilyzechman@hotmail.com

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As the ferric acid solution is further diluted and neutralized in a receiving stream and the pH rises, the ferric iron $[\text{Fe}^{3+}]$ or $\text{Fe}_2(\text{SO}_4)_3$ is hydrolyzed 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 streambanks 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 Eq. (4)



Reaction (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.

Total Maximum Daily Load Development

The total maximum daily load is a term used to describe the maximum amount of a pollutant a stream can assimilate without violating water quality standards. The units of a load measurement are mass of pollutant per unit time (e.g., mg/h, lb/day). In the case of pH, there is no associated mass unit (pH is measured in standard units). As a result, it is proposed that the total load be expressed in terms of an equivalent hydrogen ion load.

Total maximum daily loads 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. The sum of these components cannot exceed applicable water quality standards (WQs) for a given waterbody and associated watershed. In addition, the TMDL must include a margin of safety (MOS), either implicitly or explicitly, that accounts for the uncertainty in the relation between pollutant loads and the quality of the receiving water body. Conceptually, this definition is denoted by the equation

$$\text{TMDL} = \text{sum}(\text{WLAs}) + \text{sum}(\text{LAs}) + \text{MOS} \quad (5)$$

The end point or goal of a pH TMDL is to achieve a pH (and associated hydrogen ion load in lb/day) that allows for the sustainability of aquatic life in a particular stream reach. The chronic pH criterion to protect warm water aquatic habitat use in Kentucky requires that the pH be maintained between 6.0 and 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. Unfortunately, the current water quality criteria have not been specified in terms of a particular frequency of occurrence. As pointed out in the recent National Research Council (NRC) TMDL report (NRC 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. The requirement of 'no exceedances' for many water quality criteria is not achievable given natural variability alone, much less with the variability associated with discharges from point and non-point sources." Certainly, such is the case in developing TMDLs for pH impairment when the violations are caused by nonpoint sources on small intermittent streams and where the 7Q10 flow may actually be zero.

The "Technical Support Document for Water Quality-Based Toxic Control" (EPA 1991) states that daily receiving water concentrations (loads) can be ranked from the lowest to the highest without regard to time sequence. In the absence of continuous monitoring, such values can be obtained through continuous simulation or Monte Carlo analysis. A probability plot can be constructed from these ranked values, and the occurrence frequency of any 1 day concentration of interest can be determined. Where the resultant frequency exceeds that of the stated target value (e.g., 10 years), associated load reductions will be required until the resultant concentration satisfies the stated target value and its associated exceedance frequency. Where the load and the resultant target indicator (i.e., pH) can be directly related through discharge (flow rate), the frequency of the associated discharge can be directly related to the frequency of the target value (i.e., pH).

In recognition of the inherent difficulties associated with imposition of a "no-exceedance" pH criteria on potentially intermittent streams, the Kentucky Division of Water has decided to use the lowest 1 year average discharge of the most recent 10-year flow record as the flow basis for setting the appropriate TMDL and associated loading reduction. Use of an average annual flow as the basis for determining the TMDL also provides a convenient mechanism for determining the total annual load as well as the total annual reduction that would be derived from an annual summation of both the daily TMDLs and 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 annual flow) by 365 days. Likewise, the equivalent total annual load reduction can be obtained by multiplying the average annual load reduction (derived by using the average annual flow) by 365 days. Although the 10 year average lowest 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 volume of flows. For actual daily flows less than average flow, incremental load reductions may be accomplished by explicit imposition of a pH standard of 6 units.

Equivalent Hydrogen Ion Load

In the absence of any nationally recognized standard for pH TMDL development, a loading methodology is proposed in which pH is expressed in terms of an equivalent hydrogen ion load and associated flowrate. 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:

$$\{\text{H}_3\text{O}^+\} = 10^{-\text{pH}} \quad \text{or more commonly} \quad \{\text{H}^+\} = 10^{-\text{pH}} \quad (6)$$

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 measured activity is divided by an activity coefficient γ

$$[\text{H}^+] = \{\text{H}^+\} / \gamma \quad (7)$$

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 total dissolved solids (TDS) (mg/L or ppm) and applying the following relationship (Snoeyink and Jenkins 1980):

