Total Maximum Daily Loads to Address Low pH in Cherry Creek in the Deep Creek Watershed Garrett County, Maryland

FINAL

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List of Abbreviations

Al	Aluminum
AMD	Acid Mine Drainage
ANC	Acid Neutralization Capacity
BOM	Bureau of Mines
CaCO ₃	Calcium Carbonate
COMAR	Code of Maryland Regulations
CWA	Clean Water Act
CWAP	Clean Water Action Plan
EPA	Environmental Protection Agency
Fe	Iron
kg/day	Kilograms per day
km	Kilometer
lb/day	Pounds per day
LTA	Long Term Average
m^3/s	Cubic meters per second
MD	Maryland
MDE	Maryland Department of the Environment
mg/l	Milligrams per liter
mi ²	Square miles
Mn	Manganese
MOS	Margin of Safety
NPS	Nonpoint Source
pН	Negative logarithm of Hydrogen Ion Molar Concentration
PR	Percent Reduction
TMDL	Total Maximum Daily Load
USGS	United States Geological Survey
WLA	Waste Load Allocation
WQLS	Water Quality Limited Segment

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EXECUTIVE SUMMARY

This document proposes to establish a Total Maximum Daily Load (TMDL) to address low pH in Cherry Creek, which is a sub-basin in the Deep Creek watershed. The Deep Creek watershed (basin code 05-02-02-03) was identified on the State's 1996 list of Water Quality Limited Segments (WQLSs) as impaired by low pH and nutrients. The list acknowledged that only a portion of the watershed might be impaired, and that with additional information the spatial boundaries of the impairment could be refined. Maryland monitored the Deep Creek system more intensively in preparation for the TMDL analysis and determined that Cherry Creek, a subwatershed of the Deep Creek system, was impaired by acid mine drainage (AMD) as indicated by low pH measurements. This TMDL was developed in response to that determination. The nutrient impairment will be addressed at a later date.

Cherry Creek drains directly into Deep Creek, which in turn drains into the Youghiogheny River. The creek is impacted by AMD, which is causing low pH measurements that violate the water quality standard for pH. This analysis accounts for pH levels that are below the State's criterion of 6.5 and are due to natural conditions.

The water quality goal of this TMDL is to reduce the acidity concentrations of the water caused by AMD in order to maintain the pH criterion at a level whereby the designated use for Cherry Creek will be met. The TMDL was determined using statistical analyses (Monte Carlo Simulation). The maximum loads for total acidity entering Cherry Creek are established for average annual flow conditions. The TMDL is estimated as a long-term average loading because evidence indicates that pH levels are independent of flow levels.

The average annual TMDL of acidity is 743 kg/day (1,634 lbs/day) measured as calcium carbonate (CaCO₃). Baseline average annual nonpoint source loads, from which reductions are computed, are based on data collected by Maryland Department of the Environment (MDE) from 1988 to 1994. Allowable average annual loads have been allocated to nonpoint sources only, because the watershed contains no active permitted mining activities to which allocations can be made.

Two factors provide assurance that this TMDL will be implemented. First, the MDE's Abandoned Mine Reclamation Program restores eligible environments previously degraded by adverse effects of past coal mining practices, including measures for the conservation of water, fish, wildlife, and recreation resources and promotes research relating to the development of water quality control methods and techniques. In addition, there are no active mining activities in the watershed and any future mining would require permit holders to improve water quality in the region. Second, Maryland has adopted a watershed cycling strategy, which will assure that routine future monitoring and TMDL evaluations are conducted.

1.0 INTRODUCTION

Section 303(d)(1)(C) of the federal Clean Water Act and the U.S. Environmental Protection Agency (EPA)'s implementing regulations direct each State to develop a Total Maximum Daily Load (TMDL) for each impaired water quality limited segment (WQLS) on the Section 303(d) list, taking into account seasonal variations and a protective margin of safety (MOS) to account for uncertainty. A TMDL reflects the maximum pollutant loading of the impairing substance a water body can receive and still meet water quality standards.

TMDLs are established to achieve and maintain water quality standards. A water quality standard is the combination of a designated use for a particular body of water and the water quality criteria designed to protect that use. Designated uses include activities such as swimming, drinking water supply, and propagation of naturally reproducing trout. Water quality criteria consist of narrative statements and numeric values designed to protect the designated uses. Criteria may differ among waters that have different designated uses.

The Deep Creek watershed (basin code 05-02-02-03) was identified on the State's 1996 list of WQLSs as impaired by low pH and nutrients. The list acknowledged that only a portion of the watershed might be impaired, and that with additional information the spatial boundaries of the impairment could be refined. Maryland monitored the Deep Creek system more intensively in preparation for the TMDL and determined that Cherry Creek, a subwatershed of the Deep Creek system, was impaired by acid mine drainage (AMD) as indicated by low pH measurements. The TMDL described within this document was developed to address the localized low pH impairment identified within the Cherry Creek portion of the Deep Creek watershed. The pH within other portions of the Deep Creek watershed will be addressed at a future date. The nutrient impairment for the entire Deep Creek watershed will also be addressed at a later date.

