Final

pH (H⁺ Ion Mass)

Total Maximum Daily Load (TMDL)

for

Pond Creek of Green River Watershed (Muhlenberg County, Kentucky) for River Miles 9.4 to 23.8, Excluding the Beech Creek Watershed

Kentucky Department for Environmental Protection

Division of Water

Frankfort, Kentucky

April 2007



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This report has been approved for release:

David W. Morgan, Director

Division of Water

4/26/07

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List of Contributors

Dr. Lindell Ormsbee, Supervisor

Mohammad Tufail, P.E., PhD Data Analysis and Report Preparation

Kentucky Water Resources Research Institute University of Kentucky, Lexington, Kentucky 40506

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Total Maximum Daily Load (TMDL) Synopsis

State: Kentucky Major River Basin: Green River HUC8: 05110006 **County:** Muhlenberg **Pollutant of Concern:** low pH Impaired Use(s): Primary and Secondary Contact Recreation and Warm Water Aquatic Life

Impaired Waterboules for ph TWIDLS (2004 505(d) List):							
	Segment						
Waterbody Name	Length (miles)	County	Suspected Source(s)				
Pond Creek into Green River			Resource Extraction (Surface				
(from RM 9.4 to 13.6)	4.2	Muhlenberg	Mining, Petroleum Activities,				
(110111 KW1 9.4 to 13.0)		_	and Acid Mine Drainage)				
Pond Creek into Green River	2.7	Muhlenberg	Resource Extraction (Acid				
(from RM 13.6 to 16.3)	2.7	Mullenberg	Mine Drainage)				
Pond Creek into Green River	3.7	Muhlenberg	Resource Extraction (Acid				
(from RM 16.3 to 20.0)	5.7	Wullienberg	Mine Drainage)				
Pond Creek into Green River	3.8	Muhlanhara	Resource Extraction (Acid				
(from RM 20.0 to 23.8)	3.0	Muhlenberg	Mine Drainage)				

Impaired Waterbodies for nH TMDLs (2004 303(d) List).

TMDL Endpoint (i.e., Water Quality Standard): pH 6.0 to 9.0 standard units. The TMDL is expressed as hydrogen ion load.

TMDL Allocations:

Subbasin	Incremental contributing area (mi ²)	Incremental Critical Flow Rate (cfs)	Incremental TMDL for $pH = 6.0$ (lbs H^+/day)	Wasteload Allocation ¹ (lbs H ⁺ /day)	Load Allocation (lbs H ⁺ /day)
0	40.42	25.10	0.14	0.0	0.14
1	29.94	18.60	0.10	0.0	0.10
2^{2}	11.57	7.18	0.04	0.0	0.04
3	24.14	15.00	0.08	0.0	0.08
4	20.55	12.76	0.07	0.0	0.07

Load Reductions Required:

Subbasin	Allowable load for a pH	Existing load	Load reduction	Percent reduction
	of 6.0 (lbs H^+/day)	(lbs H ⁺ /day)	required (lbs H ⁺ /day)	required
0	0.14	0.00	0.00	0%
1	0.10	6.46	6.36	98%
2^{2}	0.04	0.00	0.00	0%
3	0.08	0.00	0.00	0%
4	0.07	0.00	0.00	0%

¹pH limits for existing and new discharges must be between 6.35 and 9.0. ²The TMDL for the Beech Creek Watershed was approved by EPA in February of 2006. The limits contained in the Beech Creek TMDL should be used for that watershed.

Introduction

Pond Creek in Muhlenberg County, Kentucky was determined to not support the designated uses of primary and secondary contact recreation (swimming and wading) and warm water aquatic habitat (aquatic life) because of low pH. The pH standard found within regulation 401 KAR 5:031 states that 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. Based on the assessment of Pond Creek, four segments from river mile (RM) 9.4 to 23.8 were placed on the 1998, 2002 and 2004 303(d) Lists of Impaired Waters. These four segments are: RM 9.4 to 13.6, RM 13.6 to 16.3, RM 16.3 to 20.0 and RM 20.0 to 23.8 (see Figure 1 below). The creek segments are characterized by a depressed pH, the result of acid mine drainage (AMD) from abandoned coal mining sites.



Figure 1. Map of pH-impaired Pond Creek Stream Segments

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).

This document presents the TMDLs for the four pH-impaired segments of Pond Creek. The TMDL for the Beech Creek watershed, which enters Pond Creek at river mile 15.5, has already been developed and was approved by EPA in Feb of 2006.