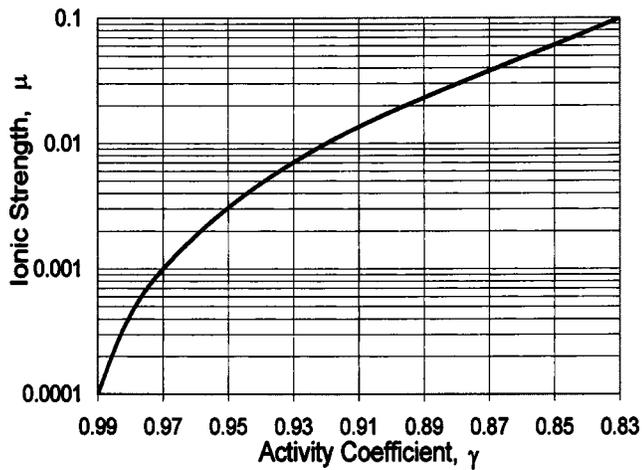


Fig. 1. Activity coefficients of H^+ as a function of ionic strength (Snoeyink and Jenkins 1980)

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

Alternatively, the ionic strength of a given source of water may be related to the measured specific conductance (SC) ($\mu \Omega/\text{cm}$) through the following relationship (Snoeyink and Jenkins 1980):

$$\mu = (1.6 \times 10^{-5}) \times \text{SC} \quad (9)$$

Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Fig. 1 (Snoeyink and Jenkins 1980). In the absence of actual measured values of TDS or specific conductance, a conservative estimate 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 1,600 measurements of specific conductance obtained from streams in the eastern Kentucky coal fields (Grubb and Ryder 1972; Kentucky Division of Water 1981; USGS 1983) has revealed a range of values from 45 to 5,920 $\mu\Omega/\text{cm}$. Use of a conservative upper limit of 6,000 $\mu\Omega/\text{cm}$ yields an ionic strength of 0.096 or approximately 0.10. Use of a conservative value of ionic strength of 0.10 yields a lower limit of the activity coefficient of approximately 0.83.

The atomic weight of hydrogen is 1 g per mole so the concentration of hydrogen ions in mol/L is also the concentration in g/L. Multiplying the concentration of hydrogen ions by the average flow rate for a given day results in a hydrogen ion load for that day in 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., 0.83), 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 Fig. 2). However, in the case of developing 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 Fig. 2).

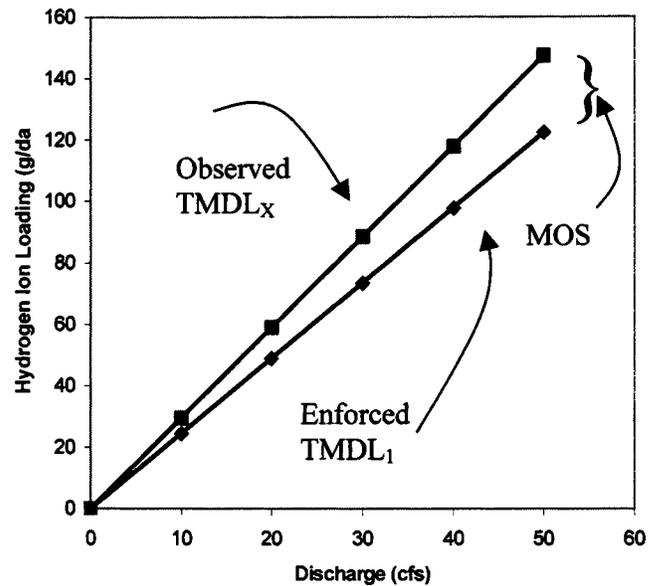


Fig. 2. Relationship between discharge and maximum ion loading for pH of 6.0

Margin of Safety

As indicated previously, all TMDLs require a margin of safety. There are two basic methods for incorporating the MOS (EPA 1997):

1. Implicitly incorporate the MOS using conservative model assumptions.
2. Explicitly specify a portion of the total TMDL as the MOS using the remainder for allocations.