Previous mining activities in the Cherry Creek watershed have lead to higher concentrations of metals than the concentrations expected in the absence of AMD. Highly acidic (pH < 3.0) solutions containing metals (e.g., iron, manganese, aluminum) are produced when water and air react with the surfaces of sulfide minerals. The process can occur naturally (acid rock drainage), but is more typically associated with active and inactive mines where coal extraction has increased access of solutions to the sulfide deposit. For these reasons, this document proposes to establish a TMDL of AMD to Cherry Creek.

2.0 TARGETED WATER QUALITY GOAL

The objective of the TMDL established in this document is to ensure that the pH levels support the Use I designation for Cherry Creek, accounting for natural conditions. The pH level is based on specific numeric criteria for Use I waters set forth in the Code of Maryland Regulations (COMAR) 26.08.02. These regulations require that the pH values of water designated as Use I need to be maintained in a pH range of 6.5 to 8.5 at all times, unless the natural conditions of a stream segment are not consistent with the criteria established for the stream. In the case of freestone streams with little or no buffering capacity, the TMDL endpoint for pH will be the pH of the natural background water quality. These pH values are typically as low as 3.5 in natural peat bogs habitats (Maryland Department of the Environment (MDE) Bureau of Mines (BOM), 2001; Morgan, Raymond, 1988)

Natural conditions of Cherry Creek, as explained in Section 3.1.1, will be the targeted water quality goal for Cherry Creek. This water quality goal has been estimated using data from sample stations that are not affected by AMD. For reasons that are explained below in the computational methodology, the water quality goal for Cherry Creek will be an acidity concentration of 30.2 mg/l as calcium carbonate (CaCO₃), and an alkalinity concentration of 0.0, which yield a net alkalinity or acid neutralization capacity (ANC) of -30.2 mg/l as CaCO₃. These conditions correspond to a natural pH value of 4.3, which is consistent with natural conditions as discussed in Section 3.1.1. See Appendix A for the natural background water quality sampling data and estimation of these endpoint values.

The natural conditions allowance is found at COMAR 26.08.02.03(A)(2):

If the natural water quality of a stream segment is not consistent with the criteria established for the stream then:

(a) The natural conditions do not constitute a violation of the water quality standards; and

(b) The water quality to be maintained and achieved is not required to be substantially different from that which would occur naturally.

3.0 SETTING AND WATER QUALITY DESCRIPTION

3.1 General Setting and Source Assessment

Cherry Creek, a subwatershed of the Youghiogheny River basin, flows into Deep Creek Lake, a highly valued recreational lake in Garrett County, Maryland. Cherry Creek is part of the Western Maryland Sub-Basin (Figure 1). Its headwaters originate near the Savage River State Forest between the Meadow and Negro Mountains. Cherry Creek drains into Deep Creek Lake, which in turn drains into the Youghiogheny River. Cherry Creek is approximately 8 miles (13 km) in length. The Cherry Creek watershed has an area of approximately 7,900 acres (12 mi²). The land uses in the watershed consist of forest and other herbaceous (5,430 acres or 69%), mixed agriculture (788 acres or 10%), wetlands (964 acres or 12%), and urban (700 acres or 9%) based on 2000 Maryland Department of Planning land use/land cover data. Figure 2 shows the geographic distribution of the different land uses. Figure 3 shows the relative amounts of the different land uses.

Cherry Creek, named for its deep reddish color produced by peat bog tannins, is a naturally acidic, low gradient, slow flowing, wadeable stream in its upper reaches and a fast flowing mountain stream in its lower reaches. Cherry Creek once supported a brook trout population. Powell (1967) reported good fishing for brook trout averaging 8 inches near Rock Lodge in 1922. In 1957, a fish kill was reported in the Cherry Creek which was attributed to low pH. Until very recently, surveys of the fish and benthic macroinvertebrates at four stations in Cherry

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Creek by the Maryland Department of Natural Resources indicated that the stream remains impacted by AMD. Recent installation of lime dosing equipment has made observable improvements in the aquatic life (Mills, August 2002).

In the Cherry Creek watershed, the estimated average annual acidity load is 6,519 kg/day (14,340 lb/day) measured as $CaCO_3^{1}$. This estimated average annual load takes into account all sources of acidity in the observed data (AMD pollution, the presence of peat bogs, atmospheric deposition, and the low buffering capacity of the geologic formation present in the area).

¹In natural waters, much of a solution's alkalinity is due to carbonate species, alkalinity and acidity are often expressed in units of mg/l as CaCO₃. The molecular weight of CaCO₃ is equal to 100 gr/mol and each mol equals 2 equivalents/mol. Acidity or Alkalinity measured as mol/liter or equivalents/liter, can also be expressed as mg/l as CaCO₃ by multiplying the acidity or alkalinity in eq/l by "(100 gr/mol)*(1 mol/2 eq)* (1000 mg/gr)".



