



Total Maximum Daily Load For:
Upper Harshaw Creek, Sonoita Creek Basin,
Santa Cruz River Watershed,
Coronado National Forest,
near Patagonia, Santa Cruz County, Arizona

HUC: 15050301-025A
Parameters: Copper and Acidity

June 30, 2003

Publication Number OFR 07-09

**NOTE: Since initial publication the contact information has been updated.
For more information please contact:**

**TMDL Unit Supervisor
602-771-4468
800-234-5677
TDD 602-771-4829**

ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY

Proposal of a Total Maximum Daily Load For:
Upper **Harshaw Creek**, Sonoita Creek Basin,
Santa Cruz River Watershed,
Coronado National Forest,
near Patagonia, Santa Cruz County, Arizona

HUC: 15050301-025A
Parameters: **Copper and Acidity**

June 30, 2003

APPROVALS

Prepared & Submitted by: _____ Date: _____

Robert Scalamera, Hydrologist, TMDL Unit

Approved by: _____ Date: _____

Nancy LaMascus, Supervisor, TMDL Unit

Approved by: _____ Date: _____

Linda Taunt, Manager, HSA Section

ACKNOWLEDGMENTS

The author would like to thank the following people for advice, general and background information:

- Kenyon Carlson and Lilly Thompson, ADEQ - Quality Assurance Unit
- Various personnel of the Arizona Department of Health Services, State Laboratory
- Andy Cajero-Travers, Hydrologist, ADEQ
- Robert Wallin, Geologist, ADEQ
- Floyd Gray, Economic Geologist, U.S. Geological Survey, Tucson, Arizona
- Robert Lefevre, Watershed Manager; Eli Curiel, Hazardous Material Coordinator; Duane Bennett, Forester, Coronado National Forest, U.S. Forest Service
- Mike Sierakoski, V.P. Metallurgy, Silver Eagle Resources (now Mercator Minerals), Tucson, Arizona
- Duane Yantorno, Division Environmental Manager; Stu Bengson, Chief Agronomist, Asarco, Tucson, Arizona

Note: ADEQ has rewritten this report based on comments submitted in response to the previous (12/06/01) report and to reflect changes in Arizona's Surface Water Quality Standards resulting from the 2002 triennial review.

Project Manager: Robert J. Scalamera, Hydrologist
Arizona Department of Environmental Quality
Water Quality Division
Hydrologic Support & Assessment Section, TMDL Unit
E-mail: scalamera.robert@ev.state.az.us
Telephone: (602) 771-4515

Mail Address: Arizona Department of Environmental Quality
Water Quality Division
Hydrologic Support & Assessment Section, TMDL Unit
Robert J. Scalamera / Mailstop 5415A-1
1110 W. Washington St.
Phoenix, Arizona 85007

ACRONYMS

ADEQ	Arizona Department of Environmental Quality
HEC-HMS	Hydrologic Modeling System produced by the U.S. Army Corps of Engineers, Hydrologic Engineering Center, Sacramento, California
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act, commonly known as Superfund
CWA	Clean Water Act
HUC	Hydrologic Unit Code
LA	Load Allocation (Non-Point Sources)
MOS	Margin of Safety
NPDES	National Pollutant Discharge Elimination Systems (CWA source permits program)
TMDL	Total Maximum Daily Load
USEPA	United States Environmental Protection Agency (also EPA)
USGS	United States Geological Survey
USFS	United States Forest Service
WLA	Waste Load Allocation (Point Sources)
WQS	Water Quality Standards (AZ)
cfs	cubic feet per second (commonly used discharge measurement unit)
ft	feet
mg/L	milligrams per liter (pollutant concentration measurement unit)
µg/L	micrograms per liter (pollutant concentration measurement unit)
kg/day	kilograms per day (pollutant load measurement unit)

DEFINITIONS OF TERMS USED IN THIS REPORT

Bankfull (discharge)	The flow in the stream at the point of incipient flooding; i.e., the largest non-flood discharge.
Baseflow (discharge)	The perennial portion of the stream discharge; the flow not directly dependent on precipitation events. In the case of an ephemeral stream, baseflow equals zero.
Ephemeral	A stream that has a channel that is at all times above the water table and that flows only in direct response to precipitation
Intermittent	A stream or reach of a stream that flows continuously only at certain times of the year, as when it receives water from a spring or from another surface source, such as melting snow. (AAC R18-11-101(30))
Mining Residue	Residue that is a result of mine related activities and takes the form of waste material piles and spills.
Perennial	A surface water which flows continuously throughout the year. (A.A.C. R18-11-101(38))
Point source	Any discernible, confined, and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fixture, container, rolling stock, concentrated animal feeding operation, landfill leachate collection system, vessel, or other floating craft from which pollutants are or may be discharged. (40 CFR 122.2)
Significant Mining	Mine related activities which result in an observable impact, such as adit drainage or a large volume of exposed mining residue.

NOTE: ADEQ uses USGS maps as the source of names for streams, mines, and other features.
Where local usage varies, such differences are noted.

TABLE OF CONTENTS

1.0 PREFACE.....	1
1.1 The Clean Water Act (CWA) §303[d] and Its Significance.....	1
1.2 TMDL Defined.....	1
1.3 The TMDL Process.....	1
1.4 Project History.....	2
2.0 PHYSICAL SETTING.....	3
2.1 Overview.....	3
2.2 Climatology.....	3
2.3 Hydrology.....	3
2.4 Geology.....	4
2.5 Vegetation/Wildlife.....	4
2.6 Land Use/Land Ownership.....	5
2.7 Problem Statement.....	5
3.0 NUMERIC TARGETS.....	8
3.1 Surface Water Quality Standards.....	8
3.2 In-stream Indicators.....	9
3.3 Data Supporting Delisting of Zinc.....	13
4.0 SOURCE ANALYSIS.....	14
4.1 Current Conditions.....	14
4.2 General Sources.....	14
4.2.1 Natural Background.....	14
4.2.2 Adit Drainage.....	15
4.2.3 Mining Residues.....	15
4.2.4 Streambeds.....	16
4.3 Existing, Known Sources.....	16
4.3.1 Headwaters/Uppermost Tributaries.....	16
4.3.2 Middle Portion of the Subject Basin.....	17
4.3.3 Bottom of the Subject Reach.....	17
4.4 Source Summary.....	17
5.0 LINKAGE ANALYSIS.....	19
5.1 Linkage of Sample Sites and Sources.....	19
5.2 Critical Conditions.....	19
6.0 LOAD CALCULATIONS AND TMDL.....	21
6.1 Model Considerations.....	21
6.1.1 Data Sources and Limitations.....	21
6.1.2 Conceptual Model.....	22
6.1.3 Flows.....	22
6.1.4 Loads.....	23
6.1.5 Modeling Scenarios.....	23
6.1.6 Calculation of Flow-extrapolated Concentrations.....	23

6.2 Load Capacity	23
6.3 Margin of Safety	27
6.3.1 Explicit Margin of Safety	27
6.3.2 Implicit Margin of Safety	27
6.4 Allocations and TMDL.....	28
6.4.1 TMDL Calculations.....	28
7.0 IMPLEMENTATION.....	33
8.0 PUBLIC PARTICIPATION AND RESPONSIVENESS SUMMARY.....	34
9.0 BIBLIOGRAPHY AND REFERENCES	35
APPENDIX A - Data Collection	36
APPENDIX B - Calculation of Concentration Extrapolation Factors.....	39

1.0 PREFACE

1.1 The Clean Water Act (CWA) §303[d] and Its Significance

The CWA §303[d][1][A] requires that "Each State shall identify those waters within its boundaries for which the effluent limitations...are not stringent enough to implement any water quality standard applicable to such waters." This act also requires states to establish Total Maximum Daily Loads (TMDLs) for such waters.

The CWA §303[d] requires states to submit to the United States Environmental Protection Agency (USEPA) a list of the surface waterbodies for which the designated use (e.g. irrigation, partial body contact, etc.) of that waterbody is impaired or "water quality limited". Surface water quality data are compared with water quality standards and other criteria to determine whether the waterbody is meeting its designated uses. ADEQ publishes a report on the status of surface water and groundwater quality in Arizona every two years (in accordance with the CWA §305(b)) and from this report derives the "Impaired Waters" or "303[d] List".

The TMDL process provides a flexible assessment and planning framework for identifying load reductions or other actions needed to attain surface water quality standards; i.e. water quality goals to protect aquatic life, drinking water, and other water uses. The CWA established the TMDL process to guide application of state surface water quality standards to individual waterbodies and their watersheds.

1.2 TMDL Defined

The requirements of a TMDL analysis are described in 40 CFR §130.2 & §130.7, based upon CWA §303[d]. A TMDL is described as "the sum of the individual wasteload allocations for point sources and load allocations for non-point sources and natural background" and a margin of safety such that the capacity of the waterbody to assimilate pollutant loadings is not exceeded. Represented as a mathematical equation:

$$\text{TMDL} = \sum \text{WLA} + \sum \text{LA} + \text{MOS},$$

where WLA is the wasteload allocation consisting of loads from point sources, LA is the load allocation consisting of non-point source loads, and MOS is a Margin of Safety which serves to address uncertainties in the analysis and the natural system.

1.3 The TMDL Process

A TMDL analysis is a tool for implementing state surface water quality standards and is based on the relationship between pollution sources and in-stream water quality conditions. The TMDL process is a method used in balancing the pollution concerns for a waterbody and allocating the acceptable pollutant loads among the different point and non-point sources allowing the selection and implementation of suitable control measures to attain water quality standards.

In implementing TMDLs, certain criteria must be taken into account. These criteria include loading capacity, load allocation, wasteload allocation, natural background, and the margin of safety. The loading capacity is the greatest amount of loading that a waterbody can receive without violating water quality standards. Load allocation is the portion of a receiving water's loading capacity that is attributed either to one of its existing non-point sources of pollution or to natural background sources. The portion of the receiving waters' loading capacity that is attributed to existing point sources of pollution is known as the wasteload allocation. Finally, the margin of safety is the factor that accounts for any uncertainty in the relationship between

the pollutant loads and the quality of the receiving waterbody (40 CFR §130.2[f-g]). Total pollutant loads are determined by combining the point, non-point and background sources of pollution.

ADEQ has adopted a stakeholder process for many of its programs, including TMDLs. ADEQ works closely with affected stakeholders in developing the TMDL by holding meetings to solicit input on a variety of topics including background information; potential modeling scenarios; identifying possible pollutant sources for allocation; and discussing potential implementation strategies. Once TMDLs are developed for all the water quality problems, they are submitted to the EPA for review and approval.

The TMDL process is not complete once wasteload allocations and load allocations have been determined. Assessment of the TMDL effectiveness must be made. Ideally, this would begin within two years after implementation and continue for the period necessary to measure effectiveness.

1.4 Project History

ADEQ performed this investigation of upper Harshaw Creek in response to the stream being listed for violations of water quality standards on the 1996 and 1998 303[d] Lists. Because Harshaw Creek is one of three stream segments in the Sonoita Basin that was listed on the State's 303[d] List of impaired waters, ADEQ decided to perform investigations of these segments simultaneously. The other waterbodies in this study are Alum Gulch and Three R Canyon. This project was started in 1997 and site monitoring was performed between 1997 and 2000 by ADEQ staff.

In 2000, ADEQ hired Hydro Geo Chem (HGC) of Tucson, AZ to review available data, select an appropriate model, and conduct flow and load modeling for the three listed segments within the Sonoita Basin. HGC used ADEQ field measurements to support modeling. The first draft of this TMDL investigation was based solely on ADEQ field measurements and modeling performed by HGC. It was released for public review in December, 2001 and it received considerable public comment.

In the spring of 2002, the USGS completed a six year long study in the Sonoita Basin. USGS staff has made available to ADEQ staff all monitoring data and findings which would be considered pertinent to the three TMDL investigations. All references to their data and findings included herein were received through personal communication with USGS staff. Currently, results from their investigation are being synthesized into a draft report.