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. The difference between the maximum TMDL_X (based on the observed ion activity coefficient of X) and the minimum TMDL_1 (based on an activity coefficient of 1.0) provides an explicit margin of safety in setting the TMDL for the stream as well as for calculating the associated load reduction (see Fig. 2). Thus, in developing a TMDL for a particular watershed, the TMDL for each subbasin will be established assuming an activity coefficient of 1.0, while the observed load will be determined using an observed activity coefficient of X (where $X < 1.0$), thus providing for an upper limit for an explicit margin of safety of approximately $(1.0 - X) \times 100\%$ (see the Appendix for an example application).

Application

The 2002 303(d) list of waters for Kentucky (Kentucky Division of Water 2002) indicates that 3.4 miles of Beech Creek, from the headwaters to the confluence with Pond Creek in Muhlenberg County, does not meet its designated use for both contact recreation (swimming) and aquatic life. The Beech Creek watershed is entirely contained within Muhlenberg County in southwestern Kentucky (Fig. 3). Muhlenberg County is bounded on the northeast by the Green River, on the southeast by the Mud River, and on the west by the Pond River. The Beech Creek watershed provides a classic example of impairment caused by AMD. Bituminous coal mine drainage, like that found in the Beech Creek wa-

Western Kentucky

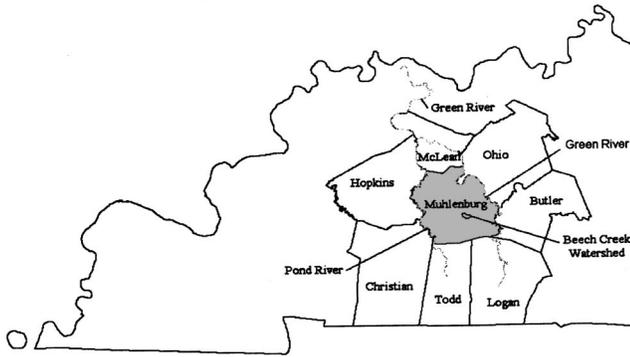


Fig. 3. Location of Beech Creek watershed

tershed, contains very concentrated sulfuric acid and high concentrations of metals, especially iron, manganese, and aluminum.

Hydrologic Information

Beech Creek, a third-order stream, originates in southeastern Muhlenberg County and flows westward to discharge into the Pond Creek 25.06 km (15.62 mi) upstream from its confluence with the Green River. The Green River carries the runoff northward to discharge into the Ohio River.

Beech Creek's mainstem is approximately 5.47 km (3.4 mi) long and drains an area of 1,067 ha (2,637 acres or 4.12 sq mi). The average gradient is 2.4 m/km (12.8 ft/mi). Elevations for Beech Creek range from 152 m (500 ft) above mean sea level (MSL) in the headwaters to 137 m (450 ft) above MSL at the mouth. Like most of the smaller watersheds, many of the tributary streams are intermittent.

Geologic Information

The Beech Creek watershed is in the Western Coal Field physiographic region. The surface bedrock is of Pennsylvanian age. Formations of the Pennsylvanian age are mostly sandstone, siltstone, coal, and interbedded limestone and shale; alluvial deposits of siltstone and cross-bedded sand or sandstone underlie the extensive lowland areas (USDA 1980). The relief of the Beech Creek watershed ranges from nearly level to steep. Gently sloping (2–6%) to steep soils (12–35%) are found in the uplands and nearly level soils are found on the floodplain.

Land-Use Information

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

Soil Information

Beech Creek watershed is dominated by nearly level loamy and clayey soils near to the mouth and level to steep loamy soils in the

Table 1. Lowest 10 Year Mean Annual Flow Rates (cfs) for Stations in Regional Analysis

Station numbers	3384000	3321350	3320500	3383000
Area (mi ²)	2.10	58.20	194.00	246.00
Area (ha)	544	15,073	50,244	63,712
Q (cfs)	0.69	49.10	99.70	166.00
Q (L/s)	19.5	1,390	2,823	4,701

headwaters. Most of the watershed is Udorthents soil, which consists of strip mine spoil containing rock fragments (USDA 1980).