Figure 1: Location Map of the Cherry Creek Drainage Basin within Maryland



Figure 2: Land Uses in the Cherry Creek Drainage Basin



Figure 3: Proportions of Land Use in Cherry Creek Drainage Basin

3.1.1 Low pH and Natural Conditions of Cherry Creek

In the Cherry Creek, four important factors affect the pH of the water. Two of these factors are anthropogenic (AMD and atmospheric deposition); the other two are the naturally occurring conditions of the creek (the presence of peat bogs that are natural sources of acidity, mostly due to the organic carbon decomposition of the organic material in the water, and the low buffering capacity of the geology formation of the area). These natural conditions, which must be accounted for in the TMDL analysis, are discussed in further detail below:

a) The presence of peat bogs

The Cherry Creek watershed contains naturally occurring *Sphagnum spp*. wetlands. These wetlands, composed of bogs and coniferous forests, have natural high organic acidity and lower pH waters. Bogs are one of North America's most distinctive wetlands. These wetlands are characterized by spongy peat deposits, acidic waters, and a floor covered by a thick carpet of sphagnum moss. Bogs receive most or all of their water from precipitation rather than from runoff, groundwater or streams. As a result, these bogs have very low concentrations of nitrogen, potassium and phosphorus that are needed for plant growth. Over time, many feet of acidic peat deposits build up in bogs. The natural pH can be as low as 3.5.

Bogs support some of the most interesting plants in the United States. Plants common to these bogs are acid-thriving and acid-resistant plants, such as varieties of carnivorous plants (i.e., sundew, pitcher plant), *Sphagnum* moss, sheep laurel, leatherleaf, and larch. Bogs also serve an important ecological function in preventing downstream flooding by absorbing precipitation. The unique and demanding physical and chemical characteristics of bogs result in the presence

of plant and animal communities that demonstrate many special adaptations to low nutrient levels, waterlogged conditions, and acidic waters.

Bogs in the United States are mostly found in the glaciated northeast and Great Lakes regions, but also occur in the southeast. Their acreage declined historically, as they were drained to be used as cropland and mined for their peat, which was used as a fuel and a soil conditioner. Recently, bogs have been recognized for their role in regulating the global climate by storing large amounts of carbon in peat deposits. Bogs are unique communities that can be destroyed in a matter of days, but require hundreds, if not thousands, of years to form naturally. Because these peat bogs are valued habitats, it is important that pH values in Cherry Creek only be mediated in areas of disturbance and these unique natural areas be protected. Increases in ambient pH to 6.5 would be incompatible with these valuable and rare habitats; it would change the present plant community and disturb the peat and the pH gradient, resulting in impairment to species that have adapted to low pH levels.

b) Geology of the Cherry Creek Watershed

Cherry Creek is confined within the northeast-southwest trending of the Berlin Syncline. This coal basin is located along the eastern edge of the main bituminous coal field. The rocks exposed in the area are almost exclusively of Pennsylvanian age system, however, a small amount of Mississippian age system rocks are at the mouth of the creek. The groups of rocks within the Pennsylvanian system that are located in the Cherry Creek watershed are the Allegheny Formation and the Pottsville Formation. Description of these two formations are as follows (Maryland Geological Survey, 1968):

<u>Allegheny Formation</u>: Interbedded sandstone, siltstone, claystone, shale, and coal beds; Upper Freeport coal at top; where present, Brookville coal defines base; thickness 275 feet in northeast, increases to 325 feet in south and west.

<u>Pottsville Formation</u>: Interbedded sandstone, siltstone, claystone, shale, and coal beds; conglomeratic orthoquartzite and protoquartzite at base; thickness 60 feet in northeast increases to 440 feet in southeast.

As can be noted from the descriptions above, both formations lack the acid-neutralization capacity of the limestone. Limestone is not present in the area. A map from the Maryland Geological Survey of the area can be found in Appendix B.

3.1.2 Natural Conditions of pH in Cherry Creek

There are several cases of streams in Western Maryland that have a natural background pH below the criterion of 6.5. In Cherry Creek, the naturally acidic water from peat bogs remains acidic as it continues to flow down stream. This is due to the lack of mineral buffering capacity of the local geology.

Six water quality stations in Cherry Creek known to be unaffected by AMD were assessed to establish a reasonable water quality endpoint that accounts for the natural conditions. The

monitoring stations and associated data used for this analysis are described in Appendix A. For reasons described below, the findings apply generally across the entire Cherry Creek basin.

The water quality analysis revealed moderately low pH, and low iron and sulfate values. These findings support the claim that the areas are unaffected by AMD, which otherwise would be expected to have high iron and sulfate associated with low pH caused by AMD. Instead, the findings are consistent with situations resulting from waters with high bicarbonate or carbonic acid concentrations emanating from siderite-rich areas, or a similar dissolved carbon dioxide to bicarbonate sequence resulting from plant respiration and decay of organic matter. The later is clearly the case in Cherry Creek, where naturally low pH is mostly due to the decomposition of organic matter in the peat bogs.

The naturally low pH values vary from 4.2 to 4.6, with an average value of about 4.3. Because Maryland's pH criteria apply at all times, it would be reasonable to make use of the minimum value of the range of observed naturally low pH values. However, as a conservative assumption intended to offset the potential effect of atmospheric deposition of acidic compounds, the TMDL analysis makes use of the higher average values in the observed data presented in Table 1, including the pH of 4.3.