Location

Pond Creek watershed is entirely contained within Muhlenberg County, in southwestern Kentucky (Figure 2). Muhlenberg County is bounded on the northeast by the Green River, on the east by the Indian Camp Creek, and on the west by the Pond River.



Figure 2. Location of the Pond Creek Watershed

Hydrologic Information

Pond Creek, a fifth order stream, originates in southern Muhlenberg County and flows northeast to discharge into the Green River 94.1 miles upstream from its confluence with the Ohio River. It's main stem is approximately 23.8 miles long and drains an area of 81,038 acres (126.6 sq. miles). The average gradient is 16.0 feet per mile. Elevations for Pond Creek range from 760 ft above mean sea level (msl) in the headwaters to 370 ft above msl at the mouth. Like most of the smaller watersheds, many of the tributary streams are intermittent.

Geologic Information

The Pond Creek watershed is in the Western Coal field physiographic region. The surface bedrock is of Pennsylvanian age. Formations of the Pennsylvanian age are mostly sandstone, siltstone, coal, and interbedded limestone and shale; alluvial deposits of siltstone and crossbedded sand or sandstone underlie the extensive lowland areas (US Department of Agriculture, 1980). The relief of the Pond Creek watershed ranges from nearly level to steep. Gently sloping to steep soils are found in the uplands and nearly level soils are found on the floodplain.

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 Pond Creek watershed contains three main landuses: resource extraction (mining and disturbed land area), forest, and agriculture.

Soils Information

Pond Creek watershed is dominated by nearly level loamy and clayey soils near to the mouth and level to steep loamy soils in the headwaters. Most of the watershed is Udorthents soil, which consists of strip mine spoil containing rock fragments.

Mining History

Mining activities in the Pond Creek Watershed have occurred since 1967. A list of the various mining permits that have been issued for Pond Creek is provided in Table 1. 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.

Table 1. Permits in the Pond Creek Watershed (data based upon file reviews, dashed lines indicate that the information could not be determined through file reviews)

Permit #	Permitted	Disturbed	Associated	Date	Date
	Area (ac)	Area (ac)	Company	Opened	Released
089-0033	144	-	West Kentucky Coal Corp.	2/28/80	6/15/89
089-0044	214	-	West Kentucky Coal Corp.	12/11/80	5/3/85
089-0046	5.36	-	Pond Creek Coal Co. Inc.	12/11/81	12/15/86
089-9001	45	-	West Kentucky Coal Corp.	1/8/81	10/11/84
289-0133	15	-	West Kentucky Coal Corp.	12/9/74	1/20/83
289-0354	-	-	Badgett Mine Stripping	2/14/78	12/27/83
407-68	71	-	Caney Creek Coal Inc.	12/18/68	1/3/73
407-69	48	-	Caney Creek Coal Inc.	12/18/69	11/7/74
407-70	59	-	Caney Creek Coal Inc.	12/18/70	10/8/74
407-71	58	-	Caney Creek Coal Inc.	12/18/71	6/16/76
407-73	89	-	Caney Creek Coal Inc.	12/18/73	4/10/81
453-67	54	-	Wright Coal Company	9/29/67	2/13/76
489-9001	42.4	-	West Kentucky Coal Corp.	8/24/84	1/20/95
889-0016	415.5	-	West Kentucky Coal Corp.	1/30/84	1/20/95
889-0035	92.7	-		2/6/86	2/27/95
889-0038	57	-	Pond Creek Coal Co. Inc.	11/7/86	3/6/90
889-0041	223.8	-	West Kentucky Coal Corp.	7/17/87	1/24/95
889-0043	22.6	-	West Kentucky Coal Corp.	7/15/87	1/20/95
889-0045	11.1	11	Taylor/Thompson Joint Venture	7/15/97	-
889-0046	324.7	280	Pond Creek Coal Co. Inc.	8/25/92	-
889-0051	16		Taylor/Thompson Joint Venture	8/25/89	7/15/97
889-0057	57	56	Crown Energy Corp.	9/30/97	-
889-0062	80.3	56	Beech Creek Energy Inc.	1/29/97	-
889-0069	60.5	38	Pond Creek Coal Co. Inc.	1/6/93	-
889-0084	5.45	5.45	Beech Creek Energy Inc.	11/30/98	-
889-8001	44.5	-	West Kentucky Coal Corp.	8/24/84	1/20/95
889-9000	60.2	-	West Kentucky Coal Corp.	2/24/84	10/24/91
889-9001	206	-	West Kentucky Coal Corp.	2/17/84	4/23/87