After the public review period, when the USGS data and findings became available, ADEQ tasked HGC with reviewing this information and updating the model as necessary. HGC determined that the USGS data supported and enhanced ADEQ's understanding of pollutant sources and critical conditions; however, the USGS data did not offer new flow related events which could be used in the model. ADEQ revised the report based on this additional analysis. Additionally, USEPA approved ADEQ's proposed 2002 triennial review changes to surface water quality standards. The TMDLs were recalculated using the new standards and applicable revised designated uses. This draft of the report incorporates the additional data and changes to Arizona's water quality standards.

2.0 PHYSICAL SETTING

2.1 Overview

The Harshaw Creek Basin is in Santa Cruz County, Arizona. The closest town is Patagonia, Arizona. The approximate center of the basin is, latitude: 31° 29' N, longitude: 110° 44' W. Basin elevation ranges from 6,600 ft. to 4,800 ft. The subject reach (the 303[d]-listed reach) is referred to as "upper Harshaw Creek" for the purposes of this project. The primary tributary to the listed portion of Harshaw Creek is an un-named canyon containing the Endless Chain Mine and an undisturbed basin that provides natural background measurements. There are no active mines in the subject basin. Figures 1, 2, and 3 provide views of the project location, overall area, and the subject basin.

For purposes of this study, upper Harshaw Creek is divided into three sections:

- The headwaters and uppermost tributaries occupied by the Morning Glory Mine adits, shafts and mining residues. The Endless Chain Tributary (unofficial name for purposes of this study) containing the Endless Chain Mine and mill site, and an undisturbed basin.
- The middle portion between the mouth of the Endless Chain tributary and the Trench Camp Mine containing the Augusta Mine, Blue Nose Mine and several other small mines.
- The bottom portion of the subject reach includes dump number 3 of the Trench Camp Mine and a spring near the downstream end of the subject reach with the only observed constant drainage in the subject basin.

2.2 Climatology

The climate of the Harshaw Creek basin varies from high desert in the Sonoita Valley to the steppe-like climate of the higher elevation grasslands and scrub forest. Below-freezing temperatures are to be expected during the winter months, and precipitation, both rain and snow, occurs most winters. Most summers bring "monsoon" thunderstorms. Snow may remain on the higher elevations for periods ranging from hours to weeks.

The closest weather stations to the subject basin, at Canelo Pass, Nogales, and San Rafael Ranch, have different climatic settings (e.g., elevation, position relative to mountains) and do not accurately reflect the conditions found in the Harshaw Creek basin.

2.3 Hydrology

The 3-mile long subject reach is primarily ephemeral with a perennial spring located approximately 50 ft. above the downstream end of the listed reach. During baseflow conditions, when runoff was not present, flow from the springs was not observed beyond approximately 50 ft. downstream from the springs. Based upon field observations, groundwater (from the springs) is the sole source of flow during baseflow conditions.

Measured and modeled discharges on the subject reach varied from 0.75 to 75 cfs. Upper Harshaw Creek drains approximately 2,300 acres and no flow gaging stations exist on the subject waterbody. Field observations confirm that all of the tributaries to upper Harshaw Creek are ephemeral. During the 2002 ADEQ triennial review of standards, a flow-related designated use change, from perennial to ephemeral, was adopted for Harshaw Creek from the headwaters

to its mouth on Sonoita Creek.

2.4 Geology

The Harshaw Basin lies within the Basin and Range physiographic province. This province, typified by north-northwest trending normal faults, has broad, gentle sloping valleys, such as the upper Sonoita Creek valley, separated by sharply rising mountain ranges.

The USGS map and sections of the Nogales and Lochiel quadrangles show the Harshaw Creek Fault is the dominant feature within this basin. The Harshaw Creek Fault is a north-northwest trending left-lateral strike-slip fault which shows more than 4 mile displacement at its southernmost end. It is thought to be associated with the Laramide Orogeny, making it Late Cretaceous. From its headwaters, Harshaw Creek trends northeast for about one-half miles until it makes a gradual ninety degree turn to the northwest. Harshaw Creek parallels the fault, staying just west of it, for about 3 miles where it takes a fifty degree turn to the northeast and crosses the fault. The bedrock of this westernmost portion of Harshaw Basin is a 2,000 foot section of Lower Cretaceous Bisbee Formation which has been down-dropped between the Harshaw Creek Fault and the Bluenose Fault, to the west. The Bisbee formation is a sedimentary unit composed of siltstone and mudstones, some sandstone, limestone and conglomerate. It is weakly to strongly hornfelsed and pyritic. The Morning Glory, Endless Chain, Augusta, and Blue Nose Mines lie within this formation. It should be noted that the Bisbee Formation limestone lines much of the stream channel. The basal section of the Bisbee Formation is a conglomerate which lies unconformably on top of greater than 750 feet of Jurassic/Triassic silicic volcanic rocks.

After crossing the fault, Harshaw Creek continues in the northeast direction for several miles, although only two miles of it lies within the study area. The Bisbee Formation to the west of the fault has been juxtaposed, in the northern area, to a greater than 2,000 foot section of Jurassic/Triassic silicic volcanic rocks that contain local outcrops of limestone conglomerate. In the northeasternmost portion of this basin, the silicic volcanics are unconformably overlain by more than 1,000 ft. of Upper Cretaceous trachyandesite.

The Naco Group, a continuous section of Middle-Upper Pennsylvanian to Permian limestones, dolomitic, sandy, and/or fossiliferous in areas, underlies the silicic volcanics in the northeast. In the southeast, faulting has exposed different portions of this unit at the surface via a series of upthrown and downthrown blocks. Below the Naco Group is a 2,000 foot section of conformable but non-continuous pre-Cambrian to Middle Paleozoic rocks. The upper 1,500 ft. contains a series of limestone units and the lower 500 ft. contains a quartzite which is underlain by a biotite quartz monzonite.

In this watershed, ore deposition occurred during the Laramide Orogeny. The deposits are considered to be polymetallic vein replacements, such as the Morning Glory vein. Associated skarns also host minerals of economic significance. An oxide rind, extending 30 to 45 ft. subsurface, has developed in the vein deposits. (personal comm, Floyd Gray, USGS, 07/25/2002)

2.5 Vegetation/Wildlife

Upper Harshaw Creek flows through a narrow steep-walled valley. Where the valley widens and has a flat layer of alluvium (terrace), it is vegetated with the cottonwoods, sycamores, willows, and other plants typical of arid area riparian zones.

A review of the U.S. Fish and Wildlife Service web site did not reveal the presence of threatened or endangered species in the subject basin.

2.6 Land Use/Land Ownership

The Harshaw Creek basin is almost wholly contained within the Coronado National Forest and is available for recreational usage and limited cattle grazing.

The Harshaw Creek basin contains areas of mineralization (primarily zinc, lead and copper) that have been mined since prior to the arrival of the first Spanish explorers, approximately 500 years ago (personal comm, Arizona Department of Mines and Minerals; personal comm, Sheila Dean, USFS). Large-scale mining, consisting of mainly sub-surface workings, began in the mid-1800s and continued for approximately 100 years. The region is covered with abandoned mine workings and mining residue. The upper Harshaw Creek basin contains one privately owned mine, the Trench Camp Mine, owned by Asarco.

There is some privately owned land occupied by ranches, farms and vacation cabins/homes in lower Harshaw Creek downstream from the study area.

2.7 Problem Statement

This segment was listed for impairments due to copper, zinc, and acidity (pH). The overall purpose of this project was to provide an assessment of the sources of these pollutants and to calculate TMDLs for listed pollutants on the affected reaches. Lower Harshaw Creek, starting at the downstream end of the study reach and continuing approximately 11 miles to its mouth on Sonoita Creek, is not included on the 303[d] List and, therefore, not addressed in this TMDL.

Flow in upper Harshaw Creek carries measurable quantities of copper and has excessively low pH. The pollutants of concern result from the chemical weathering of sulfide-mineralized rock which produces sulfuric acid. Sulfuric acid acts to disassociate metals from the mineral matrix and make them available for transport, in the dissolved form, in the water column. Sulfide minerals are naturally occurring in the mining district. They can also be found in stockpiled mine materials.

As a result of the changes to the Arizona surface water quality standards during the 2002 triennial review, and because human-caused exceedances were not observed nor noted during modeling, ADEQ will not calculate a TMDL for zinc at this time, but will keep zinc on the list of parameters to be monitored. Copper measurements also only exceeded the new water quality standards at the natural background sampling point; however, modeling indicates exceedances will occur at higher discharges. Therefore, ADEQ has calculated a TMDL and load allocations for copper on the subject reach.



Not to Scale

Figure 1 - Project Location
Sonoita Creek Basin TMDL Projects



Bob Scalamera
ADEC/WQD/HSAS/TMDL Unit
10/22/01

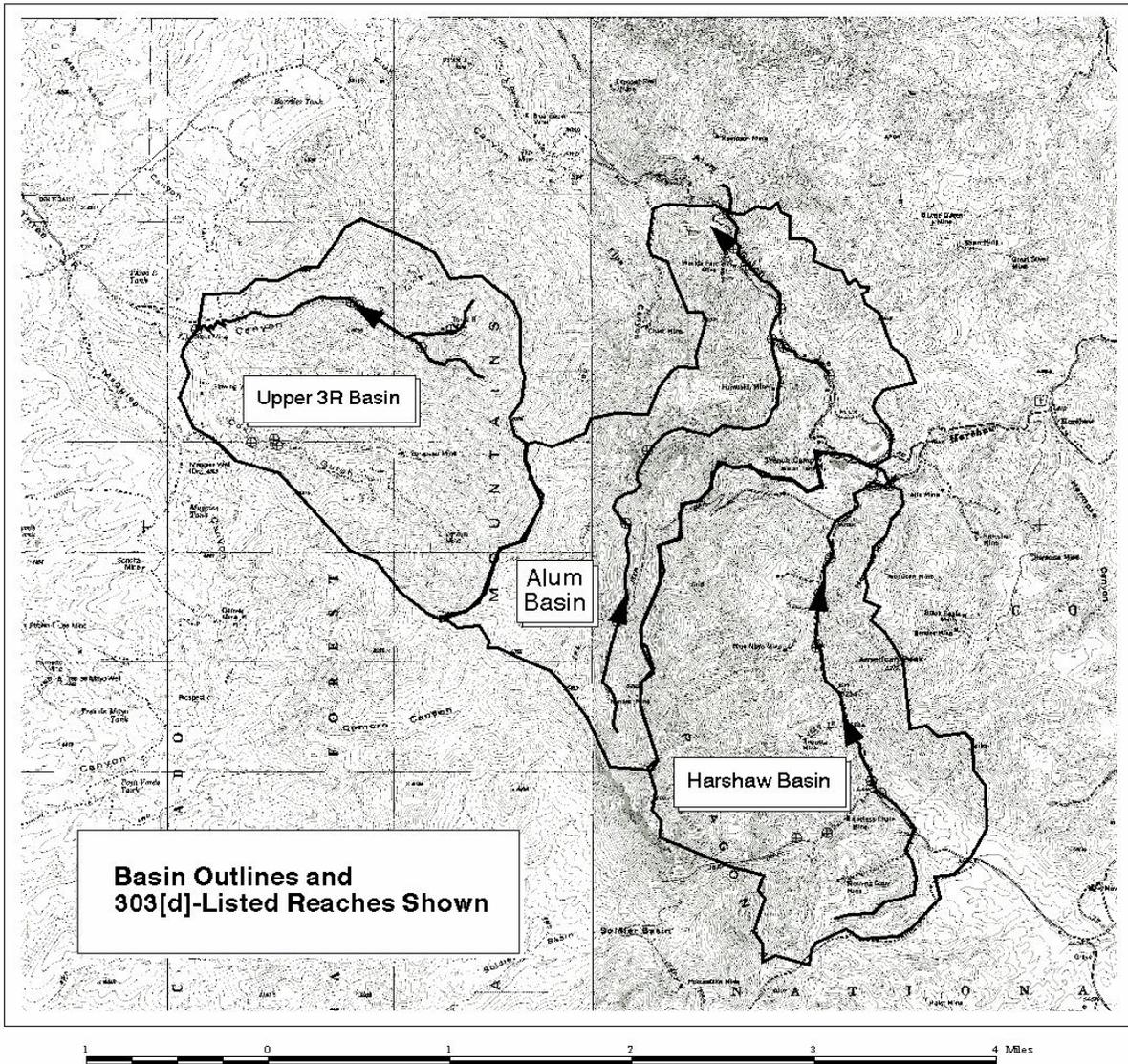


Figure 2 - Project Area
 Sonoita Creek Basin TMDL Projects



Bob Scalamera
 ADEQ/WQD/HSAS/TMDL Unit
 10/11/01

3.0 NUMERIC TARGETS

3.1 Surface Water Quality Standards

The State of Arizona has adopted numeric water quality standards (Table 1) which protect the designated uses of each surface water. During the 2002 triennial review of surface water quality standards, ADEQ modified designated uses for several segments within the study area. The State also repealed the chronic water quality standards on ephemeral waters; therefore, only the acute standards apply to ephemeral waters. The revised standards were approved by the USEPA on October 22, 2002.