Watershed History

Mining activities in the Beech Creek watershed occurred prior to 1977. The waters of Beech Creek were monitored as early as 1978 by the Kentucky Division of Water (1981). In 1997, the KYDOW conducted another intensive survey of streams in the Western Kentucky Coal Fields, including Beech Creek. The Kentucky DOW reported that on July 2, 1997, Beech Creek could not support aquatic life and swimming use based on an observed pH reading of 2.7. The observed cause of pH impairment was surface mining activities and resource extraction.

Total Maximum Daily Load Development for Beech Creek Watershed

Because hydrogen ion loading values can be directly related to discharge (e.g., Fig. 2), an associated allowable ion loading exceedence frequency can be directly related to the frequency of the discharge. In order to find the lowest 10 year average annual discharge for the Beech Creek watershed, a regional hydrologic frequency analysis was used. Regional analysis can be used to develop an inductive model using data that has been collected at streamflow gauging stations that are located in the same hydrologic region as the watershed of interest. For this study, the following USGS gauging stations were selected: 03320500, 03384000, 03383000, and 03321350. The data from these gauges were used to estimate the lowest average annual flows of the most recent 10 years (see Table 1). These discharges were then regressed with watershed area to produce Fig. 4. Using this figure, the lowest 10 year mean annual discharge for a given watershed area can be readily determined.

Application of Fig. 4 for the Beech Creek watershed yields a lowest 10 year mean annual discharge of 72.5 L/s (2.56 cfs), assuming a watershed area of 1,067 ha (4.12 mi²). Use of this discharge with the lower curve in Fig. 2 yields a TMDL of 6.26 g/day (0.014 lb/day) of hydrogen ions. The lowest 10 year mean annual discharges for each individual subbasin are obtained using a simple mass balance technique. For a mass balance to be obtained, the flow at the outlet must equal the summation of the incremental flows at each subbasin. Therefore, the calculated outlet flow is distributed throughout the watershed based on subbasin area. This process gives the larger subbasins a larger incremental flow; likewise, it gives the smaller subbasins a lesser flow. These incremental flows can be used in conjunction with Fig. 2 to obtain incremental TMDL's for each subbasin (see Table 2).

Incorporation of a Margin of Safety into Total Maximum Daily Load

Specific conductance values in Beech Creek have been found to range from 1,650 to 1,900 $\mu\Omega/\text{cm}$, which yield ionic strength

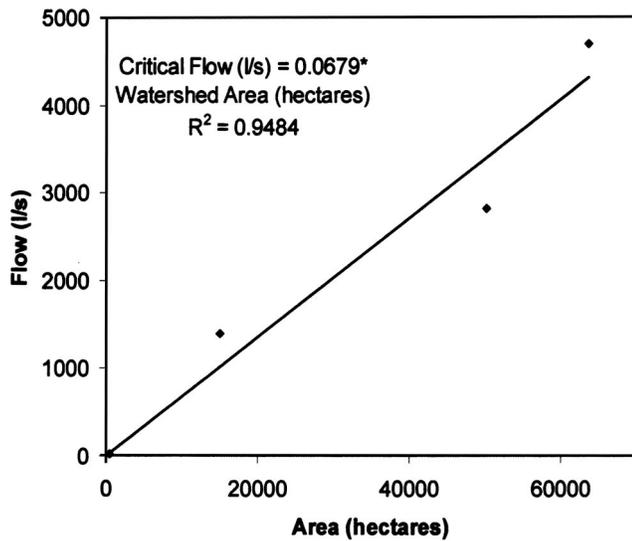


Fig. 4. Relationship between basin area and lowest 10 year mean annual flow

values of between 0.026 and 0.030. Application of Fig. 1 for the observed ionic strengths in Beech Creek yields an activity coefficient of approximately 0.88. In developing a pH TMDL for Beech Creek, a conservative activity coefficient of 1.0 was assumed, thus providing for an explicit margin of safety of approximately 12% in determining the associated TMDL. As a result, Eq. (5) can be rewritten in terms of the enforced TMDL₁ as follows:

$$\text{TMDL}_1 = \text{sum(WLAs)} + \text{sum(LAs)} \quad (10)$$

where

$$\text{TMDL}_1 = \text{TMDL}_x - \text{MOS} \quad (11)$$

Total Maximum Daily Load Allocation

Once the TMDL for the watershed has been determined, the associated load must be allocated between both point loads (wasteload allocations) and nonpoint source loads (load allocations). There are no known permitted point sources in this watershed. As a result, the wasteload allocations for the Beech Creek Watershed are assumed to be zero. Thus, the remaining load allocations are directly equal to the enforced TMDL₁ as follows:

$$\text{sum(LAs)} = \text{TMDL}_1 \quad (12)$$

Thus, the load allocations for each subbasin are simply equivalent to the associated incremental TMDLs as shown in Table 2.

