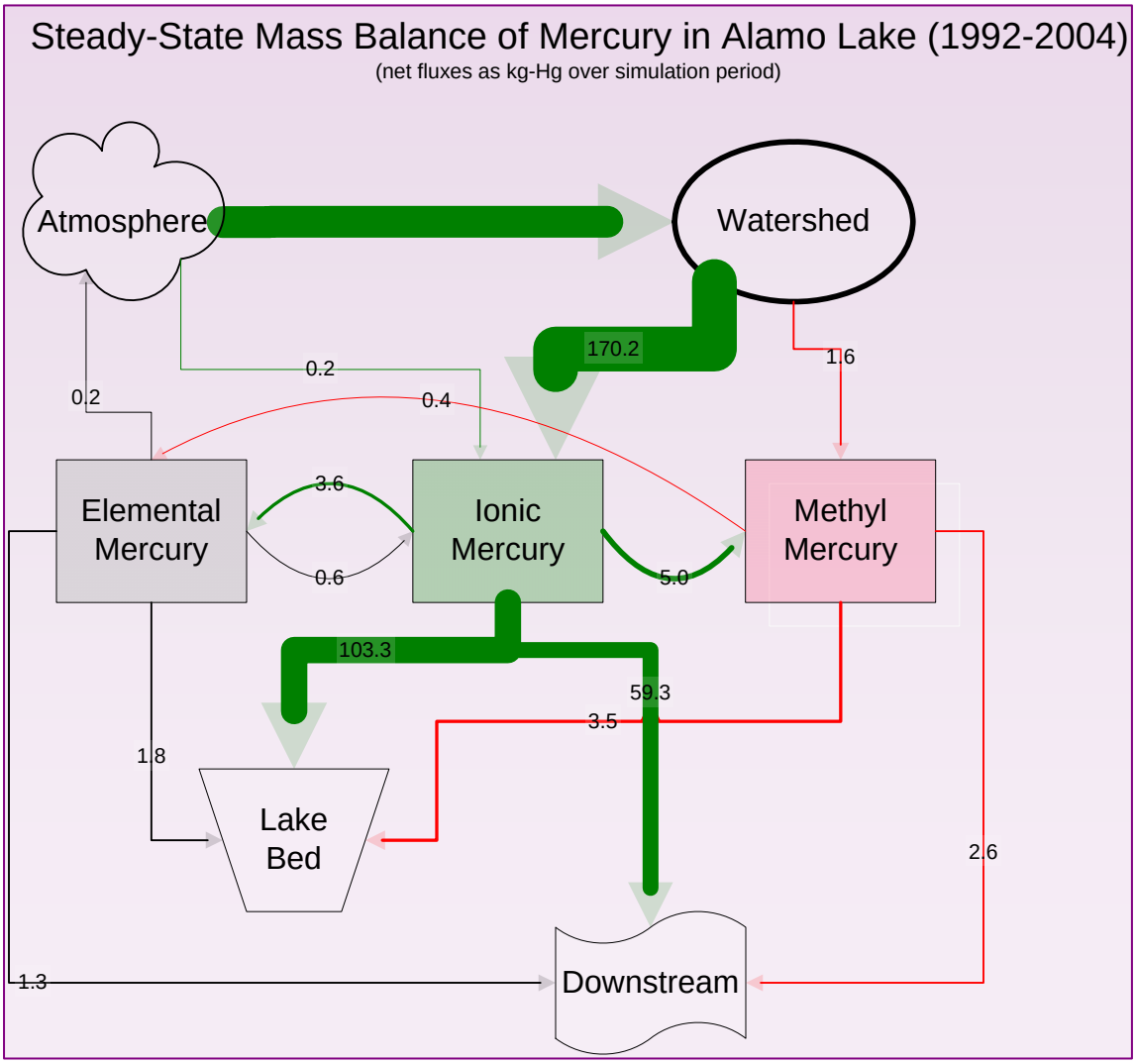
Draft Final Mercury TMDL for Alamo Lake, AZ



Arizona Department of Environmental Quality
& Tetra Tech, Inc.
December, 2005

TABLE OF CONTENTS

I. EXECUTIVE SUMMARY 1

II. INTRODUCTION AND PROBLEM STATEMENT 2

A. DESCRIPTION OF TMDL PROCESS 2

B. CLEAN WATER ACT SECTION 305 (B), 303 (D), AND SIGNIFICANCE 3

II. WATERSHED CHARACTERIZATION 5

A. WATERSHED OVERVIEW 5

B. LAKE OVERVIEW 5

C. CLIMATE 6

D. HYDROLOGY 7

E. GEOLOGY 7

F. LAND COVER/VEGETATION 8

G. LAND USE 9

H. POTENTIAL SOURCES 11

1. MINING 11
2. NATURAL: GEOLOGY AND SOILS 12
3. ATMOSPHERIC DEPOSITION: EMISSIONS AND FIRE 13

III. DATA REVIEW 17

A. DATA COLLECTION 17

B. WATERSHED SAMPLING: DRY PERIOD (SPRING '02 – SUMMER '04 17

C. WATERSHED SAMPLING - WET PERIOD (FALL '04 – SPRING '05 18

D. ALAMO LAKE SAMPLING 19

E. FISH TISSUE SAMPLING 20

IV. TMDL MODELING 21

A. CONCEPTUAL APPROACH 21

B. WATERSHED LOADS USING LOAD DURATION CURVES 22

C. WATERSHED SOURCE ID AND LOAD DELIVERY USING THE WCS MODEL 27

V. LINKAGE ANALYSIS USING WASP5/TOXI5 & HEC-5 30

A. WATERSHED LOADING 32

B. B. LOADING TO ALAMO LAKE 33

C. C. LAKE SAMPLING RESULTS (RESETTING OF MERCURY EXPOSURE HIGH FLOW EVENTS) 36

D. D. LINKAGE OF MERCURY LOADING TO FISH IMPAIRMENT 38

E. E. DERIVATION OF BIOACCUMULATION FACTORS *40*
VI. MODELING CONCLUSIONS **42**
A. WATERSHED AND AERIAL LOADING *42*
B. LAKE LOADING *42*
VII. TMDL AND ALLOCATIONS **43**
A. TMDL CALCULATION *43*
B. NUMERIC TARGETS *43*
C. NARRATIVE STANDARDS *44*
D. FISH CONSUMPTION ADVISORY AS IMPAIRMENT *44*
E. TMDL TARGET *45*
F. MARGIN OF SAFETY *45*
G. CRITICAL CONDITION *46*
H. TMDL ALLOCATIONS *46*
I. WASTELOAD ALLOCATIONS (WLAS) *47*
J. LOAD ALLOCATIONS (LAS) *47*
VIII. PRIORITIES FOR TMDL IMPLEMENTATION **48**
IX. PROPOSED ACTIONS FOR IMPLEMENTATION **49**

LIST OF TABLES

Table 1. History of Alamo Lake Assessment 4
Table 2. Percentage of Rock Types 8
Table 3. Land Use in Bill Williams Watershed 10
Table 4. Comparison of Simulated and Observed Mercury Concentrations 35
Table 5. Results of Alamo Lake Sampling, August 24, 2005 37
Table 6. MeHg BAFs and Predicted Tissue Concentrations for Lower Trophic Level Biota in Alamo Lake 41 .....
Table 7. Arizona Numeric Water Quality Standards for Mercury 44
Table 8. Eg.Confidence Levels/Required Load Reductions to Meet the Numeric Target 46
Table 9. Watershed Total Mercury Load Allocations 47

LIST OF FIGURES

Figure 1. Bill Williams watershed; three major sub-watersheds contribute to Alamo Lake 5
Figure 2. Weather Stations and Rainfall Distribution 6
Figure 3. Hydrologic Network and Stream Gages 7
Figure 4. Distribution of Rock Types Comparison of Simulated and Observed Mercury Concentrations 8 .....
Figure 5. Land Cover Distribution (GAP Analysis) 9
Figure 6. Land Use Distribution for Alamo Lake Watershed 10
Figure 7. Historic Gold Mining Sites 11

Figure 8. Distribution of All Types of Mining 12
Figure 9. Soil mercury values (from Gustavsson et al., 2001) 13
Figure 10. Dry Deposition in Alamo Lake Airshed (CMAQ, 2005) 14
Figure 11. Dry Deposition in Alamo Lake Airshed (CMAQ, 2005) 14
Figure 12. Forest Fire Areas Reported by the BLM (1982-2002) 15
Figure 13. Average Size of Historical Fires within Modeled Sub-basins 16
Figure 14. Analysis of Forest Fire Impacts on Estimation of Mercury Loads at Locations in the Alamo Lake Watershed 16
Figure 15. Sampling Locations 17
Figure 16a. Hydrograph for Big Sandy 18
Figure 16b. Photograph at Big Sandy Gage 19
Figure 17. MeHg Results against Depth and ORP, August 25, 2005 20
Figure 18. Total Mercury in Relation to Length in Largemouth Bass Tissue 20
Figure 19. Histogram of Mercury Concentrations in Largemouth Bass, Alamo Lake 21
Figure 20. Stations Used for Flow and Load Duration Curves 23
Figure 21a. Load Duration Curves for Mercury (Hg) and Suspended Sediment Concentration (SSC) at Big Sandy River Station 24
Figure 21b. Load Duration Curves for Mercury (Hg) and Suspended Sediment Concentration (SSC) at Burro Creek Station 25
Figure 21c. Load Duration Curves for Mercury (Hg) and Suspended Sediment Concentration (SSC) at Santa Maria River Station 26
Figure 22. Processes Simulated by WCS 27
Figure 23. Sub-basins in Alamo Lake Watershed..... 28
Figure 24. Soil Erosion Factors 29
Figure 25. Stations Surrounding Arizona (Note: none in Arizona) 29
Figure 26. Generalized Lake Mercury Cycle 31
Figure 27. MeHg vs. Total Hg Load Relationship for Santa Maria River 32
Figure 28. MeHg vs. Total Hg Load Relationship for Burro Creek 32
Figure 29. MeHg vs. Total Hg Load Relationship for Big Sandy River 32
Figure 30. Analysis of Tributary Sediment Size Data 32
Figure 31. Linkage of WASP Model Compartments 33
Figure 32. Model Representation of Mercury Transformation Kinetics 34
Figure 33. Simulated and Observed Avg Hg Concentrations 35
Figure 34. 12-yr Model Trajectory for Hg..... 36
Figure 35. Comparision of 2005 and 2003 Mercury Samples at Station BWALA-A (Alamo Lake near Dam) 38 .....
Figure 36. Response of Average MeHg Concentrations in the Water Column of Alamo Lake to Reductions in Watershed Load 39
Figure 37. Modeled changes to Inflow/Outflow 42

I. EXECUTIVE SUMMARY

Alamo Lake was issued a fish advisory in the spring of 2003 based on unacceptable levels of mercury in bass, catfish and crappie. The Arizona Department of Environmental Quality (ADEQ) has recently completed a Total Maximum Daily Load (TMDL) analysis to determine pollutant load reductions necessary to protect human health and wildlife. This TMDL was calculated using both empirical data and modeling of the lake and its watershed.