All post-Kentucky Primacy permits are secured through reclamation bonds. A reclamation bond is a financial document submitted to the Office of Surface Mining prior to mine permit issuance. A bond guarantees mining and reclamation operations will be conducted by mining companies according to regulations and the terms of the approved permit. If a coal company cannot comply with these conditions, the bond is "forfeited" (paid to the Office of Surface Mining) for eventual use by the Division of Abandoned Mine Lands (DAML) in reclaiming the mined area. Reclamation bonds may be submitted in the forms of cash, certificate of deposit, letter of credit or surety (insurance policy).

A reclamation bond may be returned to a coal company by either of two methods: administrative or phase (on-ground reclamation). Administrative releases occur when new bonds are substituted for the original bonds. Administrative releases are also given for areas of a mine site that are

permitted but never disturbed by mining or for areas that are included under a second more recently issued permit.

Phase releases occur in three stages and according to specific reclamation criteria: Phase One – all mining is complete, and backfilling, grading and initial seeding of mined areas has occurred; Phase Two – a minimum of two years of growth on vegetated areas since initial seeding, the vegetation is of sufficient thickness to prevent erosion and pollution of areas outside the mine area with mine soils, and any permanent water impoundments have met specifications for future maintenance by the landowner; and Phase Three – a minimum of five years of vegetative growth since initial seeding and the successful completion of reclamation operations in order for the mined area to support the approved post-mining land use. Up to 60 percent of the original bond amount is released at Phase One. An additional 25 percent is returned at Phase Two, with the remainder of the reclamation bond released at Phase Three. Once a permit is released and the reclamation bond returned, the state cannot require additional remediation action by the mining company unless it is determined that fraudulent documentation was submitted as part of the remediation process.

Monitoring History

The waters of Pond Creek were monitored as early as 1978 by the Kentucky Division of Water (KDOW) as reported in *The Effects of Coal Mining Activities on the Water Quality of Streams in the Western and Eastern Coalfields of Kentucky*, published in 1981 by the KDOW as part of an agreement with the DAML. The locations of the sites that were sampled as part of the survey are shown in Figure 3. The recorded pH levels are shown in Table 2. As can be seen from the table, several readings were below 6.0. The information shown for Site 999 should be considered suspect. A very low pH value (2.6) is indicated. However, the observation is listed as occurring on a different date then the other observations made for Pond Creek (end of June 1978 instead of mid-April 1978). Additionally, there is also little mining in this portion of the watershed and data collected for this TMDL at a site located just downstream indicated no low pH problem (P3 in Table 3). However, this information was used as part of the 303(d) listing process for Pond Creek.

Station	Date	pН
999	6/28/78	2.6
991	4/12/78	5.9
986	4/12/78	2.8
983	4/11/78	4.5
982	4/11/78	4.4
978	4/11/78	5.2
998	4/11/78	6.8
985	4/11/78	6.6
984	4/11/78	6.4
975	4/11/78	6.8
997	4/11/78	6.2
03011912	6/19/80	7.2

Table 2.	Historic	Monitoring	Data	(1978 an	d 1980)
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Figure 3. Historic Sampling Sites in Pond Creek Watershed

In 1997, the 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. A pH reading of 6.5 was made at river mile (RM) 3.5 of Pond Creek. This indicated no impairment in the lower reach of Pond Creek. More recent data collected in the lower reach as part of the TMDL development also indicated that the lower reach of Pond Creek was not impaired because of low pH. As a result of this information, the listing for Pond Creek as impaired for aquatic life and swimming uses because of low pH (resulting from resource extraction activities) included the reach from RM 9.4 to RM 23.8.

Problem Definition

The 1998 and subsequent Lists of Waters for Kentucky (Kentucky DOW, 1998, 2003, and 2005) indicate that 14.4 miles of Pond Creek do not meet the designated uses of primary and secondary contact recreation (swimming and wading) and aquatic life due to low pH. The Pond Creek watershed provides a classic example of impairment caused by acid mine drainage (AMD). Bituminous coal mine drainage like that found in the Pond Creek watershed, may contain concentrated sulfuric acid and elevated 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). At low pH levels, the iron associated with AMD is soluble. However, in downstream reaches where the pH begins to improve, most of the ferric sulfate $[Fe_2(SO_4)_3]$ is hydrolyzed to essentially insoluble iron hydroxide $[Fe(OH)_3]$. The stream bottom can become covered with a sterile orange or yellow-brown iron hydroxide deposit that impacts benthic algae, invertebrates, and fish.