Table 2. Lowest 10 Year Mean Annual Incremental Flows and Corresponding Total Maximum Daily Loads

Location	Area (ha)	Area (mi ²)	Q (L/s)	Q (cfs)	Incremental TMDL	
					(g/day)	(lb/day)
Total watershed	1,067	4.12	72.5	2.56	6.26	0.014
Subbasin 1	324	1.25	22.1	0.78	1.90	0.004
Subbasin 2	743	2.87	50.4	1.78	4.36	0.010

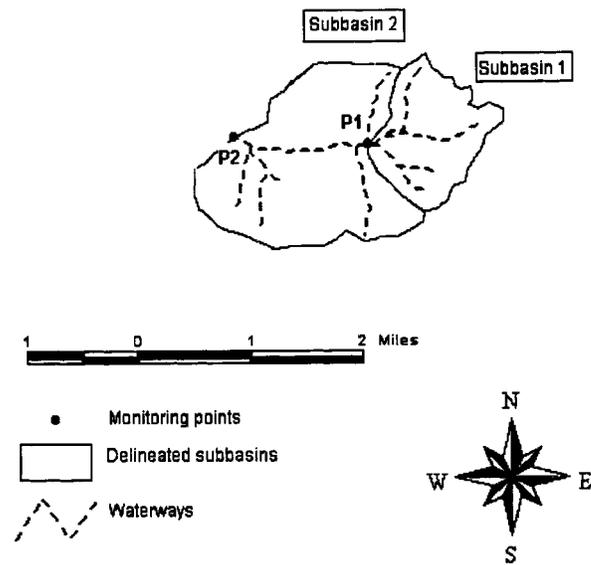


Fig. 5. Beech Creek watershed sampling sites monitored by Murray State University personnel

Predicted Load Assessment

Point Source Loads

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

Nonpoint Source Loads

Several nonpoint loading sources were identified in the Beech Creek watershed. In order to provide a more recent characterization of the pH levels in the watershed, the University of Kentucky (as part of the study contract with the KYDOW) subcontracted with Murray State University to collect additional data from the watershed at the sites indicated in Fig. 5. A summary of the results obtained from these sites is shown in Table 3.

Based on a physical inspection of the watershed, it is hypothesized that the degradation of the pH in the stream is directly related to the oxidation of sulfur that occurs as runoff flows over the spoil areas associated with previous mining activities in the basin. Using the most recent monitoring data, inductive models were developed for each monitoring site that relate total hydrogen ion loading to streamflow. The models developed for subbasins 1 and 2 are shown in Figs. 6 and 7 and were developed using a conservative estimate of 0.88 for the associated ion activity coef-

Table 3. Murray State Sample Results

Date	Site P1			Site P2		
	Q (L/s)	Q (cfs)	pH	Q (L/s)	Q (cfs)	pH
10/24/2000	0.28	0.01	2.74	0.85	0.03	2.6
11/7/2000	1.7	0.06	3.12	5.1	0.18	2.89
11/9/2000	12.46	0.44	3.49	53.8	1.9	3.06
3/27/2000	13.03	0.46	3.15	26.62	0.94	3.31
4/20/2001	0.57	0.02	3.3	15.01	0.53	3.19
8/13/2001	0.28	0.01	2.94	3.68	0.13	2.85
8/22/2001	0	0.0	—	2.83	0.1	2.93
1/9/2002	4.25	0.15	3.58	14.44	0.51	4.5