Data were collected by ADEQ and the U.S. Fish and Wildlife Service between 1990 and 2005 and compiled by ADEQ. Tetra Tech Inc. was hired to calculate watershed inputs and lake response using a combination of empirically derived load duration curves and linked watershed and lake models, the Watershed Characterization System (WCS) developed by Tetra Tech, and a receiving water model known as WASP5/TOXI5 (Ambrose, et. al., 1993). The U.S. Corps of Engineers provided the HEC-5 water balance model used for Alamo Lake. Modeling was performed using national and local geographic datasets in attempt to attribute mercury inputs from background geology and soils as well as air deposition.

Because the Alamo Lake watershed is so large, ADEQ and EPA Region IX agreed to establish mercury loading endpoints based on flow and water quality data at three USGS gages: Big Sandy River near Wikiup, Burro Creek at Hwy 93, and Santa Maria near Bagdad. Several additional sites were also sampled within each sub-watershed in attempt to isolate possible impacts from historic gold mining. The results of this study show that mercury is naturally present in the watershed in association with volcanic and granitic rocks, their soil derivatives, and in geothermal springs. Runoff from historic gold mining areas shows elevated mercury levels but more work is needed to survey and identify specific sources. Most of the mercury is delivered to the lake in large watershed runoff events, such as was experienced in the fall/winter of 2004/2005. Air deposition appears to play a lesser role (contributing about 15%) but local air monitoring is needed to confirm this projection.

The form of mercury that is toxic to humans and higher trophic level wildlife is methyl-mercury (MeHg), but most of the mercury entering Alamo Lake is not in that form and must be converted by microorganisms. Lake data from August 2005 show that conditions are ripe for methyl-mercury production *in the lake* following major runoff events. Working backward from present fish tissue concentrations (average 0.7 mg/kg), Tetra Tech calculated that to achieve the EPA-established level of 0.3 mg/kg or less, there must be a 66% reduction in lake water column methyl-mercury. Based on this in-lake target, Tetra Tech determined that watershed inputs of mercury must be reduced by 77%. Mercury from the watershed is delivered to Alamo Lake in association with suspended sediment. Therefore, efforts to mitigate these inputs are likely to require 1) location of specific sources that can be cleaned up, and 2) large-scale sediment off-ramps upstream of the lake. For the lake, maintenance of water elevation, alternative discharge elevation(s) and pump-back may ameliorate methylation. This TMDL establishes load reductions as follows:

TMDL = 0 (WLA*) + 7.0 g/day (LA for Santa Maria River) + 11.7 g/day (LA for Burro Creek) + 10.7 g/day (LA for Big Sandy) + Implicit MOS

II. INTRODUCTION AND PROBLEM STATEMENT

A. Description of TMDL Process

The goal of the federal Clean Water Act (CWA) is to "protect and preserve the physical, chemical, and biological integrity of the nations waters". This is often termed the "fishable"/"swimmable" goal of the CWA and is understood to mean that a surface water is meeting the designated use standards for fishing and public recreation (including swimming, etc.). Water bodies deemed by default to be capable of supporting fishing and/or swimming in 1975 were assigned aquatic life support criteria. In cases where waters do not meet this goal, Section 303(d) of CWA requires states to develop Total Maximum Daily Loads (TMDLs) for the pollutants causing impairment with oversight from the Environmental Protection Agency (EPA). A TMDL allocates pollution control responsibilities among pollution sources in a watershed, and is the basis for actions taken to restore the chemical, physical, and biological integrity of a waterbody that has been classified as "impaired" for one or more designated uses.

Water quality standards are the criteria established to protect the designated uses of Arizona's waters. When states and local communities identify problems in meeting water quality standards, a TMDL can be part of a plan to remedy water quality problems. If the initial determination that a waterbody supports the "fishable"/"swimmable" goals was incorrect, a state may submit a "delist report" to have the waterbody removed from the impairment list. If one or more of the conditions under 40 CFR 130.10 (The goals of CWA) preclude attainment of uses, the state must conduct a "Designated Use Attainability Study". An EPA approval must be obtained in order to remove a designated use. If uses can potentially be met but require flexibility in one or more surface water quality standards (criteria), a state may pursue "site-specific", "regional" or even "seasonal" standards. This last process is similar to removing a designated use and it also requires adherence to EPA guidelines and EPA approval.

A TMDL represents the total load of a pollutant that can be discharged to a water body on a daily basis and still meet the applicable water quality standard. The TMDL can be expressed as the total mass or quantity that can enter the water body within a unit of time. In most cases, the TMDL determines the allowable pounds per day of a constituent and divides it among the various contributors in the watershed as waste load (i.e., point source discharge) and load (i.e., nonpoint source) allocations. The TMDL must also account for natural background sources, seasonal variation, and provide a margin of safety. For non-point sources such as accelerated erosion or internal nutrient cycling, it may not be feasible or useful to derive a pounds per day figure.

TMDLs must include specific information to be approved by U.S. EPA Region IX. This necessary information can be summarized in the following eight elements:

Plan to meet State Surface Water Quality Standards: The TMDL includes a study and a plan for the specific water and pollutants that must be addressed to ensure that applicable water quality standards are attained.

Account for seasonal variations and critical conditions: The TMDL must identify the conditions under which pollutant loading occurs. This usually refers to flow regime, but may also include climatic or seasonal conditions and other sources of loading such as aerial deposition.

Describe quantified water quality goals, targets, or endpoints: The TMDL must establish numeric endpoints for the water quality standards, including beneficial uses to be protected, as a result of implementing the TMDL. This often requires an interpretation that clearly describes the linkage(s) between factors impacting water quality standards.

Analyze/account for all sources of pollutants. All significant pollutant sources are described, including the magnitude and location of sources.

Describe the linkage between water quality endpoints and pollutants of concern. The TMDL must explain the relationship between the numeric targets and the pollutants of concern. In other words, the recommended pollutant load allocations must be less than or equal to the total loading capacity of the receiving water and still meet water quality criteria.

Develop a margin of safety (MOS) that considers uncertainties, seasonal variations, and critical conditions. The TMDL must describe and quantify any uncertainties regarding the ability of the plan to meet water quality standards that have been addressed. The plan must consider these issues in its recommended pollution reduction targets with a quantifiable MOS.

Assign allocations to point sources, non point sources, and background sources. Allocations are quantitative and refer to the respective loads allowed from each source contributing to the pollutant of concern. The allocations will become part of the permit conditions where an Surface Water Discharge Permit (NPDES) permit is needed.

Provide implementation recommendations for pollutant reduction actions and a monitoring plan. The TMDL should provide a specific process and schedule for achieving pollutant reduction targets. A monitoring plan should also be included, especially where management actions will be phased in over time. Results from monitoring will be used to assess the validity of the pollutant reduction goals.

Include an appropriate level of public involvement in the TMDL process. This is usually met by publishing public notice of the TMDL, circulating the TMDL for public comment, and holding public meetings in local communities. Public involvement must be documented in the state's TMDL submittal to EPA Region 9.

B. Clean Water Act Section 305 (b), 303 (d), and Significance

Water quality standards for surface waters are reviewed and revised by states every three years as criteria are refined. These criteria, or threshold levels, are developed for various potential pollutants based on the particular designated uses of a water body and the degree of exposure or risk to humans, animals, and plants. Standards may be numeric or narrative, meaning they can

be numbers, ranges of numbers, or narrative descriptions. Arizona's Surface Water Quality Standards contain both numeric and narrative criteria (A.A.C. Title 18, Chapter 11).

Every two years, each state must submit an accounting of how well their water bodies are meeting their standards. This report is known as the Water Quality Assessment Report or "305(b) Report", after the section of the Clean Water Act (CWA), requiring a report to Congress. Waters are classified as "attaining" their uses (full support), "not attaining" (partial support), "inconclusive" where there are insufficient data to assess, and "impaired" according to the number and nature of criteria violations. Based on the 305(b) Assessment Report, the state generates a list of impaired waters from a review of threatened and impaired categories (A.R.S. Title § 49-232 through 234; A.A.C. Title 18, Chapter 11, Article 6). The list is referred to as the Water Quality Limited List or "303(d) List", after the relevant CWA section. Waters on this list require a TMDL. This TMDL is based on a listing by EPA in the fall of 2002. Alamo Lake was listed by EPA for not attaining EPA fish tissue criteria for mercury. The lake already had a history of various listings, as seen in Table 1.

Table 1. History of Alamo Lake Assessment

Year	**Status**	**Parameter(s)**
1992	**Full Compliance**	**None**
1994	**Impaired**	**DO, turbidity**
1996	**Impaired**	**DO, turbidity, sulfide**
1998	**Impaired**	**DO, Hg in fish, sulfide**
2000	**Impaired**	**(Hg pulled pending 2000 sampling), sulfide**
2002	**Impaired**	**DO, pH, sulfide; EPA added Hg back on)**
2004	**Impaired**	**Hg in fish, pH, ammonia**

Subsequent changes in Arizona Surface Water Quality Standards removed turbidity and sulfide from the list. Subsequent sampling data demonstrated that DO was no longer an issue. pH and ammonia have not been directly addressed through the mercury TMDL. Additional data will need to be collected to compare Fish and Wildlife Service field and lab protocols with ADEQ field and lab protocols in order to address impairments for ammonia and pH. In particular, it appears that a significant portion of the pH data were qualified (exceeded holding time).