For Harshaw Creek, the following designated uses apply:

- Aquatic and Wildlife ephemeral (A&We),
- Partial Body Contact (PBC), and
- Agricultural Livestock Watering (AgL).

For the tributaries to the subject segment of Harshaw Creek, all of which are ephemeral, the following designated uses apply:

- Aquatic and Wildlife ephemeral (A&We) and
- Partial Body Contact (PBC)

The numeric target for each of the listed pollutants has been set so that the most stringent water quality standard for the supported designated uses can be supported. The copper and zinc standards for the listed Aquatic and Wildlife ephemeral use vary with hardness (range of 25 to 400 mg/L as CaCO₃) (A.A.C. Title 18, Chapter 11, Article 1, App. A).

Table 1 Surface Water Quality Standards (basis for numeric targets)

Designated Use	pH	Copper (µg/L)		Zinc (µg/L)	
		Total	Dissolved	Total	Dissolved
AgL	6.5 - 9.0	500		25,000	
A&We	6.5 - 9.0		6.3 - 86		344 - 3,599
PBC	6.5 - 9.0	1,300		420,000	

The minimum applicable pH standard, as shown above, is 6.5. Since this is a unitless number, it was converted to H⁺ ion concentration in µg/L for the load calculations. The formula is $10^{(-pH)}$ which results in a hydrogen concentration in moles and, since the atomic weight of hydrogen is one, this equates very closely to mg/L. Multiplying by 1,000 gives hydrogen ion concentration in µg/L. Using this formula, the H⁺ concentration of 0.00032 µg/L is equivalent to the standard of 6.5. The larger the H⁺ concentration, the lower the pH.

Tables 2A-2C include a summary of measured concentrations in comparison to applicable standards. Figure 3 displays the relative locations of ADEQ and USGS sample sites.

3.2 In-stream Indicators

Reliable in-stream indicators that are solely related to water quality have not been observed in the subject watershed. The "normal" indicators (i.e., insects, fish, and vegetation) are also adversely affected by the huge variations in water quantity (dry to flood). The presence of evaporative salts (precipitates) on the dry portions of the streambed may be considered in-stream indicators, but much more data needs to be collected to determine and quantify the relationship to in-stream water quality. Attributing a cause to an in-stream indicator is therefore tenuous at best. Hillslope conditions hold some promise as indicators, but, again, much more data needs to be collected to determine and quantify the relationship to in-stream water quality. Therefore, for this phase of the TMDL, ADEQ has chosen to rely solely on in-stream concentrations of the pollutants of concern.

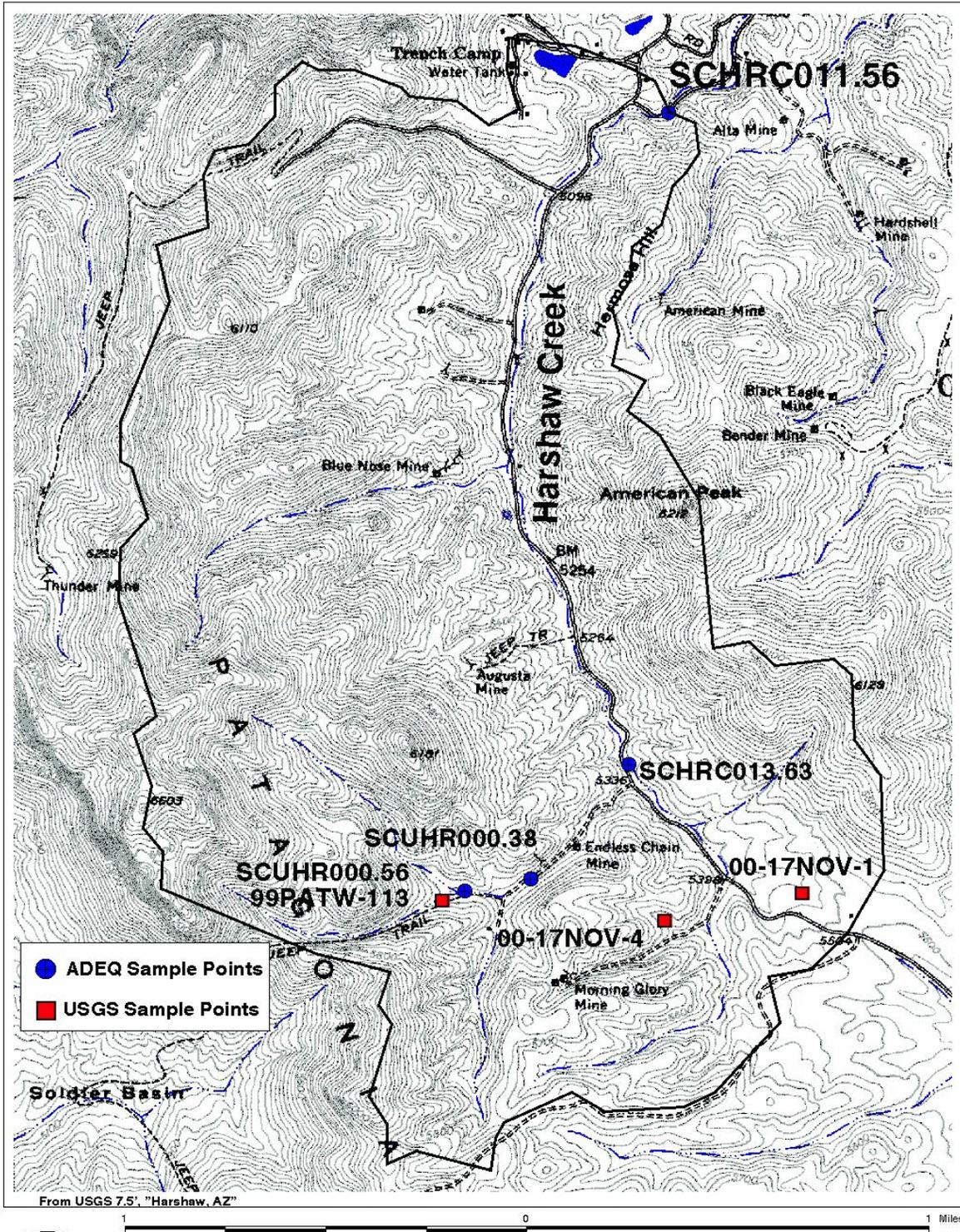


Figure 3 - Harshaw Creek TMDL Project Sample Points



Bob Scalamera
 ADEQ/WQD/HSAS/TMDL Unit
 11/27/02

POLLUTANT MONITORING DATA

Table 2A pH Data (standards exceedances in bold)

Site	Date	Discharge (cfs)	pH WQS	Data pH
SCUHR000.56 (nat. back.)	07/19/99	0.02	6.5 - 9.0	5.2
99PATW-113 (nat. back.) (USGS) SCUHR000.56 (nat. back.)	09/24/99	not measured	6.5 - 9.0	not measured
SCUHR000.56 (nat. back.) ¹	08/16/99	0.04	6.5 - 9.0	6.3
SCUHR000.38	07/22/99	0.22	6.5 - 9.0	6.2
00-17NOV-1 (nat. back.) (USGS)	11/17/00	not measured	6.5 - 9.0	7.5
00-17NOV-4 (nat. back.) (USGS)	11/17/00	not measured	6.5 - 9.0	7.1
SCHRC013.63	07/22/99	0.11	6.5 - 9.0	4.6
SCHRC011.56	12/04/97	0.15 (est)	6.5 - 9.0	6.6
SCHRC011.56	02/03/98	0.21	6.5 - 9.0	6.6
SCHRC011.56	03/31/98	1.9	6.5 - 9.0	7.0
SCHRC011.56	06/02/98	0.17	6.5 - 9.0	7.5

Notes:

1 Flow stopped before sample could be collected.

Table 2B Copper Data (standards exceedances in bold)

Site	Date	Discharge (cfs)	Hard ² (calc/adj)	A&We WQS (µg/L)	Data Cu diss (µg/L)	PBC WQS (µg/L)	AgL WQS (µg/L)	Data Cu total (µg/L)
SCUHR000.56 ¹ (nat. back.)	07/19/99	0.02	59/59	14	ND ^{3,4}	1,300	--	ND ^{3,4}
99PATW-113 (nat.back.) (USGS) SCUHR000.56 ¹ (nat. back.)	09/24/99	not measured	1,175/400	86	1,450	1,300	--	not measured
SCUHR000.38 ¹	07/22/99	0.22	30/30	7.5	ND ^{3,4}	1,300	--	ND ^{3,4}
00-17NOV-1 (nat. back.) (USGS)	11/17/00	not measured	706/400	86	3.59	1,300	500	not measured
00-17NOV-4 ¹ (nat. back.) (USGS)	11/17/00	not measured	746/400	86	2.01	1,300	--	not measured
SCHRC013.63	07/22/99	0.11	57/57	14	62	1,300	500	67
SCHRC011.56	12/04/97	0.15 (est)	1,777/400	86	19	1,300	500	132
SCHRC011.56	02/03/98	0.21	1,687/400	86	ND ^{3,5}	1,300	500	484
SCHRC011.56	03/31/98	1.9	444/400	86	38	1,300	500	201
SCHRC011.56	06/02/98	0.17	1,025/400	86	ND ^{3,5}	1,300	500	16

Notes:

- 1 Harshaw Creek reach: A&We (acute), PBC, and AgL apply; tributaries to Harshaw Creek: A&We (acute) and PBC apply.
- 2 Hardness values less than 25 mg/L were adjusted to 25 mg/L; values greater than 400 mg/L were adjusted to 400 mg/L. (A.A.C. Title 18, Chapter 11, Article 1, Appenidx A)
- 3 Not Detected
- 4 Method Reporting Limit is 10 µg/L.
- 5 Method Reporting Limit is 15 µg/L.

3.3 Data Supporting Delisting of Zinc

Results from sampling support delisting zinc in this segment. Table 2C shows that only one exceedance, measured by the USGS at 99PATW-113 (a natural background site), and occurred during the sampling period. The surface water quality standards address exceedance of standards due to natural background as follows: “where the concentration of a pollutant exceeds a water quality standard and the exceedance is not caused by human activity but is due solely to naturally-occurring conditions, the exceedance shall not be considered a violation of the water quality standard” (A.A.C. R18-11-119).

Table 2C Zinc Data (standards exceedances in bold)

Site	Date	Discharge (cfs)	Hard ² (calc/adj)	A&We WQS (µg/L)	Data Zn diss (µg/L)	PBC WQS (µg/L)	AgL WQS (µg/L)	Data Zn total (µg/L)
SCUHR000.56 ¹ (nat. back.)	07/19/99	0.02	59/59	711	ND ^{3,4}	420,000	--	64
99PATW-113 SCUHR000.56 ¹ (nat. back.) (USGS)	09/24/99	not measured	1,175/400	3,599	5200	420,000	--	not measured
SCUHR000.38 ¹	07/22/99	0.22	30/30	401	70	420,000	--	ND ^{3,4}
00-17NOV-1 (nat. back.) (USGS)	11/17/00	not measured	706/400	3,599	4.6	420,000	25,000	not measured
00-17NOV-4 ¹ (nat. back.) (USGS)	11/17/00	not measured	746/400	3,599	36.6	420,000	--	not measured
SCHRC013.63	07/22/99	0.11	57/57	691	190	420,000	25,000	160
SCHRC011.56	12/04/97	0.15 (est)	1,777/400	3,599	750	420,000	25,000	1,920
SCHRC011.56	02/03/98	0.21	1,687/400	3,599	440	420,000	25,000	3,110
SCHRC011.56	03/31/98	1.9	444/400	3,599	860	420,000	25,000	880
SCHRC011.56	06/02/98	0.17	1,025/400	3,599	250	420,000	25,000	360

Notes:

- 1 Harshaw Creek reach: A&We (acute), PBC, and AgL apply; tributaries to Harshaw Creek: A&We (acute) and PBC apply.
- 2 Hardness values less than 25 mg/L were adjusted to 25 mg/L; values greater than 400 mg/L were adjusted to 400 mg/L (A.A.C. Title 18, Chapter 11, Article 1, Appenidx A)
- 3 Not Detected
- 4 Method Reporting Limit is 50 µg/L.