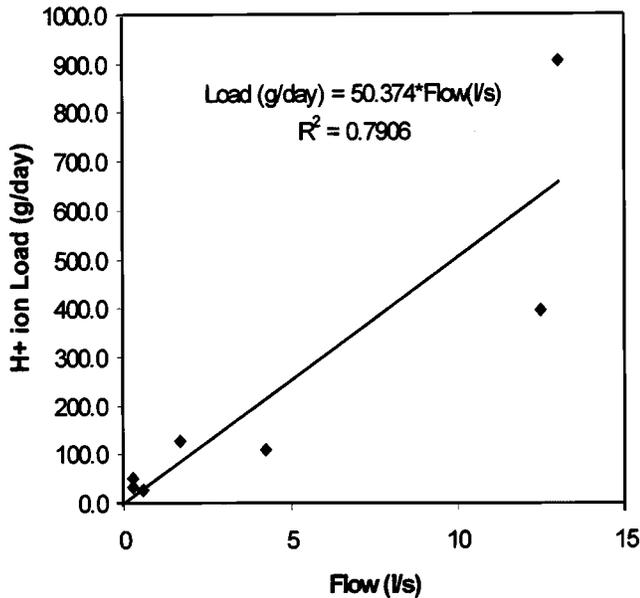


Fig. 6. Flow versus ion loading for pH for site P1

ficient (based on an upper limit of measured specific conductance values for Beech Creek of 1,900 $\mu\Omega/\text{cm}$). As can be seen from the figures, the total load increases as a function of flow, illustrating the significant relationship between the pH degradation and nonpoint sources. The developed relationships may be used to predict total ion loading to a stream on the basis of streamflow.

The predicted hydrogen ion loads for each site may be obtained using the critical discharges from Table 2 along with the associated load relationships (e.g., Figs. 6 and 7). Application of this approach yields the predicted loads for each site as shown in Table 4. Note that for an independent tributary, the incremental load is equal to the cumulative load for that tributary. On the other hand, a subbasin that has flows entering from adjacent or upstream subbasins requires a mass balance application to find the incremental load. For example, the incremental load for subbasin 2 is determined by subtracting the cumulative load for subbasin 1 from the cumulative load for subbasin 2.

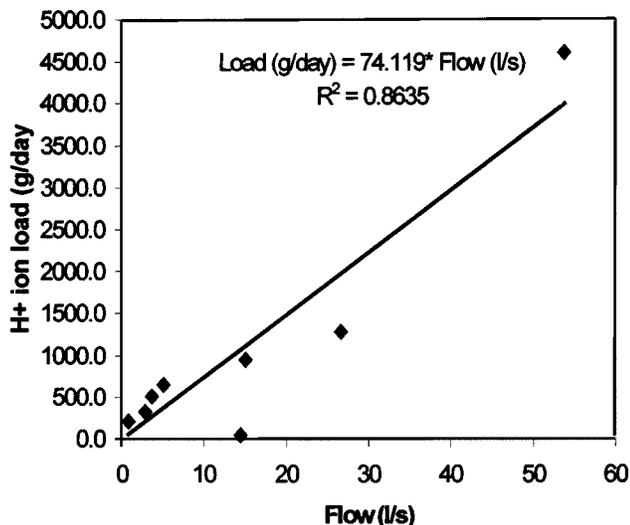


Fig. 7. Flow versus ion loading for pH for site P2

Table 4. Predicted Ion Loads

Subbasin	Q (cfs)	Q (L/s)	Load (g/day)	Load (lb/day)	Inc. (lb/day)
1	22.09	0.78	1,107	2.435	2.435
2	72.49	2.56	5,372	11.820	9.385

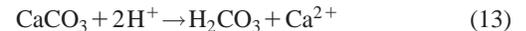
Load Reduction Allocation

Once a TMDL is developed for a watershed, the required load reductions can be found by determining the amount of load that must be reduced in order to lower the in-stream load at or below the TMDL. 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 water quality standard can then be verified through mathematical simulation. Alternatively, separate TMDLs (and associated load reductions) can be developed for individual subbasins within the watershed. In the current study, separate TMDLs and associated load reductions were developed for each of the subbasins identified in Fig. 5. Attainment of the individual load reductions should then meet the TMDL requirement for the complete watershed.