II. WATERSHED CHARACTERIZATION/POTENTIAL MERCURY SOURCES

A. Watershed Overview

Alamo Lake on the Bill Williams River is located at the confluence of the Big Sandy and Santa Maria rivers in west-central Arizona. The Alamo Lake drainage basin is extensive (Figure 1). At 5,373 square miles, the entire Bill Williams watershed constitutes 5% of the state's land area but less than 0.2% of the state's population. The Alamo Lake drainage includes 4,700 square miles of the larger watershed. Land ownership is a combination of Bureau of Land Management, U.S. Forest Service, State Trust, and private lands.

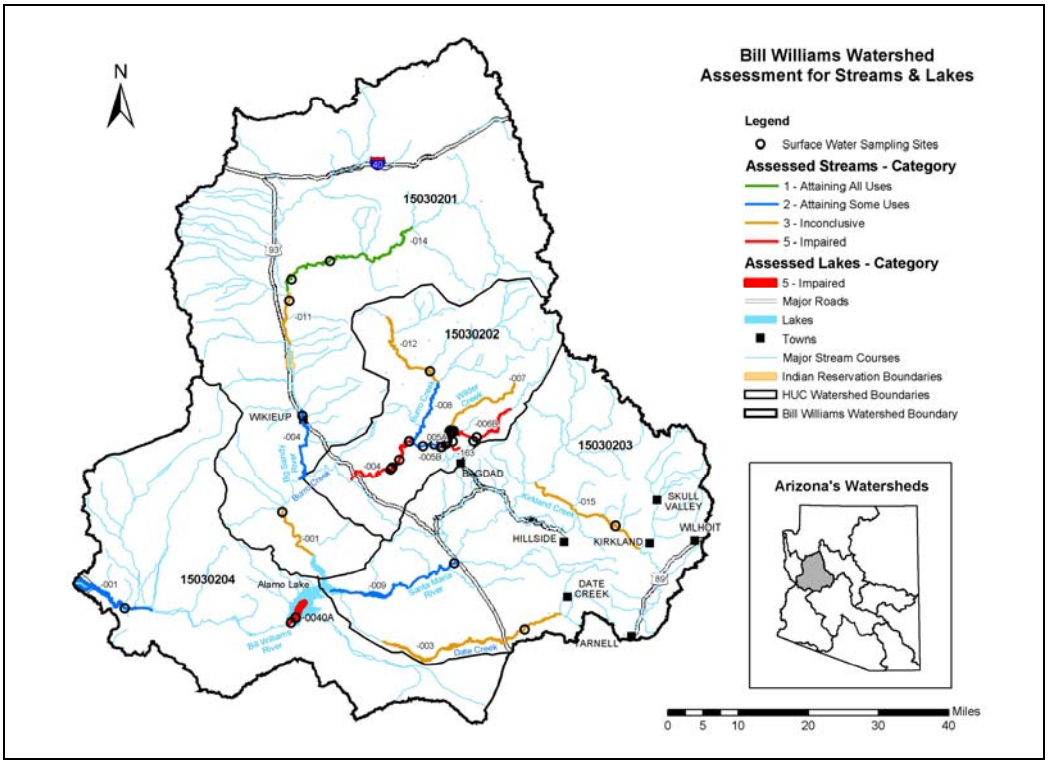


Figure 1. Bill Williams watershed; three major sub-watersheds contribute to Alamo Lake

B. Lake Overview

Alamo Dam which created Alamo reservoir was constructed between 1965 and 1968 by the Army Corps of Engineers (ACOE) for flood control on the Bill Williams River. The reservoir had an original assigned recreational capacity of 1,300 surface acres, corresponding to a lake elevation of 1070 ft above mean sea level. In 1988, to protect threatened and endangered species, the U.S. Fish & Wildlife Service (USFW) requested that the lake not be drawn down below 1,100 ft asl, which would more than double the recreational capacity to 2,737 surface acres. Subsequently, the Army Corps of Engineers (ACOE) conducted a study aimed at delineating the required storage capacity for several purposes: recreation, water conservation, flood control, and surcharge pool. The Feasibility Report and Environmental Impact Statement were released in April 1999 to operate the Alamo Dam to provide fish and wildlife benefits both upstream and downstream of the dam

without reducing flood control and recreation benefits provided by the project (ACOE, 1999). The new recreational pool (at 2,737 surface acres) is approximately 1/8th of the total flood control/dam safety capacity and about 150 feet below flood-pool elevation. Maximum capacity of the lake is reported as 17,000 surface acres. The lake has become a very popular bass fishery and contributes to wildlife habitat in the lower Bill Williams basin.

C. Climate

Precipitation data are collected at several stations within and around the Alamo Lake watershed (National Climatic Data Center (NCDC) and the Arizona Meteorological Network (AZMET). The AZMET stations also provide solar radiation; precipitation, evaporation, temperature (PET); wind; and relative humidity measurements. Eight stations within close proximity to the Alamo Lake watershed had available datasets. The locations of these weather stations and the distribution of annual average precipitation within the watershed are shown in Figure 2. Note that the majority of the watershed receives less than 12 inches of precipitation a year on average. The first half of this TMDL project (Spring 2003 – Summer 2004) took place during a particularly dry period, whereas the second half (Summer 2004-Winter 2005) experienced unusually heavy precipitation.

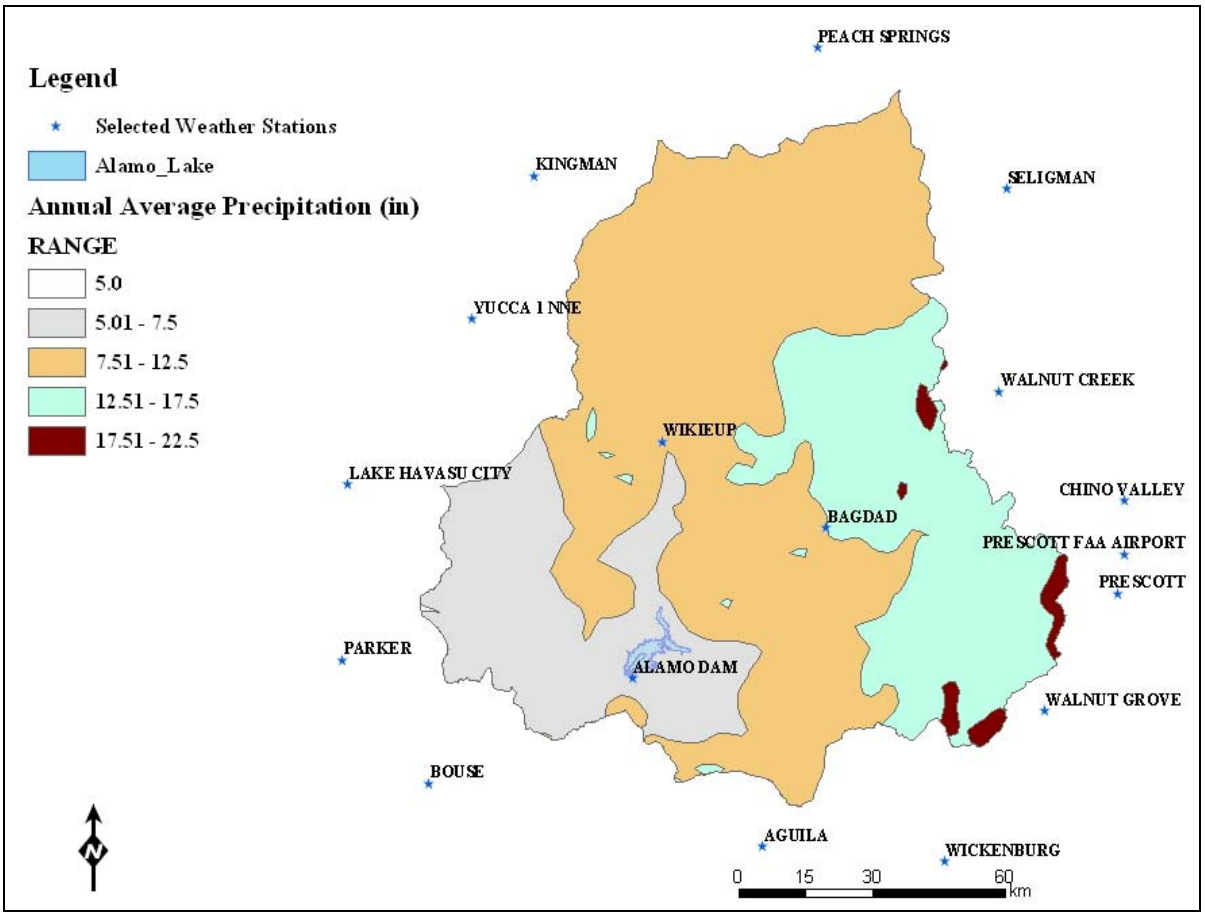


Figure 2. Weather Stations and Rainfall Distribution

D. Hydrology

Currently there are three operational USGS gaging stations above Alamo Lake, each one near the terminus of the three major tributaries. Taking into consideration the purpose and design of Alamo Lake, it becomes evident that the hydrology of the watershed is temporally and spatially dynamic. Inflows to the lake over the past 30 years have come primarily from the Big Sandy River with inputs from Burro Creek. The Santa Maria River is equally dynamic but does not contribute as much to the lake. Figure 3 shows historic and current gage locations; approximately 85% of the hydrological system is ephemeral to intermittent. Station #0942447 on lower Burro Creek has been made temporarily operational through installation of a radar sensor. The three gages provided the flow data used to develop load duration curves for suspended sediment and mercury.