4.0 SOURCE ANALYSIS

The primary project objective of this investigation was to collect data sufficient to isolate both geographically and temporally, and quantify, relative to each other, the primary pollutant load sources in the project area. All significant sources have been identified and linkages between these significant sources and loads are discussed in the Linkage Analysis Section 5.0.

The data used to determine impairment which resulted in the 303[d]-listing was collected during the 1980s and 1990s in support of the goals of other ADEQ programs and is insufficient to isolate sources or calculate loads. As part of this project, ADEQ collected data specific to the goals of source quantification and TMDL calculation. Lack of precipitation during the study period made a comprehensive analysis of all sources impossible.

There are no known NPDES-permitted point sources in the subject basin; however, a complete review of all sources may result in the classification of some as “point sources” which would require NPDES discharge permits.

4.1 Current Conditions

Verification sampling events were completed between December 1997 and June 1998 on upper Harshaw Creek at a sample point (SCHRC011.56) near the downstream end of the listed reach. ADEQ conducted source identification monitoring of the subject waterbody during 1999-2000. One additional sample point in Harshaw Creek (SCHRC013.63) and two additional sample points in the (un-named) tributary containing the Endless Chain Mine were monitored to allow determination of loads from runoff in the headwaters (the Endless Chain Mine at SCUHR000.38 and natural background at SCUHR000.56). Due to lower-than-normal precipitation during this period, ADEQ was able to collect only a limited number of samples. (Figure 3 displays the ADEQ and USGS sampling locations; Tables 2A-2C display the measured data.)

4.2 General Sources

4.2.1 Natural Background

With respect to the definition of a natural background source, HydroGeoChem, Inc. (HGC) concluded:

“... there are several areally-extensive zones of alteration and mineralization associated with the ore deposits in the subject watersheds. A field inspection verified that there are large portions of the subject watersheds containing naturally occurring disseminated pyrite and iron oxides due to weathering of pyrite.” (HGC’s Task 3 report, p. 4)

ADEQ staff selected a natural background sampling site (SCUHR000.56) in the unnamed tributary containing the Endless Chain Mine which lies in the upper reaches of Harshaw Creek. This area appears geologically similar to the rest of the subject reach and does not appear to have been disturbed by mining or other human activities.

The USGS also made natural background measurements (slope runoff) in Harshaw Creek. ADEQ’s modeling contractor for this project, HGC, Inc., was tasked with determining the applicability of the USGS natural background data to the calculation of the TMDL. After review of the USGS data, field notes, conversations with USGS personnel and discussions with ADEQ, it was determined that three of the USGS measurement sets are usable to

describe natural background in the subject basin, but due to lack of corresponding discharge data, they cannot be used to calculate loads. ADEQ has included these values in tables 2A-2C.

The USGS measured dissolved metal fractions only. Because there are surface water quality standards for both, ADEQ measures both total and dissolved. Review of the data however, indicates very little difference between the two in this watershed. Because it appears that metals tend to stay in the dissolved state in this watershed, ADEQ considers the USGS measurements representative of both total and dissolved natural background. ADEQ will collect additional measurements of natural background runoff and associated discharges as part of the second phase of this TMDL.

The natural background concentrations ADEQ used in calculating bankfull loads are the flow extrapolated ADEQ measurements at sample point SCUHR000.56. The flow extrapolation factors are calculated by the methodology explained in Appendix B. These are:

H+ (pH) natural background concentration:

pH of 5.2 = 0.0063 µg/L H+ and a pH of 6.3 = 0.0005 µg/L H+

0.0009 µg/L = [(0.0063 µg/L + 0.0005 µg/L) / 2] x 0.531_(flow extrapolation factor)

ADEQ-measured copper (dissolved and total) concentrations were not detected above 10 µg/L. ADEQ used a value of one half the detection limit (5 µg/L) for model calculation purposes:

Copper natural background concentration:

dissolved = **13 µg/L** = 5 µg/L x 2.53_(flow extrapolation factor)

total = **0.7 µg/L** = 5 µg/L x 0.14_(flow extrapolation factor)

The low total copper relative to the dissolved copper is due to the difference in the flow extrapolation factor, dissolved copper increases with increasing discharge while total decreases with increasing discharge.

4.2.2 Adit Drainage

No drainage was observed from any of the mines in the subject basin.

4.2.3 Mining Residues

Mining residues are a significant source of pollutants and consist of three major categories of material:

- Waste rock removed to gain access to the ore. (This material may or may not have leachable metals.)
- Low grade ore waste that has leachable metals in quantities that were uneconomical to extract at the time of mining.
- Mill tailings which are the finely ground waste after separation from the economically useful minerals. (This material may or may not have leachable metals.)

These materials are typically mixed (layered) in the same "dumps", dependent upon mine or mill activities at the time of dumping. The dumps are exposed to precipitation and are being slowly eroded and fed into the stream by runoff. ADEQ did not observe significant

movement or erosion of this material after the low intensity (two year) precipitation event that was sampled; however, gullies and rills were noticed during a sampling trip that occurred several days after a large localized precipitation event. It should be noted that these piles, which are in contact with the stream, are being constantly eroded and undercut creating a potential for collapse into the stream.

The USGS came to the following conclusions about mining residues:

The mine sites of the watershed typically include numerous adits and shafts, waste rock, and relic tailings dumps, and the larger sites typically have the remains of mills or other ore-handling fixtures, all resting on the steep, rocky banks of the stream. These sites release concentrations of metals in the "high metal" (high concentrations) category relative to a large range of mine types compiled from world literature. (See Plumlee et al, 1993) (personal comm, Floyd Gray, USGS, 05/31/02)

4.2.4 Streambeds

Streambed sediments result from the wasting of mining residues and evaporative deposits from groundwater discharges which vary in composition as do the mining residues. Findings from the USGS investigation suggest that streambed sediments are the primary source of pollutant loading (personal comm, Floyd Gray, USGS, 05/31/02). Streambed sediments are not directly addressed by this phase of the TMDL due to a lack of data that can be used to associate sediment concentrations with water column concentrations at various discharges. Arizona does not currently have standards for sediments, but this loading source will be further characterized in a later phase of investigation.

4.3 Existing, Known Sources

Figure 4 displays the relative inputs in a graphical format. The sampling results shown in Tables 2A-2C and the modeling results shown in Tables 4 - 6 were used to support the following conclusions.

4.3.1 Headwaters/Uppermost Tributaries

The mining residues of the Morning Glory Mine occupy a portion of the channel at the headwaters of Harshaw Creek. While insufficient precipitation occurred during the study period to generate runoff in this canyon, experience suggests that this is a potential source due to the large volume of waste material and the prevalence of visible pyrite exposed at the surface.

Data collected at sample point SCUHR000.38, located downstream from the Endless Chain Mine mill site and upstream from the Endless Chain Mine was compared to data collected at sample point SCHRC013.63, located downstream from the mouth of the Endless Chain tributary. As a result, the Endless Chain Mine is considered a significant source of all the constituents of concern. The Endless Chain Mine site includes a waste pile occupying a portion of the stream channel in the Endless Chain tributary.

4.3.2 Middle Portion of the Subject Basin

The portion of Harshaw Creek between the mouth of the Endless Chain tributary and the Trench Camp Mine has a series of canyons that feed into Harshaw Creek between the Endless Chain Mine canyon and the Trench Camp Mine. Several other small mines in draws along this reach have been observed; however, none have been identified as a significant source of pollutant loading. The named mines on these tributaries are the Augusta Mine and the Blue Nose Mine.

Small mines may contribute to loading, but experience suggests that loading is usually proportional to the volume and exposed area of mining residues of similar composition. Due to lack of sufficient precipitation during the study period, direct measurements of runoff from the mines of the Middle Reach were not made.

4.3.3 Bottom of the Subject Reach

Trench Camp Mine is the only sizable mine in this reach and the only portion of the Trench Camp Mine site in the subject basin is the waste material dump number 3 which fills a tributary near the downstream end of the subject reach. (Dumps number 1, 2, and 4 are in the Alum Gulch basin.) Trench Camp Mine, formerly occupied by a mine, mill and smelter, has been remediated by Asarco, the most recent operator and current owner. The remediation included the removal of structures, filling of the main shaft, and leveling and vegetating of the four waste material dumps.

Due to lack of sufficient precipitation during the study period, direct measurements of runoff from the Trench Camp Mine were not made. Using the runoff into Alum Gulch calculated as part of the Alum Gulch TMDL project as indicative of the potential for loading contributions, Trench Camp Mine dump number 3 is most likely a minor source of loading into Harshaw Creek.

The spring near the downstream end of the subject reach has the only observed source of constant drainage in the subject basin. No baseflow exceedances were measured. During bankfull flow, the discharge from the spring is not a major source of pollutant loading due to dilution. For example, the runoff flows are two or more orders of magnitude higher than the baseflow with corresponding lower loads as shown by modeling. The results of the modeling are displayed in Tables 4 - 6. A comparison of bankfull loads to baseflow loads can be made.

4.4 Source Summary

Upper Harshaw Creek and its tributaries are narrow steep-walled canyons with limited horizontal space available to support mining activity, yet there are many small mines throughout the basin which have a potential impact. During this first phase of the TMDL project, ADEQ was able to quantify contributions of the Endless Chain Mine site and of the unnamed spring at the downstream end of the subject reach. Potentially significant contributions may come from the Morning Glory Mine and stream sediments throughout the basin. ADEQ will attempt to quantify these loads during the second phase of the investigation.