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

In the process of mining, the iron sulfide (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:

$$4 \operatorname{FeS}_2 + 14 \operatorname{O}_2 + 4 \operatorname{H}_2 0 + \operatorname{bacteria} \rightarrow 4 \operatorname{Fe} + \operatorname{SO}_4 + 4 \operatorname{H}_2 \operatorname{SO}_4 \tag{1}$$

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

$$4 \text{ FeSO}_4 + \text{O}_2 + 2 \text{ H}_2\text{SO}_4 \rightarrow 2 \text{ Fe}_2(\text{SO}_4)_3 + 2 \text{ H}_2\text{O}$$
(2)

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

$$2 \operatorname{Fe}_2(\mathrm{SO}_4)_3 + 12 \operatorname{H}_2\mathrm{O} \to 4 \operatorname{Fe}(\mathrm{OH})_3 + 6 \operatorname{H}_2\mathrm{SO}_4 \tag{3}$$

The brownish yellow ferric hydroxide ($Fe(OH)_3$) may remain suspended in the stream even when it is no longer acidic. Although the brownish, yellow staining of the streambanks and water doesn't cause the low pH, it does indicate that there has been production of sulfuric acid. The overall stoichiometric relationship is shown in equation (4):

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

Reaction (4) indicates that a net of 4 moles of H_{+} are liberated for each mole of pyrite (FeS₂) 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 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 National Research Council 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 the number of allowed flow excursions in a specified period (return period) and not in terms of the low flow or an absolute "never to be exceeded" limit. Water quality criteria may occasionally be exceeded because of the variability of natural systems and discharges from point and nonpoint sources." Small, intermittent streams are especially vulnerable to this variability.

The Technical Support Document for Water Quality-Based Toxic Control (EPA, 1991) states that daily receiving water concentrations (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 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 stream flow), 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 (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 average lowest daily 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

KPDES-Permitted Sources

During the 2000-2001 sampling period, there were no mining activities with individual Kentucky Pollutant Discharge Elimination System (KPDES)-permits. However, there were mining activities with general KPDES-permits in the watershed (see Table 1). Mining activities with individual KPDES permits received a TMDL allocation under the Wasteload allocation (WLA).

Non KPDES-Permitted Sources

Because pre-law mining existed in the watershed (see Table 1), there are also non-KPDES permitted sources of low pH. Non-KPDES permitted sources received a TMDL allocation under the Load Allocation (LA).

Monitoring

Previous monitoring has been performed in the Pond Creek watershed in conjunction with mining permits. The historic pH readings at these sites as recorded in Table 2 indicate severe impairment in selected sections of the Pond 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 KDOW) subcontracted with Murray State University to collect additional data from the watershed at the sites indicated in Figure 4. A summary of the results obtained from these sites is shown in Table 3. As can be seen from Table 3, at all sites except Site P1, measured pH values were above 6.0. Even though the pH values for Sites P0, P2, P3, and P4 were all above 6.0, the TMDL was developed for the entire watershed including Subbasins 0, 1, 2, 3, and 4. However, due to the fact that there were no violations of pH in subbasins 0, 2, 3, and 4, no load reductions were needed for these subbasins.



Figure 4. Murray State Sampling Sites

	Site	e P0	Site	P1	Site	e P2	Site P3		Site	e P4
Date	Flow rate (cfs)	рН	Flow rate (cfs)	рН	Flow rate (cfs)	рН	Flow rate (cfs)	рН	Flow rate (cfs)	рН
Location		. @ RM .5	Pond Cr 10.5, H		Pond Cr 14.3, H	. @ RM wy 176	Pond Cr 17.0, Hy	: @ RM wy 1163	RM 1	t Cr. @ 3, Hwy 63
Latitude	37°	18	37°	13	37°	11/	37°	37° 10′ 37° 09′		09/
Longitude	86°	59 [/]	87°	02′	87°	06	87°	06′	87° 05′	
2/12/00			22.0	5.3	8.0	6.4	4.0	6.2	0.0	7.1
2/27/00			215.0	5.6	365.0	6.0	122.0	7.2	63.0	6.8
3/25/00			93.0	5.6	181.0	7.3	30.0	7.7	10.0	9.9
4/8/00			343.0	6.2	109.0	7.8	51.0	8.1	19.0	8.3
4/15/00			80.0	6.0	69.0	7.2	24.0	7.8	12.0	7.1
4/28/00			60.0	6.7	139.0	6.8	17.0	7.5	34.0	7.4
5/5/00			82.0	6.4	192.0	7.4	110.0	8.0	34.0	8.0
4/7/01	74.0	8.1	84.0	7.0						
4/21/01	15.0	7.8	13.0	7.4						
6/1/01	19.0	7.1	16.0	4.7						