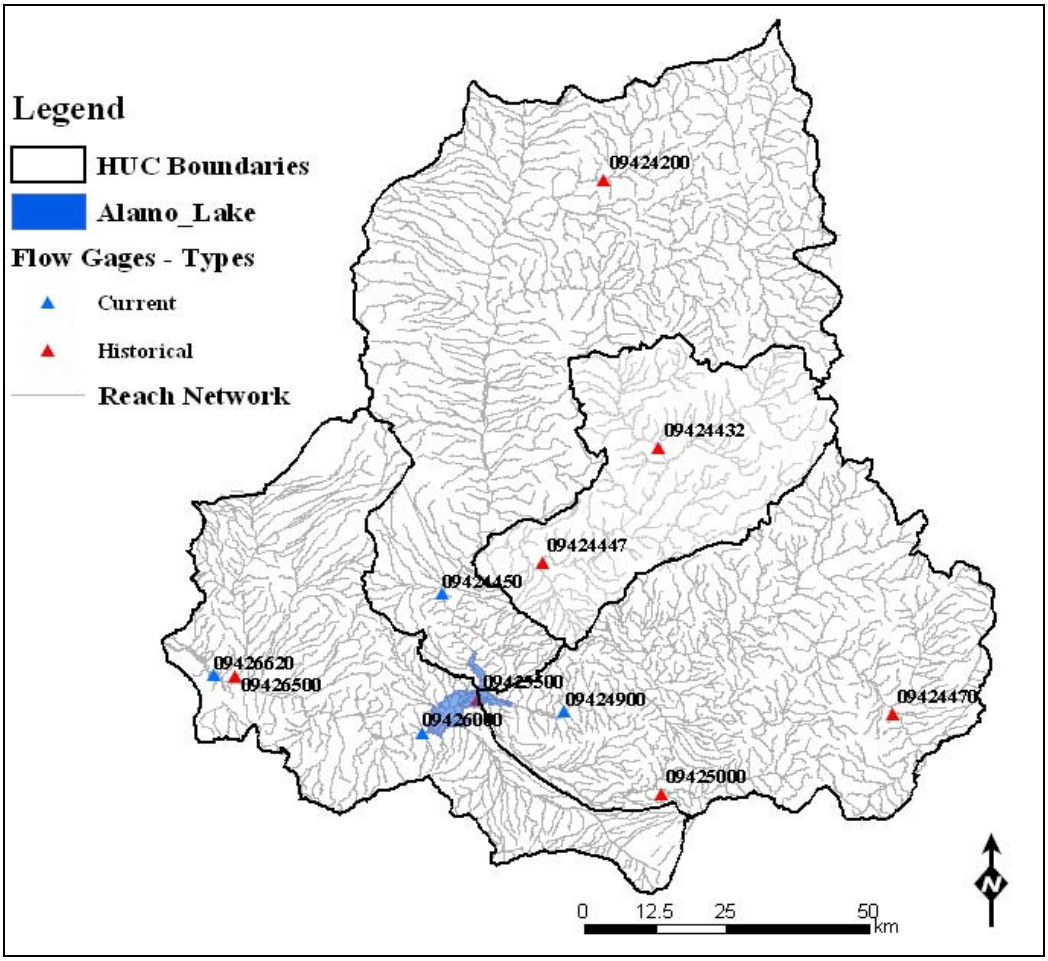


Figure 3. Hydrologic Network and Stream Gages

E. Geology

Alamo Lake is located in the Sonoran Desert portion of the Basin and Range Lowlands province. Deep elongated structural basins filled with alluvial deposits characterize the geologic environment. The mountains, pediments, and underlying bedrock are composed primarily of Precambrian granite and schist. The approximate percentage distribution of different rock types are given in Table 2.

Table 2. Percentage of Rock Types

	Percentage
Alluvium	14%
Basalt	18%
Granitic	31%
Metamorphic	3%
Sedimentary	25%
Volcanic	10%

Figure 4 represents the distribution of different rock types in the Alamo Lake Watershed. There is a prevalence of volcanic source rock (basalt, granite, and other), a massive sulfide deposit, and hard rock and placer mining in the Alamo Lake Watershed.

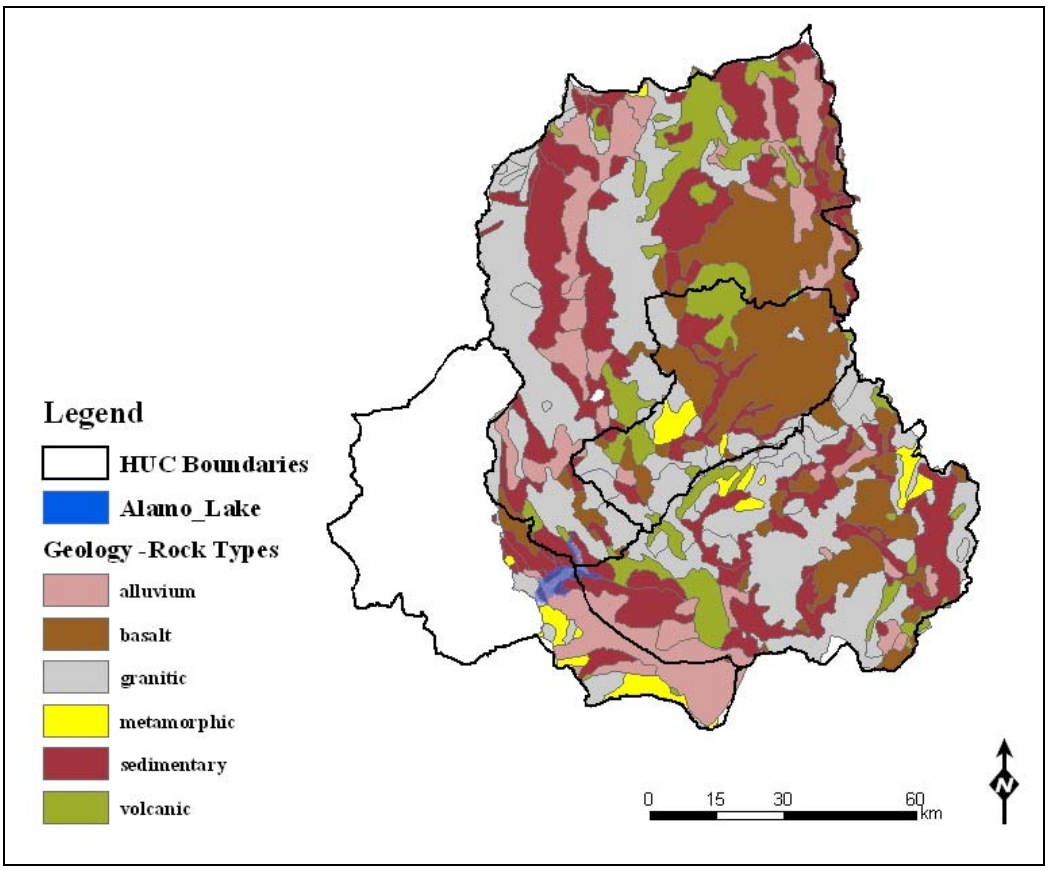


Figure 4. Distribution of Rock Types

F. Land Cover/Vegetation

Elevations within the Alamo Lake watershed range from 365 ft at the lake to 8,454 ft above mean sea level in upper reaches of the Santa Maria and Burro Creek sub-basins. Figure 5 shows the distribution of land cover based on the GAP dataset. Additional specialized vegetation

information is also available, including a high-resolution coverage of riparian vegetation developed from satellite and aerial videography imaging (AGFD, 1994).

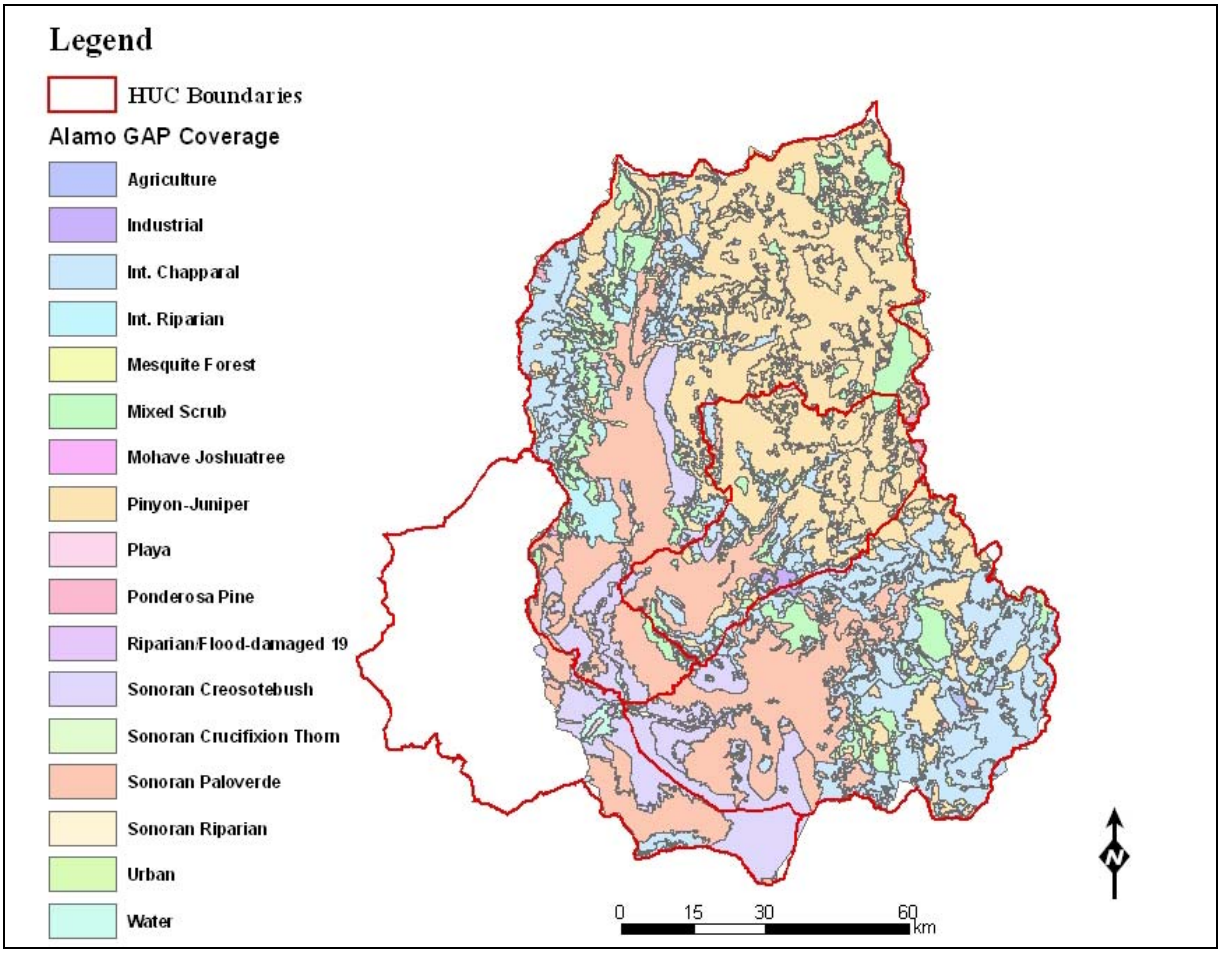


Figure 5. Land Cover Distribution (GAP Analysis)