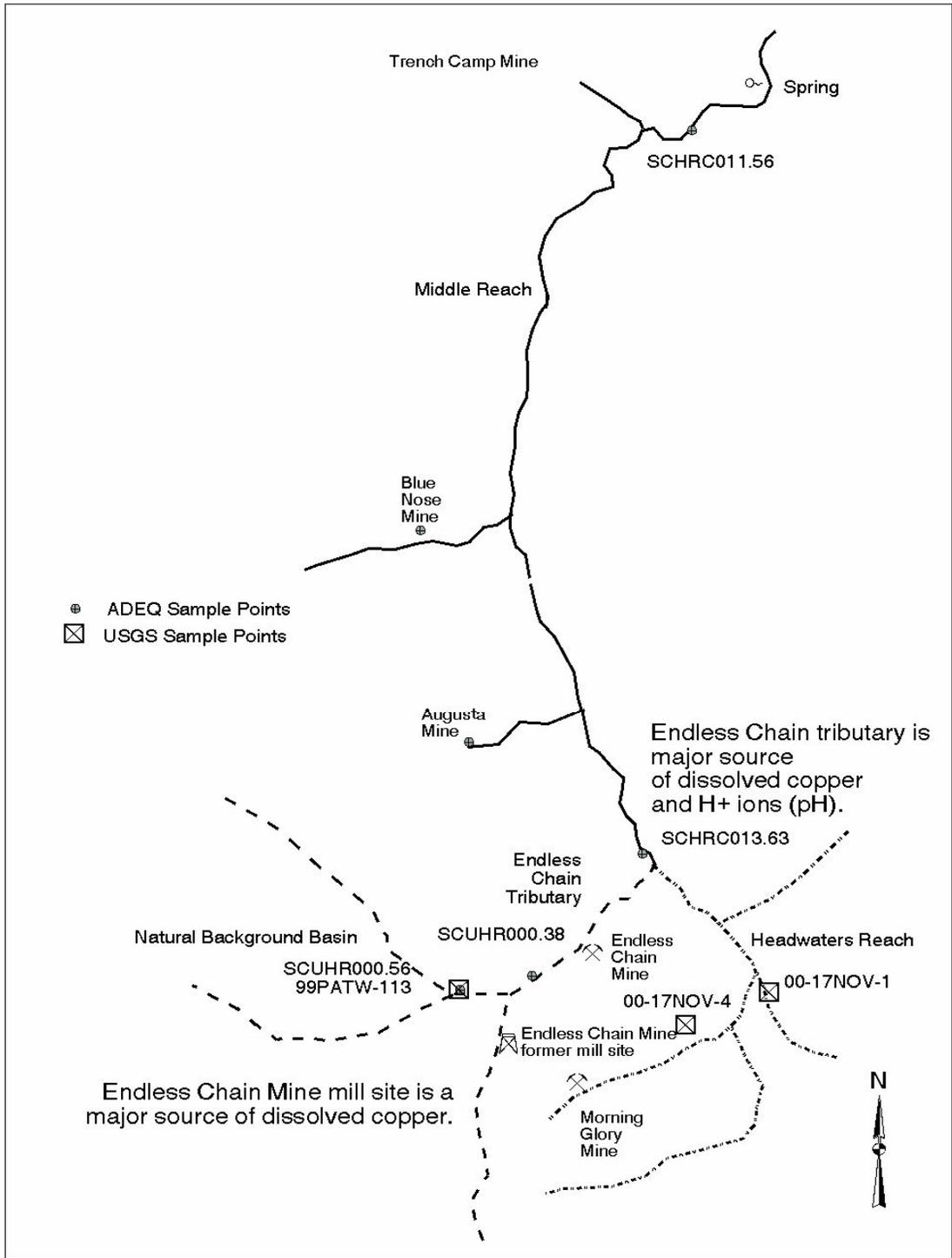


Figure 4 - Harshaw Creek TMDL Project Loading Sources Schematic

Not to Scale



Bob Scalamera
 ADEQ/WQD/HSAS/TMDL Unit
 11/27/02

5.0 LINKAGE ANALYSIS

5.1 Linkage of Sample Sites and Sources

Table 3 and Figure 4 display the linkage between each sample site (point of compliance) and the pollutant load sources corresponding to each point. Figure 4 also displays the relative significance of the load sources.

Table 3 Linkage of Sample Sites (Points of Compliance) and Sources

Site ID	Pollutant Sources
SCUHR000.56 USGS site: 99PATW-113	Upstream from mined area. Headwaters of Endless Chain Mine tributary. Natural background sample as this area appears geologically similar to the rest of the subject reach and does not appear to have been disturbed by mining or other human activities.
SCUHR000.38	Endless Chain Mine tributary - includes upstream load plus runoff from former Endless Chain Mine mill site.
USGS site: 00-17NOV-4 ¹	Sample from tributary to Morning Glory mine drainage. Natural background sample as there are no workings in the drainage area.
USGS site: 00-17NOV-1 ¹	Sample from headwater of Harshaw Creek. Natural background sample as there are no workings in the drainage area.
SCHRC013.63	Downstream from mouth of Endless Chain Mine tributary - includes Endless Chain Mine. (Flow at time of measurement did not include runoff from headwaters of Harshaw Creek.)
SCHRC011.56	Bottom of listed reach, only perennial portion in upper Harshaw. (Baseflow load is primarily groundwater (from spring), bankfull is primarily runoff.)

Notes:

1 No corresponding ADEQ site

The pollutants of concern are linked in that all result from the action of water and oxygen on sulfide minerals in mining residues, streambed sediments, and naturally occurring mineral deposits which produces sulfuric acid. The acid acts to disassociate metals from the mineral matrix and make them available for transport in the dissolved form in the water column.

5.2 Critical Conditions

Conclusions from the USGS investigation characterize the factors critical to loading in Harshaw Creek:

Periodically, almost seasonally, release of waste rock into the streams were observed with the subsequent release of metals to the water column. This metal release by waste rock movement is a significant component in low volume desert waterways.

Waste material captured in the stream during storms is transported downstream and deposited preferentially in areas of shallow gradient where the velocity and suspended load capacity of the stream is diminished. The process by which storm water is degraded appears to be via interaction with reactive detritus (e.g. sulfide-bearing siliceous waste rock, sulfate salts) from waste piles and from interaction with highly

soluble salts accumulated in stream-bed sediment via evaporation. By the combined actions of these processes the acid generating potential of downstream areas typically resembles that of upstream mine sites and thus the water chemistry changes little during transport. Therefore these stream segments have the highest potential for the release of metals into the watershed.

Metal concentrations from water and sediment samples collected downstream from dump sites by the USGS during storm runoff are substantially higher than those measured in gullies and sheet flow above the primary streambed. The USGS has concluded that mine dump erosion and the accumulation of evaporative salts from acidic, metal-enriched discharge from abandoned mine sites are the largest contributors to degraded streamflow during storm events (personal comm, Floyd Gray, USGS, 05/31/02).

This TMDL provides for attainment of water quality standards under all flow regimes by using selected critical flow and/or loading conditions as critical modeling scenarios. Loads may be different within a hydrologic event (i.e., "first flush" versus later samples) and between sample events. As previously mentioned, the USGS considers sediment, including evaporative deposits, to be the major sources of pollutant load and contend that flows through the sediment and evaporative salt deposits will trigger loading, regardless of season.

The ADEQ-chosen critical flows to model were the 2-year, 24-hour event (approximately bankfull) and baseflow. The model is capable of calculating loads at flows other than these critical flows due to the use of the extrapolation factors. Input of the selected flow into the model will result in loads and TMDLs calculated for the selected flow. ADEQ collected samples/measurements in the subject streams during baseflow conditions and, in limited quantities, during higher flows which were used to calculate extrapolation factors as explained in Appendix B. At flows ranging from zero to bankfull, the loads calculated using baseflow discharges apply; at flows equal to and greater than bankfull, the loads calculated using bankfull apply.

As mentioned in the Hydrology section, the baseflow portion of the stream is solely derived from the discharges of the springs located approximately 50 ft. above the downstream end of the listed reach. (Note: Baseflow is not be further defined as the commonly used design flow of "7Q10 flow" because of the lack of the necessary gage data and, in the case of an ephemeral stream, 7Q10 flows tend to equal zero.)

Because flow interaction with sediment is considered to be the primary source of loading (as confirmed by the USGS), bankfull was also chosen as a critical modeling condition as this is the flow during which the most sediment disturbance or movement occurs over time (Leopold, 1978). In Arizona, the bankfull event generally occurs at approximately the 1.1 to 1.8 year return interval; channels in mountainous regions (such as the subject stream) are close to the 1.4 year return interval (Moody, 1999). The 2 year return interval precipitation event is the closest to 1.4 year with sufficient data available to feed a hydrologic model. (Note: Bankfull field estimations are based upon field observations and measurements in "Regional Relationships For Bankfull Stage in Natural Channels of Central and Southern Arizona", Northern Arizona University, College of Engineering and Technology, Moody, T. O. & W. Odem, February, 1999.)

6.0 LOAD CALCULATIONS AND TMDL

6.1 Model Considerations

6.1.1 Data Sources and Limitations

Because there are no rain gauges or flow gauges within the subject reach of Harshaw Creek, historic data was not available for model calibration. Additionally, drought conditions greatly reduced the opportunity for sample collection. ADEQ did measure stream cross-sections at or near many of the sample points for purposes of hydrologic model setup.

Because of the limited amount of precipitation, flow and water quality data, load modeling requires a number of assumptions be made. For example, assumptions such as initial loss and runoff transformation can be generalized/estimated as they have less impact on model outcomes. These assumptions are not unusual in water quality analysis, regulation and TMDL development. This lack of data is one of the reasons ADEQ considers this project to be a first phase of the TMDL.

In HGC's Model Selection Report, a succinct analysis of data limitations is made.

With respect to runoff estimation, there is a good geomorphologic basis for constructing a runoff model, but calibration of the model will be difficult due to the lack of runoff hydrographs for measured precipitation events. The ephemeral nature of most flows and the lack of continuous runoff data argues for using an event-based model rather than a continuous model. The need for a simple method of rainfall runoff estimation is indicated by the inability to calibrate the model.

To model mass loading, the water quality of runoff will need to be generalized to large areas and considered steady with respect to time and discharge. The limited spatial coverage of the water quality data and the lack of information on sediment dictates that chemical processes that may potentially transfer constituents between different phases and sources cannot be considered, and that simple mixing will have to be assumed. These factors indicate that a relatively simple method of tracking the mass balance such as a spreadsheet program would be sufficient. (HGC's Task 3 report, p. E-2)

HGC concluded the Model Findings Report by stating,

Given the ephemeral nature of the subject watersheds and the limited flow and water quality data available, the runoff estimates and loading calculations reported herein are adequate as a first approximation for making water quality management decisions. (HGC's Task 4 report, p. 36)

As mentioned in the Project History section, HGC and ADEQ recently reviewed USGS data that was not available for consideration during the first draft of this report. This data was helpful because it contained additional measurements of background concentration and it confirmed the primary source of pollutant loading is from stream sediment. However, ADEQ could not use it to calculate background loads due to lack of corresponding discharge measurements. Attempts by the modeling contractor, HGC, Inc., to match existing precipitation records for the closest weather stations with the dates of the USGS samples failed to provide sufficient linkage between precipitation and discharge. The USGS has limited measurements (without corresponding discharge measurements) of the impact of springs on the stream and this was used to form their conclusions.

6.1.2 Conceptual Model

The following is excerpted from Task 3 - Report of Model Selection Findings.

"Based on the conceptual model and availability of data, an appropriate model for the Sonoita Basin simulates surface runoff and baseflow from a rural area at a watershed and subbasin scale, performs event-based simulations, requires no calibration, and allows prescription of runoff concentrations at a subbasin scale (e.g., as a function of land use) for load calculation.

Guidance for model selection is provided in the EPA's Compendium of Tools for Watershed Assessment and TMDL Development (EPA, 1997). Watershed-scale loading models described by EPA (1997) are the most appropriate for Sonoita Basin project but were generally more complex than warranted due to the lack of calibration data. Based on the review of watershed-scale loading models and the constraints on modeling due to data availability, the most appropriate method to evaluate loading was determined to be use of the rainfall-runoff model HEC-HMS developed by the United States Corps of Engineers (sic) to estimate runoff and a spreadsheet calculation procedure to estimate subreach loading." (HGC's Task 3 report, p. E-2)

6.1.3 Flows

Event based rainfall-runoff simulations were performed using HEC-HMS. Precipitation events (2 year, 24 hour rainfalls) were determined from the isopluvial contour maps in NOAA (1973). Based upon field observations, this high-frequency, low volume rainfall is the most likely to have produced the conditions under which existing discharge and water quality measurements were made. The other critical flow, baseflow, used ADEQ-measured data.

"The rainfall runoff model was constructed to represent the subject watershed to the best degree possible, although the accuracy of the predicted runoff rates and volumes cannot be quantitatively determined because there are no rainfall runoff measurements of actual storms with which to calibrate and validate the model." (HGC's Task 4 report)

6.1.4 Loads

"Well mixed conditions and non-reactive transport of hydrogen ions and metals would be assumed so that resulting concentrations could be calculated by simple mixing. This approach to loading analysis is based on standard principles of load estimation." (HGC's Task 3 report, p. 22)

The HEC-HMS estimated stream flow and ADEQ measured baseflow were combined with the measured and estimated pollutant concentrations at various locations in a Quattro Pro spreadsheet (Tables 4 - 6) to calculate loading estimates at each target site.

6.1.5 Modeling Scenarios

Several different flow scenarios were modeled to consider possible extremes. These scenarios were coupled with a synthetic rainfall distribution that is likely to occur in the Sonoita Basin.

The high-frequency precipitation events, the 2-, 5-, 10-year, and 24-hour rainfalls, were determined using isopluvial contour maps from NOAA (1973). High frequency, low volume rainfalls are the most likely to have produced the conditions during which existing discharge and water quality measurements were made. A low frequency event, the 100-year 24-hour rainfall was also evaluated. (From HGC's Task 3 report, p. E-3)

Because the critical condition for loading is flow dependent, the 2-year scenario and a baseflow scenario, developed by ADEQ, were used to develop load scenarios.