As noted above, it is reasonable to use the natural conditions findings for all the streams in the basin. This is because the peat bogs are found through out the basin, as is the geology that lacks buffering capacity. This justification is supported by the data from the six water quality stations, which are reasonably distributed throughout the basin area.

Parameters	Concentrations
pH (pH units)	4.34
Acidity (mg/l as CaCO ₃)	30.25
Alkalinity (mg/l as CaCO ₃)	0.0
Iron (mg/l)	1.00
Sulfate (mg/l)	9.06

	Table 1: Natural Condition	Values of Different Parameters	for the Cherry Creek
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3.2 Water Quality Characterization

Cherry Creek was identified as having low pH measurements due to nonpoint sources of acids (AMD) resulting in its addition to Maryland's 1996 of impaired waterbodies. Mining began in the Cherry Creek watershed in the early 1800's as small local deep mines. Extensive underground and surface mining conducted before adequate laws and regulations were enacted have produced numerous sources of uncontrolled AMD throughout the watershed. In 1969, Davis (1972) collected three species of fish at the mouth of Cherry Creek. Studies by the MDE's BOM and other state agencies documented the degradation of miles of Cherry Creek by AMD from numerous abandoned underground and surface coalmines. The first comprehensive study on the mining impacts in Cherry Creek was conducted in 1972. Skelly and Loy (1973) identified abandoned mine sources, collected stream quality information, and proposed abatement solutions for priority mine sites in the Cherry Creek and Casselman River watersheds.

Additional water quality and quantity data was collected in 1986 and 1987. Morgan assessed hydrologic conditions in 1988, and in 1987. Thompson assessed flora and fauna of the adjacent wetlands in the upper reaches and peat bog habitats of Cherry Creek. Since 1987, additional water quality data, annual stream discharge measurements, and biological community assessments have been conducted randomly throughout Cherry Creek. These studies have identified areas in the Cherry Creek watershed that support healthy naturally low pH peat bog floral and faunal populations, as well as sections of wetlands and stream that are impacted by abandoned mine drainage.

Since the late 1970s, the MDE's BOM has accomplished several mine abatement and wetland treatment projects to address the quality and quantity of water in Cherry Creek. Studies by the BOM and other state agencies have documented the degradation of miles in Cherry Creek by AMD from numerous abandoned coal mines. These studies have also identified sections of Cherry Creek Basin that support healthy peat bog floral and faunal populations.

Three key water quality parameters (pH, acidity, and alkalinity) are presented below. These data were collected by MDE and other agencies during various water quality surveys conducted in Cherry Creek from 1972 to 1994. A very extensive study (Skelly and Loy) of the watershed was conducted in 1972. Twelve sets of samples, one for each month of the year, were collected (12/6/71; 1/8/72; 3/11/72; 3/25/72; 4/8/72; 4/22/72; 5/27/72; 7/8/72; 7/29/72; 8/12/72; 9/9/72; 9/23/72; 10/14/72; 11/18/72). In addition, a total of twelve surveys were conducted from 1988 to 1994: two in 1988, 1991 and 1994, three in 1989 and 1990. The reader is referred to Figure 1 for the locations of the water quality sampling stations. Table 2 presents the distance of each station from the mouth.

Data from the Skelly and Loy study was available as 1972 monthly data for different parameters including pH, acidity, alkalinity, metals concentrations, etc. A comparative statistical analysis of this 1972 data and more recent data (from 1988 to 1994) was performed to investigate the possibility of using the 1972 data in the estimation of the TMDL. Results from the statistical analysis showed significant statistical differences between the 1972 data set and the 1988-1994

data set. It was concluded that the TMDL analysis would exclude the 1972 data set. Results from the comparative analysis can be found as Appendix C.

Water Quality Station	Miles from the Mouth of Cherry Creek	
CC-1	8.2	
CC-2	5.9	
CC-3	4.3	
CC-4	3.4	
CC-5	2.6	
CC-5b*	0.07 from intersection with Cherry Creek	
CC-6	1.0	
CC-7	0.14	

Table 2: Location of Water Quality Stations

*This station is located in an unnamed tributary of Cherry Creek

As shown in Figure 4 below, sample data for Cherry Creek between 1988 and 1994 show an overall pH ranging between 3.0 and 6.7 with an average of 4.16. The creek is showing pH water quality impairments at all stations and at all times based on the criteria of 6.5; however, based on the "natural conditions" of a pH of 4.3, the impairment occurs less frequently, with one station (CC-5) not showing impairment at any time during the sampling period. All stations sampled in the watershed showing pH impairment are known to be caused both by AMD and atmospheric deposition. All sources of acidity are taken into account implicitly by the TMDL analysis, because it makes use of observed data integrates all sources. Table 3 shows the range of pH values for each sampling station.