G. Land Use

The National Land Cover Data (NLCD) for the Alamo Lake Watershed were obtained from the USGS National Seamless Data Distribution System (USGS, 2004b). Figure 6 shows the distribution of different land uses within the Bill Williams watershed. Table 3 summarizes the land use data for the Alamo Lake watershed, which is dominated by shrubland (71%) and forest (21%).

Table 3. Land Use in Bill Williams Watershed

Land use	Area (acre)	Percent
Shrub land	2454760	71.01
Forest	717203	20.75
Barren	138990	4.02
Herbaceous	123170	3.56
Water	6620	0.19
Pasture	4881	0.14
Mines	4230	0.12
Cropland	3491	0.10
Urban	1956	0.06
Wetlands	1693	0.05
Total	3456995	100.00

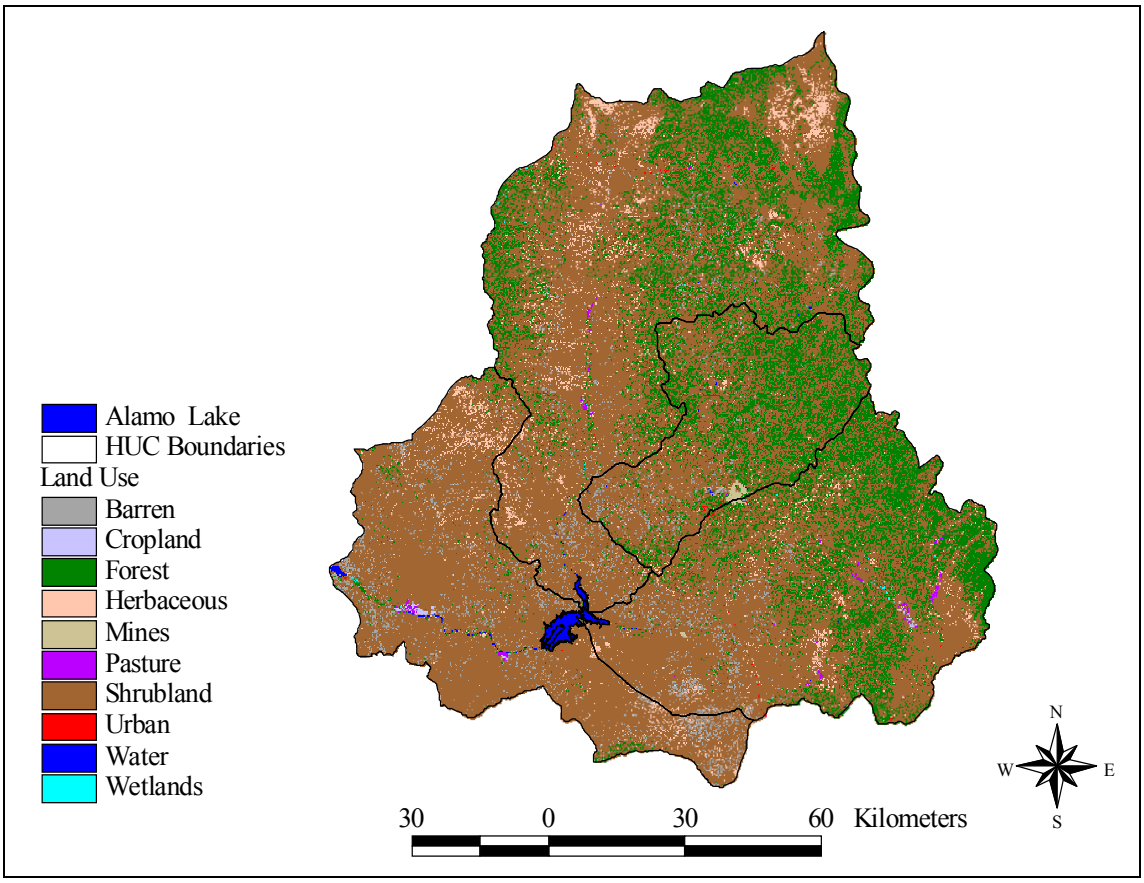


Figure 6. Land Use Distribution for Alamo Lake Watershed

H. Potential Sources

1. Mining

Mercury contamination from historic gold mines represents a potential risk to human health and the environment. Miners used mercury (quicksilver) to recover gold throughout the western United States at both placer (alluvial) and hardrock (lode) mines. The placer-gold mines that use hydraulic, drift, and dredging methods are usually a major source of mercury contamination. There are a number of mining sites within the watershed. The locations of historic gold mining are shown in Figure 7 (http\\www.mrdata.gov, USGS); other types of mines including gold mines are shown in Figure 8 (Mineral Industry Location System database). This information is critical because mining sites can be a major source of mercury.