6.1.6 Calculation of Flow-extrapolated Concentrations

Due to the ephemeral nature of the subject streams and the lack of precipitation during the period of the investigation, very few monitoring points in the Harshaw Creek basin were sampled more than once. With few exceptions, these were mostly measurements of streamflow resulting from groundwater discharge. The few measurements of runoff were less than bankfull. Therefore, ADEQ determined a means of extrapolating the limited measured concentrations and flows was needed in order to model bankfull loads. The method for determining these extrapolation factors is described below and explained in detail with examples in Appendix B.

Results from the monitoring point (SCHRC011.56, downstream from spring at bottom end of subject reach) with measurements under both high and low flow conditions were used to calculate a "bankfull extrapolation factor". The bankfull concentrations calculated using the flow-weighted extrapolation factor was tested against the measured values.

6.2 Load Capacity

The measured and modeled concentrations are used to calculate corresponding loads of the 303[d]-listed pollutants. These loads are based on the modeled hardness and flow.

Tables 4A - 4E display the Load Capacity values calculated according to the formula below and show the 20% explicit margin of safety (see section 6.3) which is based on the load capacity:

$$\text{Load Capacity} = 0.0024465 \cdot \text{Flow} \cdot \text{Numeric Target (standard)}$$

The loads and other values necessary to calculate load allocations and TMDLs (Tables 4 -6)

were calculated using the following:

The value 0.0024465 is a unit conversion factor to get from $\mu\text{g/L}$ and cubic feet per second (cfs) to kg/day:

$$[1.0 \times 10^{-9} \text{ kg}/\mu\text{g} \cdot 28.316 \text{ L}/\text{ft}^3 \cdot 86,400 \text{ sec}/\text{day}] \cdot (\text{conc}) \mu\text{g}/\text{L} \cdot (\text{flow}) \text{ft}^3/\text{sec} \cdot \text{concentration extrapolation factor},$$

which works out to:

$$[0.0024465] \cdot \text{conc} \cdot \text{flow} \cdot \text{concentration extrapolation factor} = \text{load in kg/day}$$

CALCULATING LOAD CAPACITY

Table 4A Natural Background (non-point source) - Sample point: SCUHR000.56
Bankfull discharge = 8 cfs

Parameter	Hardness (mg/L)	WQS (µg/L)	Load Capacity (kg/day)	MOS (kg/day)
Cu (diss)	42	10	0.2	0.039
Cu (total)	N/A	500	9.8	2
H+ (pH)	N/A	0.00032	0.0000063	0.0000013

Table 4B Endless Chain Mine basin (non-point source) - Sample point: SCUHR000.38
Bankfull discharge = 13.5 cfs

Parameter	Hardness (mg/L)	WQS (µg/L)	Load Capacity (kg/day)	MOS (kg/day)
Cu (diss)	25	6.3	0.21	0.042
Cu (total)	N/A	500	17	3.3
H+ (pH)	N/A	0.00032	0.000011	0.0000021

Table 4C Upper Harshaw basin (non-point source) - Sample point: SCHRC0013.63
Bankfull discharge = 27.1 cfs

Parameter	Hardness (mg/L)	WQS (µg/L)	Load Capacity (kg/day)	MOS (kg/day)
Cu (diss)	40	9.8	0.65	0.13
Cu (total)	N/A	500	33	6.6
H+ (pH)	N/A	0.00032	0.000021	0.0000042

Table 4D Spring - Sample point: SCHRC0011.56
Baseflow discharge = 0.75 cfs

Parameter	Hardness (mg/L)	WQS (µg/L)	Load Capacity (kg/day)	MOS (kg/day)
Cu (diss)	400	86	0.16	0.032
Cu (total)	N/A	500	0.92	0.18
H+ (pH)	N/A	0.00032	0.00000059	0.00000010

Table 4E Middle Harshaw basin (non-point source) - Sample point: SCHRC0011.56
Bankfull discharge = 74.9 cfs

Parameter	Hardness (mg/L)	WQS (µg/L)	Load Capacity (kg/day)	MOS (kg/day)
Cu (diss)	400	86	16	3.2
Cu (total)	N/A	500	92	18
H+ (pH)	N/A	0.00032	0.000059	0.000012

CALCULATING LOADS

Tables 5A - 5E display the Existing Load and its components: Natural Background and Human-caused calculated according to the formula:

$$\text{Existing Load} = 0.0024465 \text{ (unit conversion factor)} \cdot \text{Flow} \cdot \text{Existing Concentration}$$

$$\text{Natural Background Loading} = 0.0024465 \text{ (unit conversion factor)} \cdot \text{Flow} \cdot \text{Natural Background Concentration}$$

$$\text{Human-caused Load} = \text{Existing Load} - \text{Natural Background Loading}$$

Note: Loads resulting from runoff include a natural background load.

Table 5A Natural Background (non-point source) - Sample point: SCUHR000.56

Bankfull discharge = 8 cfs

Parameter	Existing Conc (µg/L)	Existing Load (kg/day)	Nat Back Conc (µg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Cu (diss)	13	0.25	13	0.25	0
Cu (total)	0.7	0.014	0.7	0.014	0
H+ (pH)	0.00090	0.000018	0.00090	0.000018	0

Table 5B Endless Chain Mine basin (non-point source) - Sample point: SCUHR000.38

Bankfull discharge = 13.5 cfs

Parameter	Existing Conc (µg/L)	Existing Load (kg/day)	Nat Back Conc (µg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Cu (diss)	13	0.43	13	0.43	0
Cu (total)	0.7	0.023	0.7	0.023	0
H+ (pH)	0.00000032	0.00000011	0.00090	0.00000011	0

Table 5C Upper Harshaw basin (non-point source) - Sample point: SCHRC0013.63

Bankfull discharge = 27.1 cfs

Parameter	Existing Conc (µg/L)	Existing Load (kg/day)	Nat Back Conc (µg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Cu (diss)	157	10.4	13	0.86	9.5
Cu (total)	9.4	0.62	0.7	0.046	0.58
H+ (pH)	0.000013	0.00000088	0.00090	0.00000088	0

Table 5D Spring - Sample point: SCHRC0011.56

Baseflow discharge = 0.75 cfs

Parameter	Existing Conc (µg/L)	Existing Load (kg/day)
Cu (diss)	11	0.02
Cu (total)	211	0.39
H+ (pH)	0.00000061	0.000000010

Table 5E Middle Harshaw basin (non-point source) - Sample point: SCHRC0011.56
 Bankfull discharge = 74.9 cfs

Parameter	Existing Conc (µg/L)	Existing Load (kg/day)	Nat Back Conc (µg/L)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)
Cu (diss)	38	7	13	2.4	4.6
Cu (total)	201	37	0.7	0.13	37
H+ (pH)	0.00000010	0.000000018	0.00090	0.000000018	0

6.3 Margin of Safety

6.3.1 Explicit Margin of Safety

This TMDL has been calculated based on real loads at baseflow and simulated loads at a higher flow with a return interval of two years.

The precision of measurement of the parameters of concern is plus or minus 5% (personal comm, State Laboratory, Arizona Department of Health Services). An explicit margin of safety of 5% was applied to the TMDL to account for this error.

An additional explicit margin of safety of 15% was applied to account for:

- The lack of characterization of many of the minor sources in the subject basin;
- The potential for unidentified sources to contribute pollutant loads or identified sources to provide larger loads than anticipated; and
- The modeling for the project assumes homogeneous rainfall across the entire subject basin. However, precipitation events can occur in portions of the watershed with other portions receiving none and thereby resulting in runoff patterns and stream discharges different from those modeled.

The total explicit margin of safety used is 20% of the load capacity.

6.3.2 Implicit Margin of Safety

A non-quantifiable implicit margin of safety was applied through:

Not allocating additional loading when capacity was available. When the existing load for a stream segment was less than the load capacity; i.e., standards are not being exceeded, instead of using the difference between load capacity and existing loading as additional allowable load, ADEQ chose not to allow any additional loading. This was done for several reasons:

- Even if one or more segments meet standards, the stream reach as a whole does not necessarily meet standards; therefore, additional loading was not allocated.
- To allow for non-quantifiable errors in modeling methodology.
- To allow for future sources. This allowance is not required by law, but neither is it prohibited. (Future sources are most likely to take the form of additional loading caused by the exposure of "fresh" mineralized material to runoff.)

Use of conservative modeling assumptions, for example:

- "The assumption of steady concentrations may overestimate loading because most chemical analyses are for samples collected at relatively low flows, and thus potentially represent higher concentrations, compared to the event average flows used to calculate loading." (HGC's Task 4 report, p. 35)
- The model assumes conservative mixing and does not account for physical and chemical processes occurring in-stream that may reduce concentrations between sample points.

6.4 Allocations and TMDL

The in-stream water quality in the subject waterbodies is such that loads need to be reduced in order to meet standards. The following TMDLs and associated allocations are set at levels adequate to result in the attainment of applicable water quality standards.

6.4.1 TMDL Calculations

The TMDL is represented by the mathematical equation:

TMDL = \sum WLA + \sum LA + MOS + Natural Background, where:

WLA is the wasteload allocation consisting of loads from point sources (not used in this phase of the TMDL),

LA is the load allocation consisting of non-point source loads, and

MOS is a Margin of Safety which serves to address uncertainties in the analysis and the natural system.

In order to increase clarity, ADEQ has chosen to break out **Natural Background** from the LA as the loading due to natural background sources.

There are currently no NPDES-permitted point sources identified in the subject watershed; however, ADEQ plans to conduct a detailed survey to determine if any point sources exist as part of a later phase of the subject TMDL. The final TMDLs set for the pollutants in the listed portion of Harshaw Creek will not change solely if a source currently considered to be nonpoint source is later determined to be a point source. With respect to the TMDL equation, the only change that would be made in this event would be the movement of a load from the load allocation column to the wasteload allocation column.

In this first phase of the TMDL, loads at each sample point include the upstream loads. In later phases of this TMDL, ADEQ may elect to break out the upstream load from each load when enough data has been collected to allow more accurate accounting for in-stream physical and chemical processes such as: dilution; reactions with other inputs; precipitation; binding or reacting with sediments. Additionally, load allocations might be calculated for discrete sources.