Table 3. Murray State Sample Results (2000-2001)

TMDL Development

Theory

The TMDL is a term used to describe the maximum amount of a pollutant a stream can assimilate without violating WQS, 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 associated mass unit (pH is measured in Standard Units), thus TMDLs for the Pond Creek watershed were developed for load of hydrogen ions.

TMDLs are comprised of the sum of individual wasteload allocations (WLAs) for KPDESpermitted sources, including point sources, and load allocations (LAs) for nonpoint sources that do not require a KPDES permit and natural background levels for a given watershed. The sum of these components may not result in exceedance of WQSs for that watershed unless the impairment is due to natural background conditions. In addition, the TMDL must include a MOS, either implicitly or explicitly, that accounts for the uncertainty in the relation between pollutant loads and the quality of the receiving water body. Conceptually, this definition is denoted by the equation:

$$TMDL = Sum (WLAs) + Sum (LAs) + MOS$$
(8)

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, 1997):

- 1) Implicitly incorporate the MOS using conservative model assumptions to develop allocations, or
- 2) Explicitly specify a portion of the total TMDL as the MOS using the remainder for allocations.

Model Development

The magnitude of the associated hydrogen ion load in a water column (in terms of activity) can be determined by measuring the pH of the water. The relationship between hydrogen load and pH can be expressed as follows:

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

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

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

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):

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

In the absence of actual measured values of TDS, a conservative estimate of TDS for AMD can be obtained using the cumulative probability distribution of typical terrestrial waters (Figure 5) with an associated conservative probability of exceedance of 95%.



Figure 5: Distribution Function of Total Dissolved Solids (TDS) Concentration for Terrestrial Waters (Snoeyink and Jenkins, 1980)

Use of Figure 5 along with an exceedance probability of 95% yields a TDS value of approximately 900 PPM. Substitution of a TDS concentration of 900 PPM into equation 7 yields an ionic strength of 0.0225. Ionic strength can be converted to an associated activity coefficient using the functional relationship shown in Figure 6. Use of an ionic strength of 0.0225 yields an activity coefficient of 0.89.



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

The atomic weight of hydrogen is one gram per mole so the concentration of hydrogen ions in mol/L is also the concentration in g/L. Multiplying the concentration of hydrogen ions by the average flow rate for a given day results in a hydrogen ion load for that day in grams/day. As a result, for any given flow rate, there is a maximum ion load that the stream can assimilate before a minimum pH value of 6.0 is violated. Thus for any given day a TMDL may be calculated for that day using the average daily flow and a minimum pH standard of 6 units.

Because pH and equivalent hydrogen ion load can be related as a function of discharge (flow) and ionic strength, a functional relationship can be developed between discharge and the associated ion loading for a given pH value. By specifying a minimum pH value (e.g. 6) and a minimum activity correction factor (e.g. 0.89), an envelope of maximum ion loads may be obtained as a function of discharge (see Figure 7). This figure thus provides a basis for establishing the maximum ion load for a given discharge.

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. The difference between the maximum TMDL (based on the observed activity coefficient of 0.89) and the minimum TMDL (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 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. In developing a pH TMDL for Pond Creek, a conservative activity coefficient of 1.0 was assumed, while an activity coefficient of 0.89 was used in calculating the estimated current load, thus providing for a MOS of approximately 11 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 in the model to determine the value of the TMDL.



Discharge vs. Maximum Ion Loading

Figure 7. 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, the following monitoring data for Pond Creek has been used:

- Average discharge (Q) = 53.53 cfs (cumulative flow for Site P1)
- 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

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

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

 $(0.0000283168 \text{ g/ft}^3)*(53.53 \text{ ft}^3/\text{s})*(86400\text{s}/1\text{day}) = 130.96 \text{ g/day}, \text{ or } 0.29 \text{ lbs/day}$

Assuming an activity correction factor of 0.89, the final load is 147.15 g/day, or 0.32 lbs/day:

130.96 g/day / 0.89 = 147.15 g/day, or 0.32 lbs/day

Therefore, by using an activity coefficient of 1.0 instead of 0.89 to develop the TMDL values, a MOS of approximately 11 percent is realized.