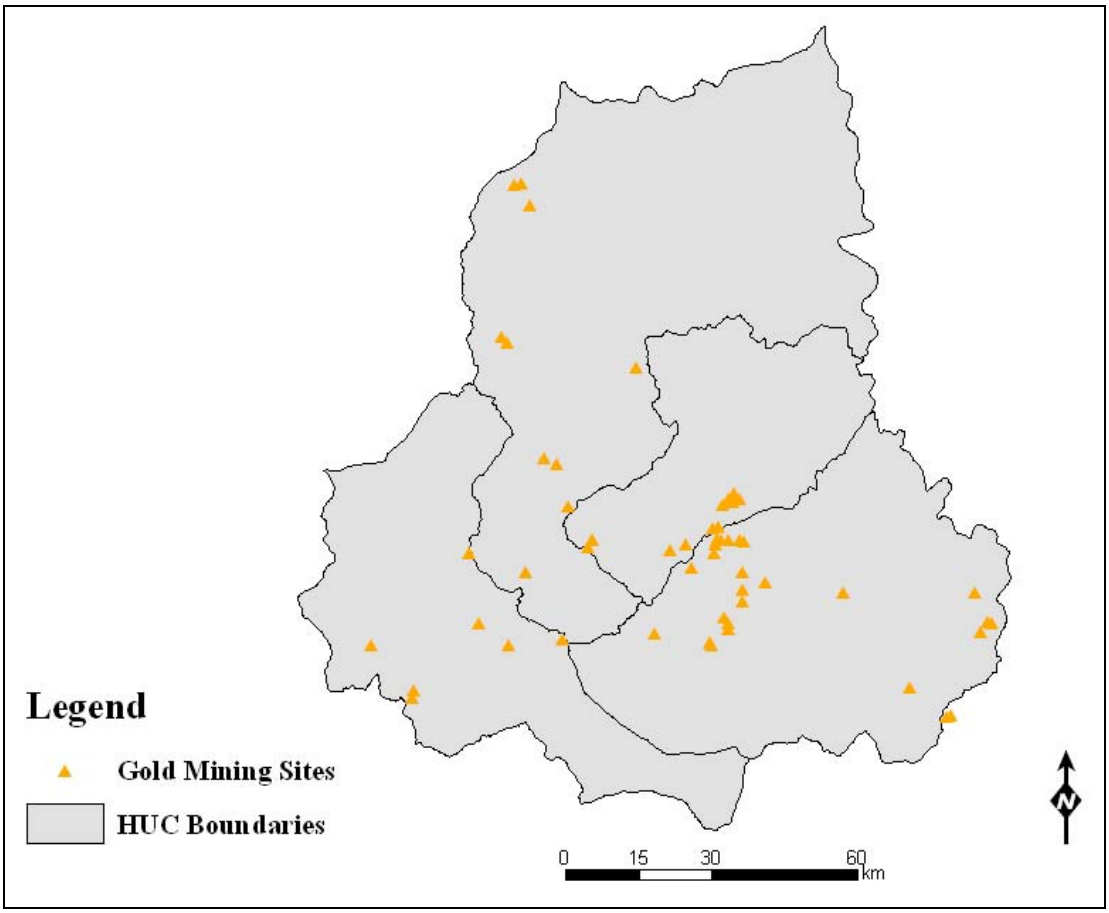


Figure 7. Historic Gold Mining Sites

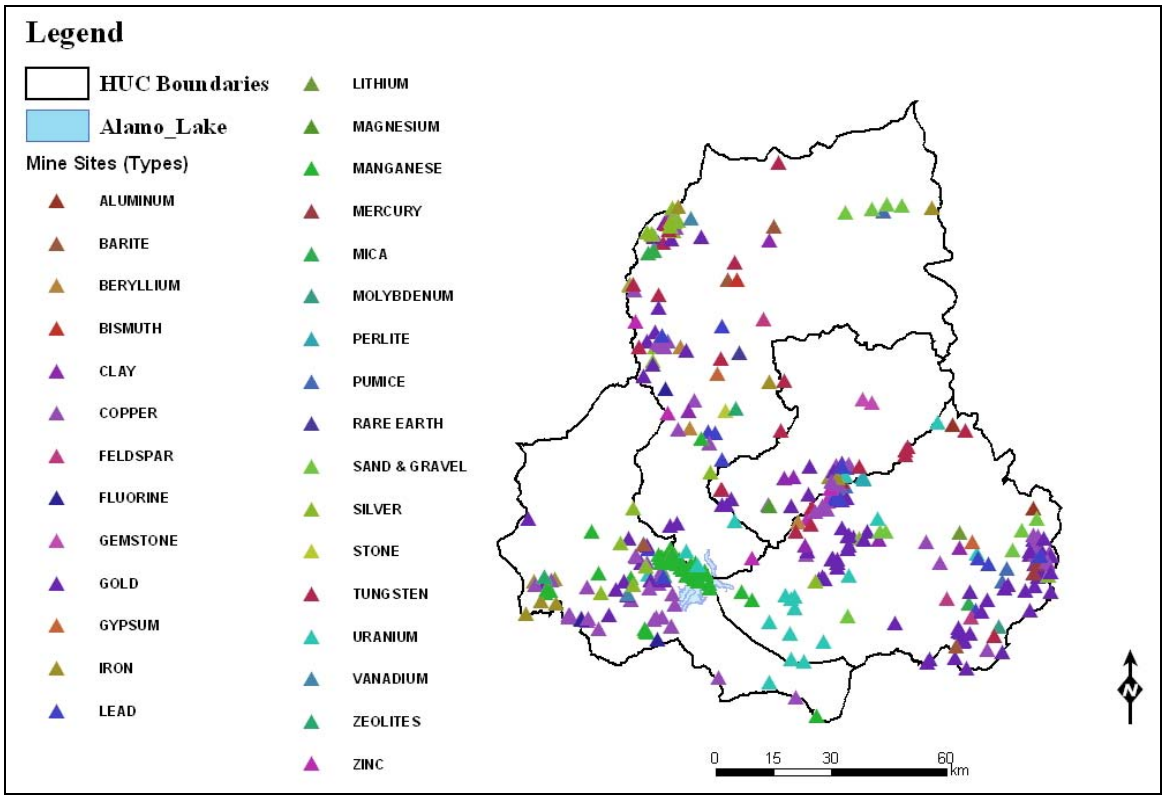


Figure 8. Distribution of All Types of Mining

Mining activities can result in watershed mercury loads in two distinct ways. First, mining activity produces tailing residues of crushed rock. If the parent material contains mercury ore, the conversion of rock to tailings increases the amount of mercury ore present in readily erodible form. Second, mercury may be directly used in the gold mining process: before the introduction of cyanidation technology at the beginning of the 20th century, mercury amalgamation of precious metal ores was common practice throughout the western United States (common at old ball mill sites). Studies of the highly contaminated Carson River area in Nevada (Lechler, 1998) demonstrate that the dominant form of mercury present in amalgamation-process tailings is still elemental mercury, approximately a century after peak mining activity, whereas stream sediments in the tailings area were dominated by elemental and exchangeable forms of mercury.

2. Natural Sources

As mentioned, the Alamo Lake watershed is comprised of approximately 59% volcanic/basaltic/granitic rocks. These rock types are known to be associated with relatively higher amounts of mercury. This relationship is supported by soil mercury concentration values for the Alamo Lake watershed, obtained from USGS (Gustavsson et al., 2001). These data were developed after processing point data collected at 1,323 stations across the conterminous US using weighted-median and Bootstrap procedures for interpolation and smoothing. Figure 9 shows the distribution of soil mercury within Arizona based on these data. A significant portion of the Alamo Lake basin is one of six or seven relatively higher soil mercury levels in Arizona.

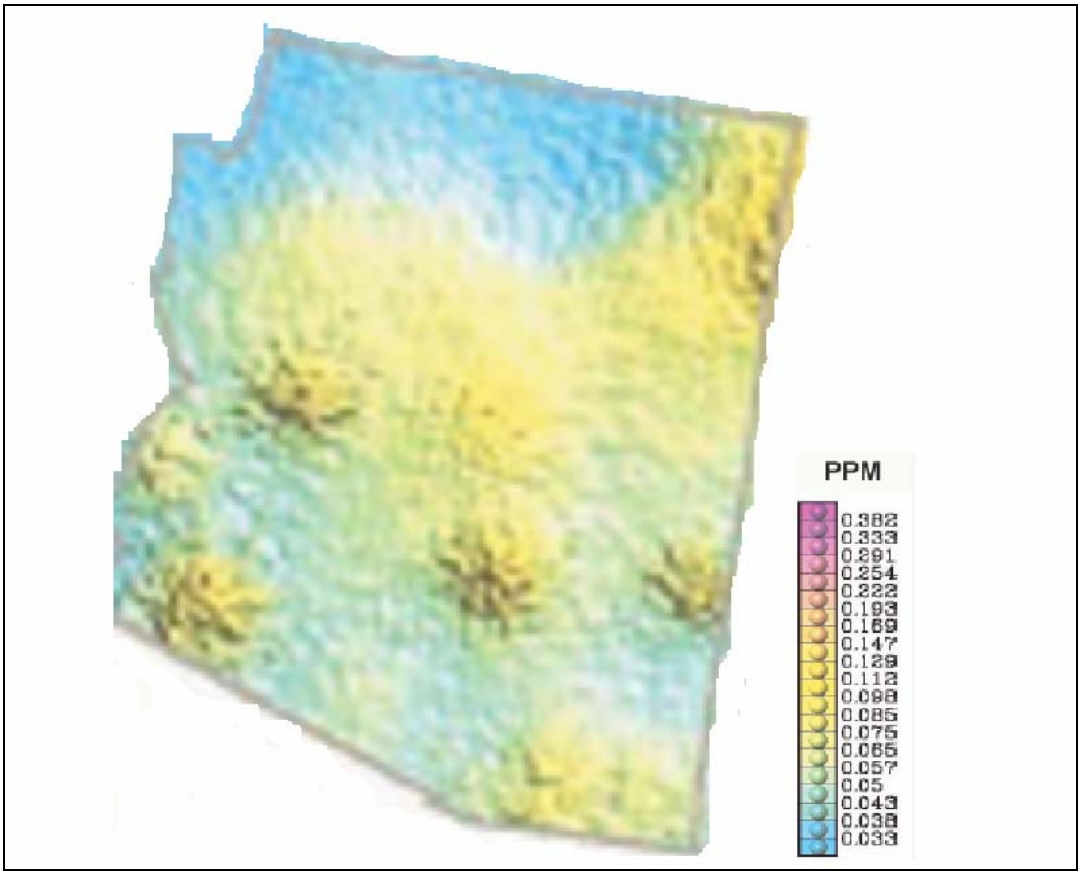


Figure 9. Soil mercury values (from Gustavsson et al., 2001)

ADEQ sampled a cross-section of geothermal springs in the Bill Williams and Big Sandy groundwater basins. Results showed mercury levels elevated approximately five times (up to 0.66 ng/L) above results from background wells, which were mostly non-detect @ 0.15 ng/L.

3. Atmospheric Deposition: Emissions and Fires

Both wet and dry atmospheric deposition can be a major source of mercury to a watershed and waterbodies. Because of the long residence time of elemental mercury in the atmosphere, deposition can be from sources located near the watershed or from regional and global sources. In general the air concentration and hence the deposition rates are typically dominated by regional values rather than local atmospheric sources, except for the chlor-alkali plants (USEPA, 1997).

USEPA has undertaken several modeling studies to develop national estimates of mercury deposition rates ((1997 EPA Mercury Study Report to Congress using Regional LaGrangian Model of Air Pollution (RELMAP)). The RELMAP modeling is believed to underestimate mercury dry deposition in the arid southwest. More recently, EPA developed a new regional mercury transport model based on the Models-3/CMAQ system (Byun and Ching, 1999; USEPA, 2005) that incorporates a more sophisticated representation of mercury chemistry. The assumptions for atmospheric deposition were updated with this information and used in the

current watershed model. Figure 10 and 11 show the atmospheric deposition rates based on CMAQ modeling results for the 2001 base case. CMAQ is believed to provide a more accurate estimate of total mercury deposition, particularly in the arid southwest.

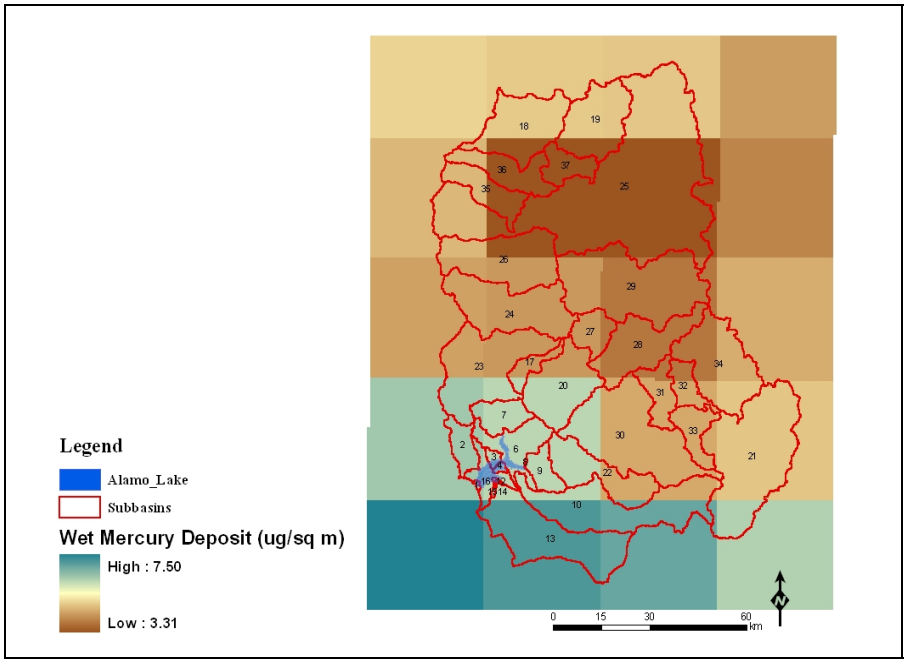


Figure 10. Wet Deposition in Alamo Lake Airshed (CMAQ, 2005)