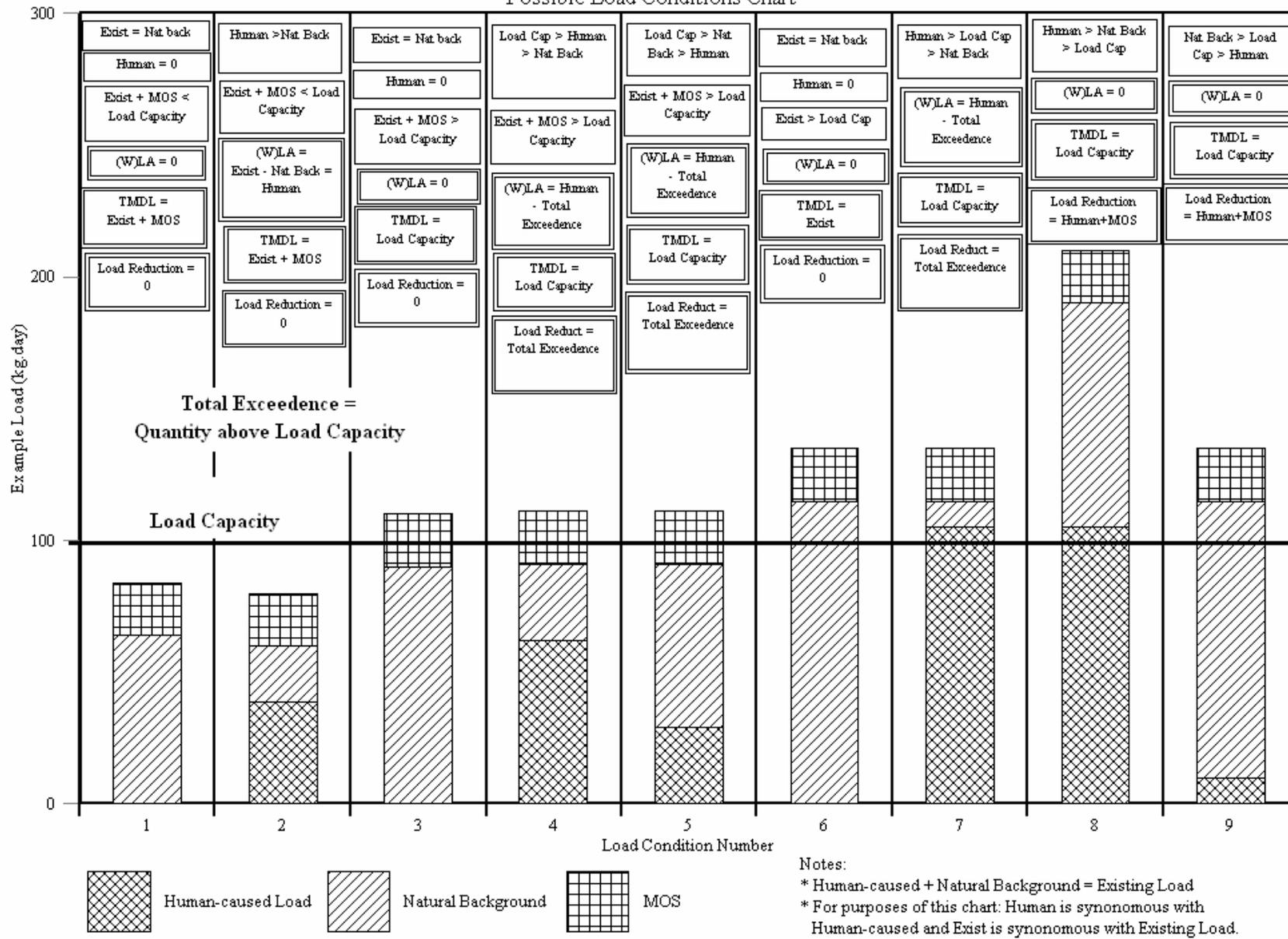
The application of the extrapolation factor to the natural background measurements is most accurate at the point of collection. When the natural background load calculated at the point of collection is applied to other sample points, apparent inconsistencies in mass balance may occur, such as the measured load being less than the estimated background load. This occurs because the model assumes conservative mixing and does not account for physical and chemical processes that reduce in-stream concentrations between the background and the downstream sample points. These processes, which include dilution with discharging ground water or other surface flows, precipitation of metal hydroxides from streamflow, and metal adsorption to stream sediment, are too complicated to be

practically modeled at the watershed scale without detailed flow measurements and chemical information for water and sediment.

ADEQ does not consider this prima facie evidence of a need for site specific standards. In later phases of this TMDL, ADEQ will collect necessary data to further characterize natural background.

Tables 6A - 6E summarize the values needed to calculate the load allocations and display the load allocations, TMDLs and the load reductions necessary to meet the TMDLs. The calculation of the load allocations are completed in accordance with the conditions displayed in Figure 5. The "load condition" column in tables 6A - 6E corresponds to the numbers along the bottom of Figure 5. Unless otherwise specified, all the tables are ordered by source. All units are kg/day.

Figure 5
Possible Load Conditions Chart



Tables 6A - 6E: Calculating Load Allocations and TMDLs

Table 6A Natural Background (non-point source) - Sample point: SCUHR000.56

Bankfull discharge = 8 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Cu (diss)	6	0.2	0.039	0.25	0	0	0.25	0
Cu (total)	1	9.8	2	0.014	0	0	2	0
H+ (pH)	6	0.0000063	0.0000013	0.000018	0	0	0.000018	0

Table 6B Endless Chain Mine basin (non-point source) - Sample point: SCUHR000.38

Bankfull discharge = 13.5 cfs. Existing dissolved copper load is due to natural background; therefore, no load reduction.

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Cu (diss)	6	0.21	0.042	0.43	0	0	0.43	0
Cu (total)	1	17	3.3	0.023	0	0	3.3	0
H+ (pH)	1	0.000011	0.0000021	0.000000011	0	0	0.0000021	0

Table 6C Upper Harshaw basin (non-point source) - Sample point: SCHRC0013.63

Bankfull discharge = 27.1 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Caused Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Cu (diss)	8	0.65	0.13	0.86	9.5	0	0.65	9.6
Cu (total)	2	33	6.6	0.046	0.58	0.58	7.3	0
H+ (pH)	2	0.000021	0.0000042	0.00000088	0	0	0.0000051	0

Table 6D Spring - Sample point: SCHRC0011.56

Baseflow discharge = 0.75 cfs. No natural background load applicable at this sample point at this discharge.

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Existing Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Cu (diss)	NA	0.16	0.032	0.02	0.02	0.052	0
Cu (total)	NA	0.92	0.18	0.39	0.39	0.57	0
H+ (pH)	NA	0.00000059	0.00000010	0.0000000010	0.0000000010	0.00000012	0

Table 6E Middle Harshaw basin (non-point source) - Sample point: SCHRC0011.56

Bankfull discharge = 74.9 cfs

Parameter	Load Cond (Fig. 5)	Load Capacity (kg/day)	MOS (kg/day)	Nat Back Load (kg/day)	Human-Cause d Load (kg/day)	Load Allocation (kg/day)	TMDL (kg/day)	Load Reduction (kg/day)
Cu (diss)	2	16	3.2	2.4	4.6	4.6	10	0
Cu (total)	2	92	18	0.13	37	37	55	0
H+ (pH)	1	0.000059	0.000012	0.0000000018	0	0	0.000012	0

7.0 IMPLEMENTATION

This investigation shows that water quality standards will be met when the load reductions are achieved. This first phase investigation has identified the major sources of pollutant loading and quantified contributions so that management decisions can be made.

The target conditions for Harshaw Creek are the removal of all mining residue dumps from the streambanks, the removal of all mine-waste originated sediments from the streambed and the isolation and treatment of all mining-impacted groundwater discharges (including springs). While TMDL calculations and values may be different between pollutants, controlling the exposure of the source material to weathering, treating the runoff and removing stream sediments from segments where needed, will reduce all the 303[d]-listed pollutants to within standards or natural background levels.

With the exception of Trench Camp Mine owned by Asarco, the pollutant sources in the subject basin are all on Coronado National Forest land. Abandoned mines represent significant technical, legal, and monetary challenges in designing and implementing remedial measures. USFS has a duty to apply for NPDES permits for both active and abandoned mines, on lands under their control, with potential to discharge to surface waters. Such permits would address discharges to surface water from mining haul roads, mine tailing and waste rock piles, and other mining-related facilities. The U.S. Forest Service has a program using CERCLA-driven actions to support remediation of sites causing harm to the ecosystem. This has not been instituted in the subject basin, but is being considered by the Coronado National Forest. If USFS addresses problems at any of these sites through CERCLA, or any other remediation program, specific permits may not be necessary; however, the requirements normally established through a permit are still required to be met.

ADEQ has divided the pollutant sources into categories based upon possible remediation strategies. These suggested strategies are general. Responsible parties must undertake site specific studies before selection, design, and implementation of a remediation method can be accomplished.

1. Mining residue dumps can be remediated by
 - a. Removing the material and either hauling to an active mine for processing with ore, or using the material to fill the abandoned mine works.
 - b. Leaving the material in place and preventing impacted runoff from reaching the stream. (This has been accomplished fairly successfully by Asarco at Trench Camp Mine.)
- 2.. Combining impacted stream sediments with the mining residue dump material and an acid neutralizing material; e.g., limestone or portland cement, for remediation.

As previously stated, the USGS (personal comm, Floyd Gray, USGS, 05/31/02) has concluded that in addition to mine dump erosion, the accumulation of deposits in the streambed resulting from the evaporation of runoff from abandoned mine sites and discharge from mining-impacted springs is another large contributor to degraded streamflow when re-dissolved during storm events. ADEQ has not made linkages between the spring discharge into the subject stream and a specific mine. Treatment of discharges, for example, through a artificial wetlands has been successfully done elsewhere and would reduce the pollutant loadings.

The second phase investigation will:

- Further develop the characterization of natural background versus human-caused loads;
- Further characterize sources;

- Require NPDES permits for point source discharges;
- Refine load allocations, possibly reclassifying some of the load allocations to wasteload allocations; and,
- Initiate formation of a watershed group focused towards implementation.

ADEQ will pursue collaboration with the USGS to continue its watershed studies in this area, including support for flow and pollutant sampling. ADEQ may conduct additional sampling when climate conditions change from drought to a wetter pattern.

HGC's Model Development Report summary includes several suggestions that should be performed as part of a second phase investigation: "[W]ork that could be undertaken to improve the basis for modeling includes the following:

- Installation and monitoring of precipitation gauges to determine rainfall intensities and site-specific daily rainfall for comparison with National Weather Service data,
- Development and continuous monitoring of stream gauging stations for measuring complete runoff hydrographs, and
- Synchronous collection of water quality samples at several locations over the duration of a complete runoff event to determine concentration as a function of location and discharge."

In sum, achieving the target conditions will reduce the human-caused loads to within standards. Additional monitoring and investigation will further develop ADEQ's understanding of loading due to natural background causing exceedences and where and when this might happen.

8.0 PUBLIC PARTICIPATION AND RESPONSIVENESS SUMMARY

Development of the Harshaw Creek TMDL included public participation in accordance with 40 CFR Parts 25 & 130.7. Public participation included review and input from stakeholder groups. Multiple presentations and meetings were held by the ADEQ in 1997 and 2001. These meetings were attended by owners/operators of mining sites, property owners; environmental groups; representatives of local, state, and federal agencies; and other interested members of the public. Written documentation of public participation is on file with ADEQ's Hydrologic Support and Assessment Section, located at 1110 W. Washington Street, 5th Floor, Phoenix, Arizona 85007.

Additionally, ADEQ released a draft of this report in December, 2001. Response to this document revealed ADEQ should:

- More clearly explain the concentration extrapolation methodology.
- Clarify its understanding of natural background conditions.
- Clearly show the linkages between sample sites and sources.

Considering this concerns and the fact that recently approved changes in Arizona surface water quality standards would affect the study, ADEQ rewrote this TMDL report and is releasing this second draft for comments.

9.0 BIBLIOGRAPHY AND REFERENCES

For availability and price information of ADEQ documents, call (602) 207-2202.

ADEQ, "Analysis of Water Quality Limited Waters in the Sonoita Creek Watershed near Patagonia, Santa Cruz County, Arizona Phase I - Confirmatory Sampling of 303[d]-Listed Parameters", October, 1998, Phoenix, Arizona.

ADEQ, "Fixed Station Network Procedures Manual for Surface Water Quality Monitoring", 1997, Phoenix, Arizona.

ADEQ, Surface Water Quality Standards, A.A.C. R18-11 (Arizona Administrative Code, Title 18, Chapter 11), 2002.

Dean, A. Sheila , "Acid Drainage from Abandoned Mines in the Patagonia Mountains, Arizona", Coronado National Forest, USDA Forest Service, Tucson, Arizona, 1982.

Eaton, Andrew D., Lenore S. Clesceri, Arnold E. Greenberg, "Standard Methods for the Examination of Water and Wastewater", 19th Edition, 1995.

Gray, Floyd, Research Geologist, USGS, personal communications, Tucson, Arizona. Various dates over the course of the project.

Leopold, Luna, and Dunne, Thomas, "Water in Environmental Planning", 1978.

Moody, T. O. & W. Odem, "Regional Relationships for Bankfull Stage in Natural Channels of Central and Southern Arizona", Northern Arizona University, College of Engineering and Technology, February, 1999.

Norris, R. James, Associate Hydrologist, and A. Michael Geddis, Associate Hydrologist. The computer model selection, modeling, and a series of reports were completed under Task Assignment Scope of Work EV01-0038 by Hydro Geo Chem, Inc. of Tucson, Arizona.

Schrader, C. Frank, USGS Bulletin 582, "Mineral Deposits of the Santa Rita and Patagonia Mountains", 1915.

U.S. Environmental Protection Agency, "Compendium of ERT Surface Water and Sediment Sampling Procedures", 1991. Washington, D.C.

U.S. Geological Survey Administrative Report "Preliminary Assessment/Site Inspection of the Alum Gulch - Flux Canyon Watershed, Northern Patagonia Mountains", Floyd Gray, Laura Norman, Oscar Duarte, Ailiang Goo, and Maurice Chafee, July 2002 (in press).