Translation of the incremental TMDLs in Table 2 into associated daily load reductions for each site may be accomplished by subtracting the incremental TMDLs from the incremental predicted loads for each subbasin (Table 4). This approach allocates the total load reduction for Beech Creek (site 2) between each of the contributing sites in the watershed, so that the entire watershed is rehabilitated and the pH is improved throughout the stream network. Application of this approach yields the values in Table 5.

Implementation Guidelines

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 $\text{pH} < 6$, CaCO_3 may be used to neutralize free hydrogen ions based on the following relationship:



Thus, the theoretical total mass of CaCO_3 required to neutralize 1 g of H^+ ions can be obtained by dividing the molecular weight of CaCO_3 (100) by the molecular weight of two hydrogen atoms (2) to yield

$$\text{required mass of limestone} = 50 \times \text{mass of hydrogen ions} \quad (14)$$

or, in terms of a required annual load

Table 5. Total Maximum Daily Load Summary for Beech Creek

Location	Incremental area (ha)	Incremental area (mi^2)	Incremental TMDL at $\text{pH} = 6.0$ (lb/day)	Predicted load (lb/day)	Required load reduction (lb/day)
Total	1,067	4.12	0.014	11.820	11.806
Subbasin 1	324	1.25	0.004	2.435	2.431
Subbasin 2	743	2.87	0.010	9.385	9.375

annual required mass of limestone

$$= 18,250 \times \text{mass of hydrogen ions (g/day)} \quad (15)$$

In practice, however, this value will represent only a lower bound of the required mass as a result of two issues: (1) the fact that not all the limestone added to a stream will be readily available as soluble CaCO_3 , and (2) the fact that 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 $\text{pH} < 4.5$ (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 2–4 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:

acidity as mg CaCO_3

$$= \frac{50,000 \times (\text{mL of NaOH}) \times (\text{normality of NaOH})}{\text{weight of sample used (mg)}} \quad (16)$$

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 and the corresponding load of CaCO_3 (required to neutralize both the hydrogen ions and other free ions) can also be determined such as the one shown in Fig. 8. In this particular case, Fig. 8 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 Beech Creek, site specific stream acidity data were not collected as part of the overall sampling effort. As a result, the required CaCO_3 loading was determined using the regional curve. It should be recognized that the loading values produced by application of Fig. 8 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, Fig. 8 is likely to provide a conservative estimate of the initial required CaCO_3 loading for a particular stream. Subsequent applications of

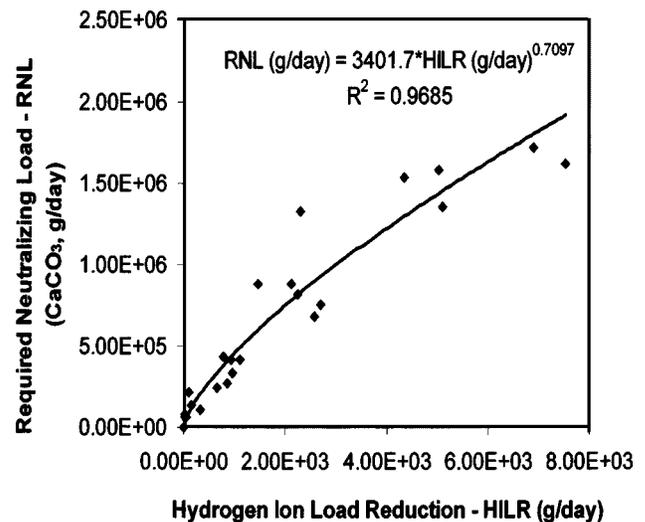


Fig. 8. CaCO_3 loading versus required hydrogen ion reduction

additional limestone can be further refined through follow-up monitoring.

Application of Fig. 8 using the required hydrogen ion load reduction values shown in Table 5, yields the corresponding values of CaCO_3 loadings shown in Table 6. A corresponding approximation of the annual loading required can be obtained by simply multiplying the daily values by 365. For actual application to the stream, it is recommended that the calculated load be multiplied by a factor of 2–4 (Clayton et al. 1998).

Phased Implementation

Practical application of pH TMDLs, especially for abandoned mine lands, 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, revegetation, and the use of agricultural limestone.