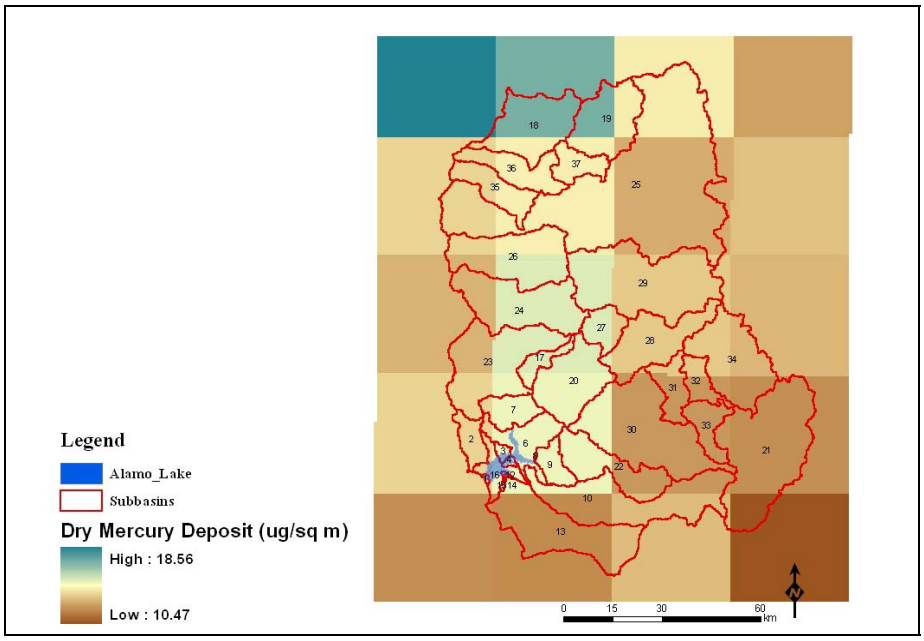


Figure 11. Dry Deposition in Alamo Lake Airshed (CMAQ, 2005)

Another factor that could impact the sediment mercury loading but is not included in the WCS modeling is the effect of major forest fires. Caldwell et al. (2000) showed that forest fires and subsequent rains in the watershed of Caballo Reservoir in south-central New Mexico resulted in increased mercury load. This increase in mercury correlated with an increase in the methylmercury concentrations within Caballo Reservoir watershed due to a combination of factors including increased erosion, mobilization of mercury from biomass, and increased opportunity for methylation.

The potential effect of historic forest fires on sediment-associated mercury loading in the Alamo Lake watershed was analyzed using the sediment mercury concentration measure monitored by ADEQ, combined with the sediment load predictions by the WCS model. Data regarding the history of forest fires within the Alamo Lake watershed was available from the U.S. Department of Interior's Bureau of Land Management (BLM). A summary of data compiled for forest fire areas in the watershed from 1982 through 2002 (Figure 12). Figure 13 shows the average area within each sub-basin that is affected by the historic forest fires. These recent fires are categorized by relative size of the area affected, but do not include exact mapping of those areas. The highest concentration of fire areas are reported in the western and southern portions of the Big Sandy River watershed, western portions of the Burro Creek watershed, and headwaters of the Santa Maria River watershed.

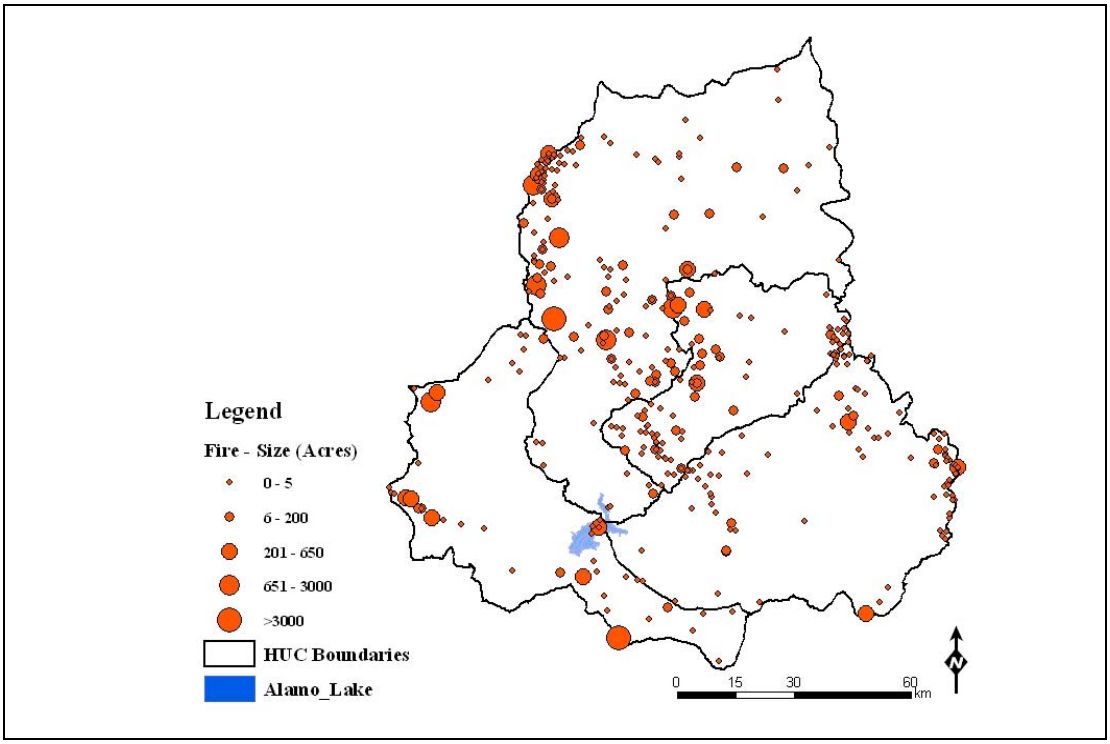


Figure 12. Forest Fire Areas Reported by the BLM (1982-2002)

Figure 14 shows a correlation between average size of historical forest fires and the unit area loading estimates of sediment associated mercury calculated based on the measured sediment

mercury concentration. Similar to the case with the relative number of mines, there is a positive correlation between the average size of historical forest fires and mercury load estimate anomalies. One difference is that the anomaly for Big Sandy watershed falls more in line with the general pattern when analyzed against fire size.