Critical Flow and TMDL Determination

Because maximum hydrogen ion loading values can be directly related to flow, 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 Pond Creek watershed, a regional hydrologic frequency analysis was used. Regional analysis can be used to develop an inductive model using data collected at stream flow gaging stations that are located in the same hydrologic region as the watershed of interest. For this study, the following USGS gaging stations were selected: 03384000, 03321350, 03320500, and 03383000. The data from these gages were used to estimate the lowest average annual flows of the most recent 10 years (see Table 4). These flow rates were then regressed with watershed area to produce Figure 8. Using this figure, the lowest 10-year mean annual discharge for a given watershed area can be readily determined.

Table 4. Lowest 10-year Mean Annual Flow for Stations in	n Regional Analysis
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	USGS Gaging Station Numbers					
Station	3384000	3321350	3320500	3383000		
Area (mi ²)	2.10	58.20	194.00	255.00		
Flow (cfs)	0.69	49.10	99.70	166.00		



Figure 8. Relation between Drainage Area and the Critical TMDL Flow

pH standards are violated only at Site P1 (Table 3). However, the TMDL will be determined for all subbasins in the watershed. Application of Figure 8 for the Pond Creek watershed yields a critical average annual cumulative discharge of 53.53 cfs at Site P1 assuming an upstream total watershed area of 86.20 mi². The incremental area for subbasin 1 is 29.94 mi², which translates into an incremental critical average annual discharge of 18.60 cfs. The TMDL can be determined using this critical discharge and Figure 7 and correcting for an activity coefficient of 1.0 instead of 0.89. For instance, for subbasin 1 (incremental flow of 18.60 cfs), the incremental TMDL can be computed as:

2.749 *18.60 *0.89 = 45.51 g/day or 0.10 lbs/day

The TMDL is given in Table 5 for all subbasins in the watershed. Note that the TMDL for the Beech Creek Watershed, which is contained within Subbasin 2, was developed and was approved by EPA in February of 2006. The limits contained in the Beech Creek TMDL should be used for that watershed.

Sub-	Cumulative	Incremental	Cumulative	Incremental	Cumulative	Incremental
basin	Area	Area	Flow	Flow	TMDL (lbs	TMDL (lbs
	(mi^2)	(mi^2)	(cfs)	(cfs)	H ⁺ /day)	H ⁺ /day)
0	126.62	40.42	78.63	25.10	0.43	0.14
1	86.20	29.94	53.53	18.60	0.29	0.10
2	56.26	11.57	34.94	7.18	0.19	0.04
3	24.14	24.14	15.00	15.00	0.08	0.08
4	20.55	20.55	12.76	12.76	0.07	0.07

Table 5. Flow and Corresponding TMDL for Pond Creek Watershed

Hydrogen Ion Loading Model

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 for monitoring Site 1 that relates total hydrogen ion loading to flow. This model is shown in Figure 9 and was derived from the data in Table 3. In developing the model for defining the current load, a conservative value of 0.89 was assumed for the activity coefficient. This model can be used in conjunction with the minimum TMDL for the subbasin to determine the total load reduction. As discussed previously, the minimum TMDL was developed assuming an activity coefficient of 1.0, thus providing for an upper limit for a MOS for the TMDL of approximately 11 percent.



Figure 9. Relationship between Flow and Ion Load for Site P1

Predicted Load

A plot of the ion loads versus flows for Subbasin 1 is shown in Figure 9. The maximum load shown in the plot is derived by using the cumulative critical flow for subbasin 1 (53.53 cfs) and the lowest observed pH value of 4.7. This results in a maximum H+ ion load of 2936 g/day, which is greater than the observed highest load of 1484.59 g/day for a flow of 215 cfs. The latter load (1484.59 g/day) is not used as the maximum load for the subbasin as it is associated with a flow (215 cfs) which is significantly greater than the critical flow for the subbasin (53.53 cfs). In examining the figure, it is observed that the ion load tends to increase as a function of flow, to reach a maximum, and then decrease as the flow increases. It is hypothesized that these results reflect two competing physical processes. At lower flows, ion loads are initially leached out of the soil areas resulting in increasing ion loads. A maximum value of ion load is reached and as the runoff volume increases, the ion loads in the spoil areas become depleted and therefore reduced because of flow dilution in the stream. As a result, ion load increases with increasing

flow, reaches a maximum, and then decreases as the flow continues to increase. On the basis of the observed data, a conservative estimate of the resulting maximum ion loads can be obtained by selecting the maximum observed ion load that corresponds to the critical flow and lowest observed pH value for the site.