Figure 4: Longitudinal Profile of pH in Cherry Creek

Station	pH Range	pH Average
CC-1	3.9 - 6.3	4.35
CC-2	3.8 - 6.5	4.16
CC-3	3.6 - 5.1	4.08
CC-4	3.6 - 6.2	4.43
CC-5	4.6 - 6.2	4.93
CC-5b	4.3 - 4.4	4.38
CC-6	3.0 - 4.2	3.49
CC-7	4.2 - 5.3	4.60

 Table 3: pH data by Sampling Station

The waters of Cherry Creek exhibit varying degrees of AMD-related pollution. Data in Table 3 show that Cherry Creek is impaired from its headwaters all the way to the junction of the creek with Deep Creek Lake where it discharges. The low pH is due in part to AMD. However, surveys and studies done by several state agencies and consulting companies demonstrate that some areas of the creek that show low pH measurements are caused not only by AMD but also by natural sources of acidity. Several sampling stations that exhibit very low pH values are located in areas unaffected by AMD. These low pH values are the natural pH condition of many smaller streams within Cherry Creek and other streams in the region.



Figure 5: Longitudinal Profile of Acidity Concentration Data in Cherry Creek

Figure 5 represents the longitudinal profile of acidity and Table 4 shows average acidity data by sampling stations. These data were collected during different surveys from 1988 to 1994. The results of those surveys indicate that the general water quality of the sampled stations is unacceptable at most times throughout the survey period. Cherry Creek has been found to exhibit significant mine drainage pollution related to mining activities. All stations shown in Figures 4, 5 and 6 are impacted by AMD. However, as stated previously, some portions of the surveyed area exhibit low pH values due to natural causes. Those stations are not shown in these figures.

Station	Acidity Range	Acidity Average
	Mg/l as CaCO ₃	mg/l as CaCO ₃
CC-1	2.2 - 140	50.8
CC-2	0.0 - 310	47.3
CC-3	14.8 - 359.4	80.1
CC-4	2.0 - 90.8	31.2
CC-5	0.0 - 94.6	28.9
CC-5b	33.6 - 41.2	36.4
CC-6	10 - 486.8	121.9
CC-7	10.5 - 87.6	36.2

As shown in Table 5 below, alkalinity concentrations in Cherry Creek were always 0.0 mg/l at all the stations in the survey area. These sample results reflect the geochemistry associated with the Pennsylvania geologic system where the Cherry Creek watershed is located (the Allegheny Formation and the Pottsville Formation). As explained above in Section 3.1.1, both formations lack the acid-neutralization capacity of limestone, which is not present in the area. A geological map of the area can also be found in Appendix B (Maryland Geological Survey, 1968).

Station	Alkalinity Range	Alkalinity Average
	Mg/l as CaCO ₃	mg/l as CaCO ₃
CC-1	0.0 - 0.0	0.0
CC-2	0.0 - 0.0	0.0
CC-3	0.0 - 0.0	0.0
CC-4	0.0 - 0.0	0.0
CC-5	0.0 - 0.0	0.0
CC-5b	0.0 - 0.0	0.0
CC-6	0.0 - 0.0	0.0
CC-7	0.0 - 0.0	0.0

Table 5: Alkalinity Concentration data by Sampling Station



Figure 6: Longitudinal Profile of Net Alkalinity Concentration Data in Cherry Creek

Because the total alkalinity of the samples is consistently 0 mg/l, the net alkalinity (alkalinity - acidity) of the stream segments is consistently negative. Consequently, the stream is not capable of neutralizing any acid loads. Figure 6 and Table 6 show the different ranges and averages of net alkalinity, also known as acid neutralization capacity (ANC), for the eight stations in Cherry Creek.

Station	Net Alkalinity Range	Net Alkalinity Average
	mg/l as CaCO ₃	mg/l as CaCO ₃
CC-1	-140 to -2.2	-50.8
CC-2	-310 to 0.0	-47.3
CC-3	-359.4 to -14.8	-80.1
CC-4	-90.8 to -2.0	-31.2
CC-5	-94.6 to 0.0	-28.9
CC-5b	-41.2 to -33.6	-36.4
CC-6	-486 to -10	-121.9
CC-7	-87.6 to -10.5	-36.2

Table 6: Net Alkalinity Computed for Each Sampling Station

3.3 Water Quality Impairment

The water quality impairment of Cherry Creek addressed by this TMDL consists of pH that is below the State's numeric criterion, after accounting for natural conditions. These violations are the result of AMD related to past mining operations in the area.

Cherry Creek, as part of the Youghiogheny River System, has been designated as a Use I water body, pursuant to which it is protected for water contact recreation, and protection of aquatic life and wildlife. See COMAR 26.08.02.03-3. Use I waters are subject to a pH criterion of not less than 6.5 and not higher than 8.5 at any time (COMAR 26.08.02.03-3A(4)), unless due to natural conditions. An analysis, summarized in Section 3.1.2 of this report, indicates that a natural pH of 4.3 is acceptable throughout the Cherry Creek basin. Low pH values, and elevated concentrations of acidity, can interfere with designated uses of the creek such as protection of aquatic life.

The data collected from 1972 to 1994 show the pH threshold of 4.3 has been exceeded at different locations throughout the stream during those surveys, including the most recent period. The pH values in Cherry Creek have been observed to reach values as low as 3.0.

4.0 TOTAL MAXIMUM DAILY LOADS AND ALLOCATION

4.1 Analysis Background and Overview

This section provides some background on pH, and its relationship to acidity and alkalinity. It also provides an outline of the methodology used to compute the TMDL.