U.S. Geological Survey "Study and Interpretation of the Chemical Characteristics of Natural Water", Water-Supply Paper 2254, John D. Hem, 1989.

Personal communications with personnel of the Arizona Department of Mines and Minerals, Phoenix, Arizona. Various dates over the course of the project.

Contractor-prepared reports are available for viewing in their entirety at the Hydrologic Support and Assessment Section, 3rd floor, ADEQ, 3033 N. Central, Phoenix, Arizona. Copies can be made available on request and are subject to a State-required copying fee.

APPENDIX A - Data Collection

Sample Sites

Figure 3 is a map of the subject basin with sample site locations. Sample sites were selected to permit meeting of project goals. ADEQ has developed a system of surface water sample point I.D.s:

Site ID: bbssddd.d bb = basin ("SC" is the Santa Cruz River); sss = stream code (e.g.: "HRC" for Harshaw Creek); ddd.dd = distance from stream mouth in stream miles along the stream channel as measured on U. S. Geological Survey maps in a scale of 1:24,000.

Sample points are listed in order from most upstream to most downstream. Where appropriate, tributary sample points are inserted between the sample points bracketing the mouth of the tributary. Complete locational data including latitude, longitude, UTM, or HUC, is stored in the project files in tabular format and available for the cost of copying from ADEQ.

SCUHR000.56	Endless Chain Mine tributary - upstream from Endless Chain Mine and mill site. Natural background.
SCUHR000.38	Endless Chain Mine tributary - upstream from Endless Chain Mine, downstream from Endless Chain Mine mill site.
SCHRC013.63	Harshaw Creek - Downstream from mouth of Endless Chain Mine tributary.
SCHRC011.56	Harshaw Creek - Approximate midpoint of 50 foot long spring-fed reach. Downstream end of listed reach.

Sample Collection Procedures and Equipment

The targeted parameters are those for which each stream is considered impaired as reported on the 303[d] List. Tributaries were monitored for the listed parameters of the downstream waters.

ADEQ followed the current USEPA-approved Quality Assurance Project Plan (QAPP) (May, 1991) and the ADEQ Fixed Station Network Procedures Manual derived from the QAPP. These contain the sampling techniques ADEQ is required to follow and which were followed as part of this project.

Commentors have suggested that ADEQ should follow EPA Method 1669, "Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels", EPA 821-R-95034 (1995) when collecting metals data. Method 1669 states: "This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 CFR parts 400-500) typically limit concentrations to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range."

Due to the heavy mining and ore processing activity in the subject basins, the concentrations of the listed metals are in the high part-per-billion range. The relevant standards for the subject streams are within the detections limits for standard EPA methods as opposed to the specialized 1600-series methods.

There were instances where results for dissolved metals are greater than those for total metals which raised questions about the validity of the reported data. The dissolved concentrations are larger than

the total concentrations due to rounding in reporting and because some samples were diluted due to matrix interference (personal comm, Carie Wilson, Bolin Laboratories, 01/23/98). Conversations with ADEQ's QA/QC Unit and the laboratory staff determined that the data is still valid.

Field Measurements and Equipment

Field water quality data was obtained with a Hydrolab Surveyor. These measurements are:

- water temperature (C)
- dissolved oxygen (mg/L & % saturation)
- specific conductance (µmhos)
- pH (a field measurement due to holding time of 15 minutes)

Other field measurements:

- Air temperature (C)
- Flow with either a Marsh-McBirney current velocity meter or, in cases of very low or very high discharge, a flow measurement was not possible and an estimate was made by field personnel.
- A hand-held Global Positioning System (GPS) receiver was used to locate sample sites.

All field measurements and observations were recorded on field sheets. All sites were photographed during each visit.

Laboratories and Analytical Methods

ADEQ is required (A.A.C. R18-11-111) to use an approved analytical method and a laboratory that is licensed by the Arizona Department of Health Services (DHS). For the subject waterbodies, ADEQ used the DHS laboratory and Bolin, a DHS-licensed laboratory.

Bolin Laboratories, Inc.
1763 N. 25th Avenue
Phoenix, Arizona 85023

Arizona State Health Laboratory
1520 W. Adams
Phoenix, Arizona 85007

Hardness data is necessary to evaluate the metals data because surface water quality standards for certain parameters change because toxicity varies with hardness. The higher the hardness, the lower the toxicity. EPA guidance and Arizona's surface water quality standards bracket the hardness values from 25 mg/L to 400 mg/L as CaCO₃. Further study is needed to determine whether the hardness equations for these metals hold for a hardness values exceeding 400 mg/L as CaCO₃. Hardness was calculated from the calcium and magnesium concentrations in accordance with the "Standard Methods for the Examination of Water and Wastewater", 19th Edition, 1995.

The laboratory analytical methods were used in this project were:

Total Ca, Fe, Mg and Zn (total & dissolved): USEPA method 200.7

Copper (total & dissolved): USEPA method 200.9

Quality Control

At least one set of quality control blanks and split samples were collected during each sample event.

Split samples were collected (using an USGS-designed churn splitter) as a check on laboratory accuracy. This is a sample split between two bottle sets which can reasonably be assumed to be identical (within 10%) of each other. All splits were within acceptable tolerances. "Blanks" were collected to verify the efficacy of field decontamination and equipment cleanliness.

ADEQ also split some samples with Asarco as a courtesy to Asarco. These were not part of the project quality assurance splits and blanks which were collected at other sample points. In one instance, zinc was detected in a blank collected at Asarco's request, and was determined to be a result of contamination of the rinse water supplied by DHS. The detected concentrations (in the rinse water) were 20 to 40 µg/L while the stream concentration was over an order of magnitude higher at 470 µg/L.

Checking all calculations and data entry was done by staff. All field equipment is maintained and calibrated on a regular basis to ensure valid field measurements. Calibration information is logged in the record book for each individual instrument.

APPENDIX B - Calculation of Concentration Extrapolation Factors

Due to the lack of precipitation and the ephemeral nature of the subject stream system, very few sample points were sampled more than once and most measurements were made under baseflow conditions in the spring-fed (groundwater) reach of this stream. These limited measurements were used as the basis for calculating (extrapolating) concentrations at higher (bankfull) flows. In order to model loads under the identified critical flows of baseflow and bankfull (high) flow, a means other than a direct linear relationship was established to calculate an estimated bankfull flow concentration from the measured low flow concentration at each sample point.

The sample point in the subject stream, with measurements under both runoff and baseflow conditions (SCHRC011.56), was identified and those measurements were used to calculate a bankfull concentration extrapolation factor. Two methods of deriving this factor were tested: a flow-weighted factor and an average ratio factor. Due to the presence of only one high-flow data point in the Harshaw study, a mathematical average was not possible; therefore, a flow-weighted extrapolation factor was used.

The bankfull concentration calculated was tested against the measured bankfull concentration at the sample point. The generally large errors are cause for concern, but when all, including extrapolated, data is plotted against flow, the general data trend is maintained by the extrapolated data. Therefore, the calculated extrapolation factors are acceptable. ADEQ intends to conduct additional monitoring in the upper Harshaw Creek basin and will adjust the TMDL as needed when the additional data is considered.

The bankfull concentration for each sample point was calculated by multiplying the selected factor by the measured baseflow concentration. This extrapolated bankfull concentration is then inserted into the loading model.

The value 0.0024465 is a unit adjustment factor to get from $\mu\text{g/L}$ and cubic feet per second (cfs) to kg/day:

$(conc) \mu\text{g/L} \cdot 1.0 \times 10^{-9} \text{ kg}/\mu\text{g} \cdot 28.316 \text{ L}/\text{ft}^3 \cdot (flow) \text{ ft}^3/\text{sec} \cdot 86400 \text{ sec}/\text{day} \cdot \text{concentration extrapolation factor}$

which works out as:

$[0.0024465] \cdot conc(\text{mg/L}) \cdot flow(\text{ft}^3/\text{sec}) \cdot \text{concentration extrapolation factor} = \text{load in kg/day}$

The general relationship, or trend, of the concentrations of each parameter with changes in flow was determined using linear regression. Due to insufficient data, the resulting ‘best-fit’ line was used solely as an indicator of general direction of change; i.e., increasing or decreasing, with increasing discharge. ADEQ intends to conduct additional monitoring in the subject basins and will adjust the TMDL as needed when the additional data is considered.

The following extrapolation factors were calculated for Harshaw Creek; the accompanying tables, formulae, examples and the logic behind the selection of each factor are explained below.

Hard:	0.704	(137% error)
H ⁺ :	0.531	(1% error)
$(H^+ \text{ concentration in mg/L} = 10^{(-pH)} \times 1000)$		
Cu (dissolved):	2.53	(25% error)
Cu (total):	0.14	(85% error)

The following are the formulae used to calculate flow extrapolation factors. The absolute value of the calculated extrapolation factor is used:

Parameter(weightedfactor) =

$$\frac{\sum(\text{High Flow Conc x High Flow Discharge}) - \sum(\text{Low Flow Conc x Low Flow Discharge})}{\sum \text{High Flow Discharge} - \sum \text{Low Flow Discharge}}$$

$$\frac{\sum(\text{Low Flow Concentration x Low Flow Discharge})}{\sum \text{Low Flow Discharge}}$$

Parameter(weightedcalc) = Parameter(weightedfactor) · Parameter(low flow average)

Parameter(weightederror) = (Parameter(meas) - Parameter(weightedcalc)) ÷ Parameter(meas)

The **average ratio** was not used for the reason given above, but the formula is provided here:

Parameter(avgfactor) = average of Parameter(high flow) ÷ average of Parameter(low flow)

Parameter(avgcalc) = Parameter(avgfactor) · Parameter(low flow average)

Parameter(avgerror) = (Parameter(meas) - Parameter(weightedcalc)) ÷ Parameter(meas)

Average Error of each stream is calculated using the absolute value of each individual error.

Hardness (Other parameters calculated by same method)

Hardness is calculated from calcium and magnesium in units of mg/L as CaCO₃. When hardness is used to calculate standards for certain metals, the hardness is always the calculated value or 400 mg/L, whichever is less. For example, a calculated hardness of 2,666 is **not** used to calculate a standard, instead 400 is used to calculate the standard, but a calculated hardness of 208 **is** used to calculate the standard. (A.A.C. Title 18, Chapter 11, Article 1, Appendix A)

In the Harshaw basin, hardness tends to decrease as discharge increases. Due to the lack of data, it is difficult to determine the accuracy of the extrapolation from baseflow to high flow. The following tables and formulae were developed to determine the concentration extrapolation factor.

Site ID	Date	Discharge (cfs)	Flow	Hard (meas)	Hard (weighted factor)	Hard (weighted calc)	Hard (weighted error)
SCHRC011.56	12/04/97	0.15	base	1,777	0.704	1,053	
SCHRC011.56	06/02/98	0.17	base	1,025			
SCHRC011.56	02/03/98	0.21	base	1,687			
SCHRC011.56	03/31/98	1.87	high	444			137%

concentration extrapolation factor =

$$444 \times \frac{(1,777 \times 0.15) + (1,025 \times 0.17) + (1,687 \times 0.21)}{(0.15 + 0.17 + 0.21)} = 0.704$$

$$\frac{(1,777 \times 0.15) + (1,025 \times 0.17) + (1,687 \times 0.21)}{(0.15 + 0.17 + 0.21)}$$

Hard(weightedcalc) = Hard(weightedfactor) * Hard(low flow average) =

$$0.704 \times \{(1,777+1,025 + 1,687) \div 3\} = \underline{\underline{1,053}} \text{ mg/L}$$

Hard(weightederror) = (Hard(meas) - Hard(weightedcalc)) / Hard(meas) = (444 - 1,053) / 444 = **137 % error**

The available data is insufficient to determine a relationship between discharge and hardness on Harshaw Creek, but there appears to be a very slight tendency towards a decrease in hardness with an increase in flow. The large error (137%) is cause for concern, but when all, including extrapolated, data is plotted against flow, the general data trend is maintained by the extrapolated data. Therefore, the extrapolation factor of 0.704 is acceptable. ADEQ intends to conduct additional monitoring in the upper Harshaw Creek basin and will adjust the TMDL as needed when the additional data is considered.