Since 1983, the Kentucky Division of Abandoned Mines has spent approximately \$17 million in restoring seven pH impaired watersheds. Although last year the total federal Kentucky AML budget allocation was \$17 million, 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, and not pH remediation projects. Based on the cost of current remediation efforts, it would appear that a significant increase in federal funding to the Kentucky AML program would be required in order for the AML program to play a major role in restoring the pH impaired streams in the state of Kentucky.

Table 6. CaCO_3 Loadings for Beech Creek

Location	Required reduction (lb/day)	Required reduction (g/day)	CaCO_3 loading (g/day)	CaCO_3 loading (lb/day)	CaCO_3 loading (ton/year)
Subbasin 1	2.431	1,105	491,553	1,081	179
Subbasin 2	9.375	4,261	1,281,111	2,817	468
Total			1,772,664	3,898	647

Summary and Conclusions

This paper presents a simple methodology for developing TMDLs for pH impaired streams. By characterizing the pH impact in terms of an associated hydrogen ion load, a functional relationship can be developed between discharge and an associated hydrogen ion loading for a given pH value. By specifying a minimum pH value (e.g., 6.0) and a conservative minimum activity correction factor, an envelope of maximum ion loads may be obtained as a function of discharge. Finally, by identifying a critical discharge for a given watershed, the maximum hydrogen ion load and associated TMDL can be obtained. Determination of the associated ion load reduction can further be accomplished by developing functional relationships between measured discharges and measured ion loads for a given watershed. Conversion of the associated hydrogen ion load reduction to an associated in-stream loading of CaCO_3 can be accomplished by a regional or site specific load reduction versus CaCO_3 loading curve. The proposed approach thus provides a simple and straightforward method for determining TMDLs for pH impaired streams, as well as the associated maximum load reduction and an estimate of the mass of neutralizing agent (e.g., CaCO_3) required to produce the reduction. As such, the development methodology should have general applicability for pH impaired streams across the United States.

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Appendix. Hydrogen Loading Example Calculation

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

- Average discharge (Q) = 72.5 L/s (2.56 cfs)
- Measured pH = 6.0

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

$$\text{pH} = -\log\{\text{H}^+\} \quad (17)$$

The resulting moles of hydrogen is the antilog of -6.0 , which is 0.000001 moles/L. The units need to be converted into g/cubic ft. This is accomplished by applying the following conversion factors:

- There is one gram per mole of hydrogen
- 1 L = 0.035314667 cubic ft

$$\begin{aligned} &(0.000001 \text{ mol/L}) \times (1 \text{ g/mol}) \times (1 \text{ L}/0.035314667 \text{ ft}^3) \\ &= 0.0000283168 \text{ g/ft}^3 \end{aligned}$$

The goal is to achieve a loading rate in terms of g/day or lb/day. If the amount of hydrogen ions in g/cubic ft is multiplied by the

given flow rate in cubic ft/s and a conversion factor of 86,400 s/day, then the load is computed as

$$\begin{aligned} &(0.0000283168 \text{ g/ft}^3) \times (2.56 \text{ ft}^3/\text{s}) \times (86,400 \text{ s}/1 \text{ day}) \\ &= 6.26 \text{ g/day or } 0.014 \text{ lb/day} \end{aligned}$$

Assuming an activity correction factor of 0.83, the final load is 7.55 g/day, or 0.017 lb/day

$$6.26 \text{ g/day}/0.83 = 7.55 \text{ g/day or } 0.017 \text{ lb/day}$$

Assuming an activity correction factor of 0.88, the final load is 7.11 g/day or 0.016 lb/day

$$6.26 \text{ g/day}/0.88 = 7.11 \text{ g/day or } 0.016 \text{ lb/day}$$

Notation

The following symbols are used in this paper:

- $\{\text{H}^+\}$ = measured activity of hydrogen ions;
- $[\text{H}^+]$ = molar concentration of hydrogen ions;
- 365Q10 = lowest average annual flow in a 10 year period;
- 7Q10 = lowest average 7 day flow in a 10 year period;
- γ = activity coefficient; and
- μ = ionic strength.

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