4.1.1 Background

pH is a measure of the concentration of hydrogen ions (H⁺) in solution, which indicates the relative acidity or alkalinity of an aqueous solution. Although pH is a good indicator of environmental conditions needed to support aquatic life, it is not conducive to the statistics needed in the TMDL analysis. Of more importance, however, is that pH does not measure latent acidity, which for example can be produced from the hydrolysis of metals. Nor does pH indicate how much acid a water body can assimilate, which involves understanding the buffering capacity of the water. Therefore, rather than use pH directly, acidity was used to conduct the TMDL analysis. A relationship between acidity and pH, developed using site-specific data, allows the results of the TMDL analysis to be translated into an endpoint for pH.

4.1.2 Overview

This analysis has three elements. First, a relationship between acidity and pH is established. This relationship is used to translate our pH goal of 4.3 to an acidity goal that is used in the TMDL computations.

Second, for each monitoring station along the river, we compute the mean and standard deviation of the acidity data. Based on these statistics we generate sets of "synthetic data" for each stream location that have the same statistical properties as the observed data. Each set of synthetic data for each station have some data points that violate the water quality criterion, including some values that are more extreme than those in the observed samples. These data sets represent the current conditions from which reductions in acidity are needed to achieve the desired pH.

Third, beginning at the upstream station, we simulate reductions in the acidity. At the given station, a reduction is determined that is sufficient to ensure that all simulated data point meet the water quality criterion. After this upstream acidity reduction is determined, the process is repeated at the next station down stream, accounting for upstream reductions and any sources of acidity that might lie between the two stations. This process is continued in a step-wise process down stream to the outlet of the creek. The sum of the reductions made at each step represent the total reduction needed to achieve the pH criterion throughout the system. The TMDL can be expressed in terms of maximum allowable acid load to the stream, and the reduction information provides guidance for future implementation strategies.

The remainder of this section describes these three steps in more detail as they apply to Cherry Creek. The TMDL analysis results are summarized, including allocations and the margin of safety.

4.2 Computational Methodology and TMDL Analysis

This section provides a more detailed discussion about the computational methodology outlined above. The TMDL analysis for Cherry Creek is also described.

4.2.1 Relationship Between Net Alkalinity, Acidity and pH

As noted above, the TMDL analysis focuses on determining an allowable acidity load, which must be related to an allowable pH. This section describes how that relationship is established in general, and for the specific case of Cherry Creek.

This TMDL analysis methodology makes use of total alkalinity and total acidity measured in field samples. By convention, these parameters are expressed in units of mg/l as CaCO₃. The difference of alkalinity minus acidity is called the "net alkalinity." The net alkalinity reflects the ANC of a stream, that is, the ability of the stream to act as a buffer when acid is added to the stream. Based on observed data, a relationship can be established between net alkalinity and pH, which can also be related to acidity. For example, a plot of pH versus net alkalinity data from a wide number of streams in Western Pennsylvania demonstrated that pH will be greater than 6.0 if the net alkalinity is zero or greater. A similar analysis, describe immediately below, is conducted for data specific to this watershed in Maryland.

As discussed above in the Section 3.1.1 Cherry Creek is known to have naturally low pH. This is due in great part to the low buffering capacity of the stream due to geochemistry that is characterized by a lack of alkalinity. Data collected from sites in Cherry Creek that have no mining activity show that the alkalinity is consistently zero. Thus, the net alkalinity is simply 0 - acidity, or the negative acidity.

Data from the 6 sites used to determine the natural pH conditions, show that the net alkalinity varies from -14 to -55, and the pH varies from 4.2 to 4.6. The data show that, if the net alkalinity is -30 or greater, then the pH water quality target of 4.3 will be maintained (See Appendix A). Because the alkalinity of this system is consistently zero, the previous result corresponds to maintaining an acidity concentration of 30 mg/l or less.

4.2.2 Monte Carlo Sampling and Synthetic Data

The next step in the analysis makes use of a stochastic analysis method called Monte Carlo Simulation. Environmental parameters typically exhibit significant natural variability. It is common to treat some environmental parameters as random variables that have a lognormal distribution. The lognormal distribution has the following properties: Negative values have zero probability of occurring, and the likelihood of large values tapers off gradually similar to a normal distribution (See discussion in Appendix D).

Typically, the analyst has a small number of observed water quality samples. However, there is more information associated with the data than the values of the individual samples by themselves. Namely, information can be extracted from the *group* of data point in terms of

relationships *between* samples. Specifically, we can estimate a central tendency of the water quality parameter such as a mean. Assuming that these water quality samples are from a real universe that has a lognormal distribution, the observed data can also be used to estimate the standard deviation of that distribution. Given these basic properties, which estimate how the real data would be distributed, the analyst can question how frequently the water quality criterion would be violated if more samples were available, or ask what the resulting magnitude of the 90th percentile of the data might be. Answers to these questions may be estimated by generating "synthetic" data and making full use of the data as a group. This process of creating synthetic data is called Monte Carlo Sampling¹. The overall analysis, in which we make use of the synthetic data, is referred to as Monte Carlo Simulation².