Subbasin 1

As indicated previously, the maximum hydrogen ion load for Site P1 may be obtained from Figure 9. However, this load is for the entire upper watershed. The incremental load for subbasin 1 may obtained by subtracting the cumulative load for Site P2 from the maximum load for Site P1. In the current case, a conservative assumption was made to assume that the load upstream of Site 2 was essentially zero (in fact it was determined to be approximately 8.0 g/day). Therefore, the incremental load contributed by subbasin 1 is assumed to be 2936 g/day). The critical flow and corresponding load for subbasin 1 is given in Table 6.

Subbasins 0, 2, 3, and 4

In the current study, a conservative assumption was made to assume that the load in all subbasins (except subbasin 1, which is impaired) was essentially zero. This is justified since there were no pH impairments in these subbasins.

Sub-	Cumulative	Predicted	Predicted	Incremental	Predicted	Predicted
basin	Critical	load	load	Critical	load	load
	Flow	Cumulative	Cumulative	Flow	Incremental	Incremental
	(cfs)	$(gm H^+/day)$	(lbs H ⁺ /day)	(cfs)	$(gm H^+/day)$	(lbs H ⁺ /day)
0	78.63	0	0.04	25.10	0	0.00
1	53.53	2,936	6.46	18.60	2,936	6.46
2	34.94	0	0.00	7.18	0	0.00
3	15.00	0	0.00	15.00	0	0.00
4	12.76	0	0.00	12.76	0	0.00

Table 6	Critical	Flow and	Correspon	nding Pre	dicted Hy	drogen Ion	heo]
	Cinical	Flow and	Conceptor	iung rie	uicieu IIy	ulogen ion .	LUau

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 separate TMDL and an associated load reduction was developed for Subbasin 1 of the Pond Creek Watershed. Additionally, a TMDL is developed for all other contributing subbasins of the watershed. Since there is no pH impairment in any other subbasins (except Subbasin 1), no load reductions are needed for these subbasins. Again, the TMDL for

the Beech Creek Watershed, which is contained within Subbasin 2, was developed and was approved by EPA in February of 2006. The limits contained in the Beech Creek TMDL should be used for that watershed.

Translation of the TMDL in Table 5 into associated daily load reductions for Subbasin 1 may be accomplished by subtracting the TMDL for Subbasin 1 from the predicted load for Subbasin 1. The values are given in Table 7. Note that since only subbasin 1 is impaired for low pH, no load computations and associated load reductions are given for subbasin 0, 2, 3, and 4. The total incremental load reduction for subbasin 1 is 6.36 lbs/day. The limits contained in the Beech Creek TMDL should be used for that watershed.

Subbasin	Incremental	Incremental	Incremental	Predicted	Load
	contributing	critical flow	TMDL for a	incremental	reduction
	area (mi ²)	(cfs)	pH of 6.0 (lb	load (lbs	needed (lbs
			H ⁺ /day)	H ⁺ /day)	H ⁺ /day)
0	40.42	25.10	0.14	0.00	0.00
1	29.94	18.60	0.10	6.46	6.36
2	11.57	7.18	0.04	0.00	0.00
3	24.14	15.00	0.08	0.00	0.00
4	20.55	12.76	0.07	0.00	0.00

Table 7. TMDL Summary and Reduction Needed for
Subbasins in Pond Creek Watershed

Permitting

Permitting Other than in Subbasin 1

Permitting for locations in the Pond Creek watershed other than in Subbasin 1 would require no special considerations related to the 303(d) list. Remediation of the abandoned mine areas in Subbasin 1 should result in improved water quality at Site P1.

Permits in Subbasin 1

Existing and new permits (except for new remining permits) for discharges to streams in Subbasin 1 of the Pond Creek watershed could be allowed, 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 or 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 cannot 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. 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. A lower pH limit of 6.35 provides an explicit margin of safety for the Wasteload Allocations.

Remining Permits in Subbasin 1

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. Followup, 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.

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.