Monte Carlo Sampling was used to generate synthetic data sets containing 5,000 data points for each of the eight sampling stations in the basin (CC-1, CC-2, CC-3, CC-4, CC-5, CC-5b, CC-6, and CC-7). The locations of theses stations are presented in Figure 1. Summary statistics of the simulated initial conditions of acidity for each of these stations are presented in Table 7. The means and standard deviations are based on observed data, and the percentile observations are based on synthetic data.

Station	Standard ^a	Minimum ^b	Mean ^a	Median	90 th	Maximum ^b
	Deviation	(mg/l) ^c	(mg/l)	(mg/l)	Percentile	(mg/l)
					(mg/l)	
CC-1	36.3	9.3	50.8	41.4	94.1	422.7
CC-2	58.2	3.2	47.3	29.8	101.3	930.8
CC-3	92.2	6.2	80.1	52.5	170.4	1786.2
CC-4	19.9	6.7	31.2	26.3	55.6	285.7
CC-5	22.9	4.5	28.9	22.6	55.3	368.9
CC-5b	3.4	29.2	36.4	36.2	40.7	51.5
CC-6	125.5	11.7	121.9	84.9	252.4	2721.4
CC-7	25.8	6.6	36.2	29.5	66.9	403.0

Table 7: Summary Statistics of the Initial Conditions of Acidity Concentrations in Chern	ry
Creek based on Monte Carlo Sampling	

a. The means and standard deviations are based on observed field data. The other values are based on synthetic data from Monte Carlo Sampling, which made use of observed standard deviations in the data.

b. The minimum and maximum are the 1st and 100th percentile values of the 5,000 observation synthetic data sets.

c. Acidity concentrations are expressed in mg/l as CaCO₃.

¹ The term "Monte Carlo sampling" is being used loosely in this context. Techniques vary widely, from crude techniques, to more sophisticated techniques that make use of stratified sampling to increase precision and efficiency.

² These computations were implemented using @Risk, Risk Analysis and Simulation Add-in for Microsoft Excel, Palisade Corporation, Newfield, NY, 2001.

4.2.3 TMDL Computation

The synthetic data, generated by Monte Carlo Sampling, provides an estimation of distribution of acidity concentrations. Based on the information from the actual field samples, these synthetic values represent the expected results if many samples were collected over time under existing conditions. These synthetic values serve as the starting point of the TMDL computation, which is a mass balance approach that makes use of the synthetic distributions at each sampling station.

As described in the analysis overview, the analysis method of the TMDL involves a series of computational steps that proceed from upstream stations to downstream stations. Each step in the process involves simulating reductions in acidity loads that reduce the mean concentration at the given water quality monitoring station. This change in mean, in turn, reduces the standard deviation of the lognormal distribution, shifting it towards lower concentrations. Iterative load reductions are simulated for the given station until the 100th percentile value of the distribution is equal to the water quality endpoint of 30.3 mg/l, which corresponds with a pH of 4.3.

After the reduction is determined for each individual station, and allowable concentrations at each station are estimated, reduced loads starting at the most upstream station in the stream are passed downstream. The allowable load at the downstream station is adjusted to reflect the load reduction made upstream before performing the load reduction calculations at that station. If a downstream station has more than one branch feeding it from upstream, the analysis accounts for the combined effects of the reduction in loads from the multiple upstream stations. Part of the series of computations is presented as an example below.

Station CC-1 Computation:

Station CC-1 is located at the headwaters of the watershed (See Figure 1). Given an average annual flow of 0.0246 m³/s, and an existing observed average concentration of 39.4 mg/l, the existing load to CC-1 is calculated to be 83.7 kg/day. Based on the synthetic data distribution for CC-1, the maximum allowable average concentration that ensures that a peak acidity concentration of 30.3 mg/l is never exceeded was determined to be 2.3 mg/l. This translates to a necessary load reduction of 78.9 kg/day (94.2%), from 83.7 kg/day to an allowable load of 4.9 kg/day.

Station CC-2 Computation:

Station CC-2 is the next station down stream of CC-1. Given an average annual flow of 0.0567 m^3/s , and an existing observed average concentration of 39.4 mg/l, the existing load to CC-2 is calculated to be 533.4 kg/day. Based on the synthetic data distribution for CC-2, the maximum allowable average concentration that ensures a peak acidity concentration of 30.3 mg/l is never exceeded was determined to be 3.5 mg/l. For the given flow, this concentration translates to an average allowable load of 47.4 kg/day. To reach this load requires a reduction of 486.0 kg/day (91.1%). Accounting for the upstream reduction of 78.9 kg/day associated with station CC-1 implies that a remaining reduction of 407.1 kg/day is needed (please see the following equation):

533.4 kg/day (Existing Load) <u>- 78.9</u> kg/day (Reduction from upstream CC-1 analysis) 454.5 kg/day (Balance) <u>-407.1</u> kg/day (Additional Reduction Needed) 47.4 kg/day (Allowable Load)

The entire set of computations is summarized in Appendix E.

4.2.4 Summary of Total Maximum Daily Load and Allocations

Based on the average annual flows and observed average concentrations, an existing average annual acidity load of 2,379,362 kg/year, expressed in mg/l as $CaCO_3$ (6,518.8 kg/day) can be estimated. The series of calculations described above necessitate a load reduction of 2,108,207 kg/year (5,775.9 kg/day) to ensure that the criterion is achieved at all times. This represents an 88.6% reduction, on average across the entire basin.

In summary, the maximum allowable load, based on average annual computations, is as follows:

For Acidity Expressed as CaCO₃ (kg/year):

TMDL	=	LA	+	WLA	+	MOS
271,155	=	271,155	+	0	+	Built-in

On average, this TMDL can be expressed as an allowable load of about 742.9 kg/day.

4.2.5 TMDL Sensitivity Analysis and Margin of Safety

The small number of samples at each sampling stations leads to a rather large estimated variance in the data set for the given station. This, in turn, is translated into large extreme values in the synthetic distributions computed using Monte Carlo sampling. Because Maryland's pH criterion are stated in terms of being met "at all times", the extreme values in the synthetic distribution lead to extreme results which are conservative with respect to protection of the environment. Although the true variances are unknown, this section provides insight regarding how the TMDL results would change if the extreme values were removed from the synthetic distributions.

For this sensitivity analysis, the removal of acidity values beyond the 99th and 90th percentiles were considered. The extreme values in the distribution were removed from the data set and the necessary load reductions were recomputed.

Scenario	Allowable Load	Percent Reduction	
	(kg/day)	Basin-wide	
Current TMDL Analysis	743	88.6 %	
Removal of 99 th Percentile *	940	85.6 %	
Removal of 90 th Percentile *	1,442	77.9 %	

Table 8: Comparison of Estimated Maximum Allowable Acidity Load with Estimates based on Removal of Extreme Values from the Synthetic Lognormal Distribution

* Although this table could be interpreted in terms of meeting the criterion 99% of the time (or 90% of the time), we caution against this view. Because, the variance is suspected to be larger than might actually be the case, this analysis might be better interpreted as a quick sensitivity analysis of the results to the variance in the observed data.

These sensitivity results suggest that the TMDL analysis is conservative with regard to protection of the environment. Because a small sample size tends to result in a larger estimated variance of a data set, it is reasonable to suspect that the extreme values observed in the synthetic data sets are unlikely to be observed in the environment. This, for example, leads to a 21% difference in loadings between cases computed on the basis of 100^{th} percentile (743 kg/day) and the 99th percentile (940 kg/day). This suggests that the analysis includes a built-in margin of safety.

In addition, when selecting the pH water quality endpoint under conditions of natural low pH, an average value was used rather than the minimum observed pH. Given that the State water quality standards apply "at all times", it would have been reasonable to use the minimum value. The use of the average value represents another built-in margin of safety.

5.0 ASSURANCE OF IMPLEMENTATION

This section provides the basis for reasonable assurances that the acidity TMDL will be achieved and maintained. Since 1998, the Maryland Department of the Environment Bureau of Mines has constructed three passive treatment systems for the Glotfelty, Everhart, and Teets sites and one in-stream lime doser in the watershed to neutralize the highly acidic mine drainage into Cherry Creek.

Several reports have been published since the early 1970's with recommendations for treating the abandoned mine drainage problem in the Cherry Creek watershed. The earliest of these reports is the Mine Drainage Pollution Watershed Survey for the Cherry Creek and Casselman River Watersheds (Skelly and Loy, 1971). This report recommended an abatement plan, mostly consisting of strip mine reclamation. They also recommended that all abatement measures should be protected after construction to ensure effectiveness. In addition, sources of pollution other than mine drainage, such as poor land use practices resulting in siltation should be remedied. Possible future sources of acid mine drainage pollution should be strictly regulated. Other reports include the "Cherry Creek Acid Mine Drainage Mitigation Plan" by the MDE's Bureau of Mines (2001).

Abandoned mine reclamation is the major step required in returning this area to a near natural state. Benefits from mine reclamation will not only be realized by new stretches of fishing water but also by the restoration of the natural environment.

Two factors provide assurance that this TMDL will be implemented. First, the MDE's Abandoned Mine Reclamation Program restores eligible environments previously degraded by adverse effects of past coal mining practices, including measures for the conservation of water, fish, wildlife, and recreation resources and promotes research relating to the development of water quality control methods and techniques. In addition, there are no active mining activities in the watershed and any future mining would require permit holders to improve water quality in the region.

Secondly, Maryland has recently adopted a five-year watershed cycling strategy to manage its waters. Pursuant to this strategy, the State is divided into five regions and management activities will cycle through those regions over a five-year period. The cycle begins with intensive monitoring, followed by computer modeling, TMDL development, implementation activities, and follow-up evaluation. The choice of a five-year cycle is motivated by the five-year federal National Pollutant Discharge Elimination System (NPDES) permit cycle. This continuing cycle ensures that, within five years of establishing a TMDL, intensive follow-up monitoring will be performed. Thus, the watershed cycling strategy establishes a TMDL evaluation process that assures accountability.

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