Allocations

Existing and new KPDES-permits in Subbasin 1 must meet pH limits in the range of 6.35 to 9.0 standard units (Table 8). This is the WLA for the subbasins. The Load Allocation is set at the allowable TMDL in lbs H^+/day . The allocations contained in the Beech Creek TMDL should be used for that watershed.

	Incremental Critical Flow Rate (cfs)	TMDL for pH = 6.0 (lbs H ⁺ /day)	Wasteload Allocation* (lbs H ⁺ /day)	Load Allocation (lbs H ⁺ /day)
Subbasin 0	25.10	0.14	0.00	0.14
Subbasin 1	18.60	0.10	0.00	0.1
Subbasin 2	7.18	0.04	0.00	.04
Subbasin 3	15.00	0.08	0.00	.08
Subbasin 4	12.76	0.07	0.00	.07

Table 8. Wasteload and Load Allocation for Subbasins in the Pond Creek Watershed

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

Implementation/Remediation Strategy

Section 303(e) of the Clean Water Act and 40 CFR Part 130, Section 130.5, require states to have a continuing planning process (CPP) composed of several parts specified in the Act and the regulation. The CPP provides an outline of agency programs and the available authority to address water issues. Under the CPP umbrella, the Watershed Management Branch of KDOW will provide technical support and leadership with developing and implementing watershed plans to address water quality and quantity problems and threats. Developing watershed plans enables more effective targeting of limited restoration funds and resources, thus improving environmental benefit, protection and recovery.

Watershed plans provide an integrative approach for identifying and describing how, when, who and what actions should be taken in order to meet water quality standards. At this time, a comprehensive watershed restoration plan for Pond Creek has not been developed; thus specific recommendations for remediation are both limited and conditional pending additional watershed planning. This TMDL provides a foundation for developing a detailed watershed plan.

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 DAML is charged with performing reclamation to address the impacts from pre-law mine sites in accordance with priorities established in SMCRA. Environmental problems are listed as a third priority in the list of abandoned mine land (AML) problem types.

The Kentucky DAML has had several remediation projects in the Pond Creek watershed (in excess of \$7 million). The work included grading and covering of acidic refuse with spoil or soil material, drainage improvements, revegetation, and tree planting. The federal Natural Resource Conservation Service has also performed an AML reclamation project in the watershed.

Recently, additional acid mine drainage remediation work was funded in the Pond Creek watershed. The Division of Water awarded \$1,171,884 in federal Clean Water Act Section

319(h) Nonpoint Source Grant funds (FFY2006) to the Division of Abandoned Mine Lands to remediate acid mine drainage from the Ebenezer abandoned mine land site located along RM 12.5-13 of Pond Creek (Figure 10). The Ebenezer site, located in the impaired Subbasin 1, includes 80 acres of fine refuse from an abandoned slurry impoundment and 5 acres of coarse refuse. While restoration of the Ebenezer site has been approved and funded, the project has been placed on hold pending a potential remining operation. A resolution (reclamation via 319(h) funding or via remining) is expected in early 2007.

Additional funding, via Kentucky Division of Abandoned Mine Land restoration funds, Clean Water Act Nonpoint Source Section 319(h) grants, Appalachian Clean Streams Initiatives funding, and other funding opportunities, is needed in order to reclaim the multitude of abandoned mine land acres in the Pond Creek watershed. Remining operations will continue to be evaluated as a viable means for both extracting additional coal and reclaiming abandoned mine sites in the watershed. Lastly, pollutant trading may also be a viable management strategy to consider for meeting the TMDL load reduction goals.



Figure 10. Ebenezer Refuse Pile (photograph from 2000 courtesy of Division of Abandoned Mine Lands)

Public Participation

This TMDL was placed on 30-day public notice and made available for review and comment from March 14 through April 13, 2007. The public notice was prepared and published as an advertisement in The Times-Argus and the Leader-News, newspapers with wide circulation in the communities impacted by these TMDLs. A press release was also distributed via a mailing list, which is maintained by the Governor's Office, of media outlets across the Commonwealth.

The TMDL document 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 document 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. (Ex. Hopkins County = 54).

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

If 200 has been added to the county number, the permit was originally issued prior to May 3, 1978, and carried through into the interim program. Ex. 254 (Hopkins)

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. Ex. 454 or 654 (Hopkins)

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. Ex. 854 (Hopkins)

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

Limestone
Clay
Sand/Gravel
Oil Shale
Fluorspar