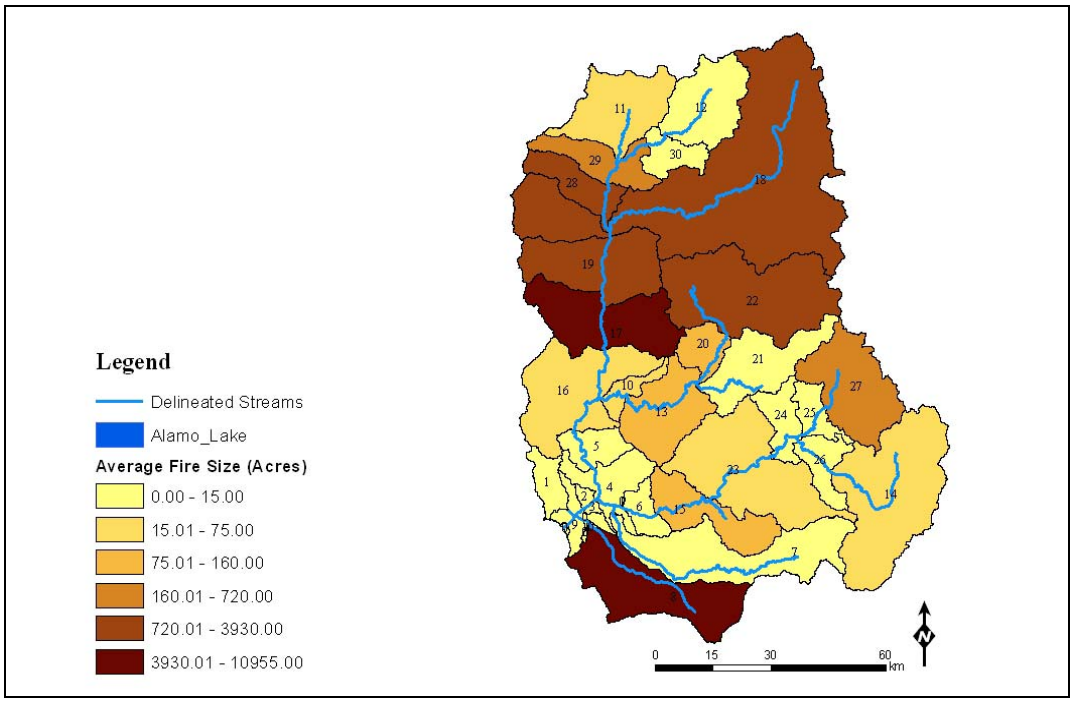


Figure 13. Average Size of Historical Fires within Modeled Sub-basins

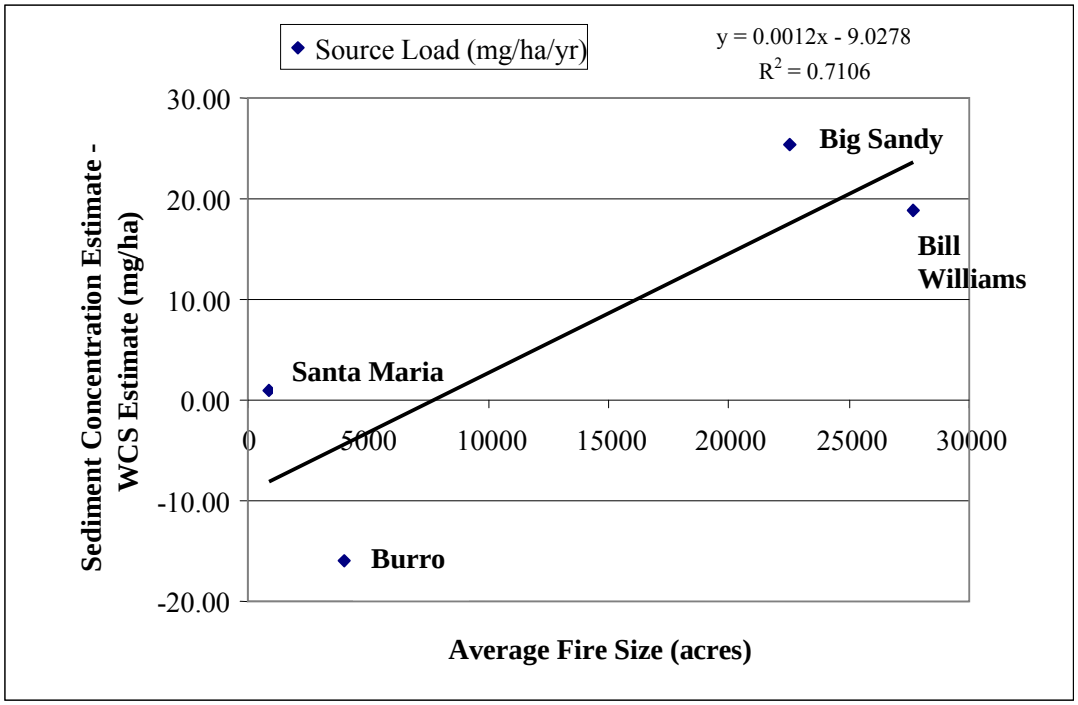


Figure 14. Analysis of Forest Fire Impacts on Estimation of Mercury Loads at Locations in the Alamo Lake Watershed

III. DATA REVIEW

A. Data Collection

Modeling of Alamo Lake included analysis of water quality data collected by USFWS between 1991 and 2004 and by ADEQ between 2002 and 2005. Grab samples were collected at several lake locations and six to twelve surface water locations within each Hydrologic Unit Code (HUC) (Figure 15). Lake sampling included a complete suite of water and sediment chemistry (nutrients, general chemistry, total & dissolved metals) plus chlorophyll-a, organic carbon, algae, zooplankton, sulfide, and sulfur-reducing bacteria. Water and sediment mercury sampling were conducted using EPA Clean Hands protocols and submitted for analysis using ultra-low level detection for total, dissolved, and methyl-mercury (EPA Method 1669 and 1631e). Tributary sampling focused on collection of general chemistry, suspended sediment concentration, flow, organic carbon, sulfate, and mercury (total, dissolved, and methyl).

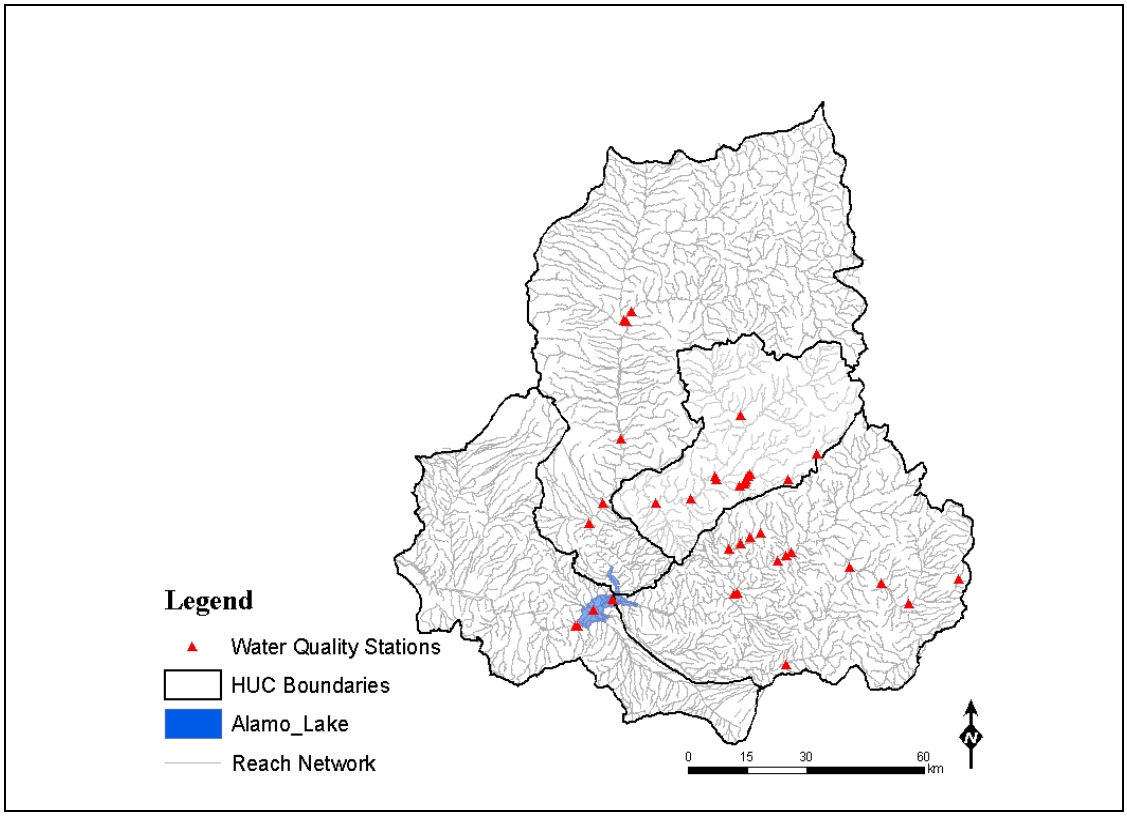


Figure 15. Sampling Locations

B. Watershed Sampling: Dry Period (Spring '02 – Summer '04)

Results supported the hypothesis that mercury is elevated in soils and sediments within or downstream of historic mining. Given the size of the Alamo Lake watershed as well as the difficulties in accessing remote areas, comprehensive background soil sampling was not attempted for this study. Such an effort may be necessary to adequately distinguish natural background from

elevated source areas. Spring watershed sampling produced mercury results within a range of 0.15 nanograms per liter (ng/L or parts per trillion) to 627.0 ng/L for surface water. For comparison, Arizona's surface water standard is 10 ng/L for protection of aquatic and wildlife. The highest value was found in runoff downstream of a massive sulfide deposit and area of historic lead and zinc mining. This sample was collected from an ephemeral stream that drains to the Santa Maria River southeast of the town of Bagdad. The second highest value of 168 ng/L was found in a pool (non-flowing) adjacent to the historic Hillside Mine. In ground water, the range was 0.15 ng/L to 66.0 ng/L, with highest values from geothermal springs. For soils/sediments, all initial samples were submitted to a lab that did not possess low-level analysis capability and results were for the most part non-detect at <0.1 mg/kg. The exception were results from 0.22 mg/kg to 0.46 mg/kg in soils and tailings within or downstream of historic mine sites. Arizona does not have sediment standards.

C. Watershed Sampling - Wet Period (Fall '04 – Spring '05)

Starting in August of 2004, the Alamo Lake watershed received several very large precipitation events, producing some of the highest flows on record (Figure 16a shows one example) and the logistics of sampling became very challenging. Never-the-less, data obtained from the primary tributary sites represent an adequate cross-section of flows for projection of sediment and mercury load duration curves. These curves and other model results will be discussed in the next section. Suspended sediment concentration was very high, as evidenced in a photograph of the same station taken during the same period (Figure 16b).

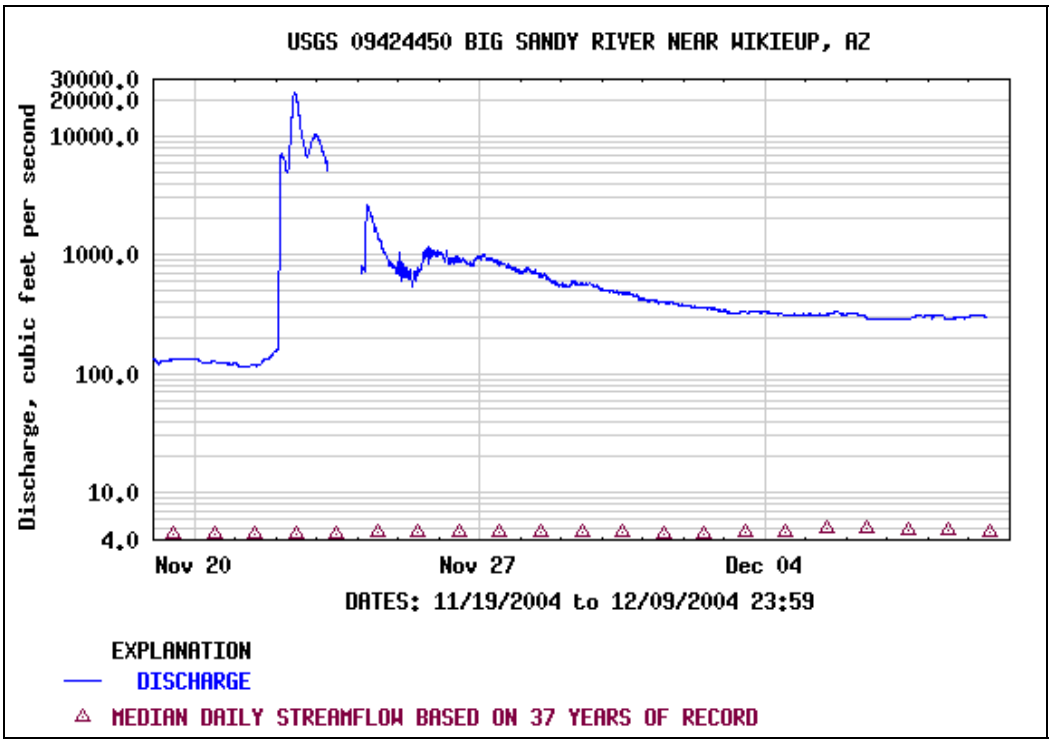


Figure 16a. Hydrograph for Big Sandy

Figure 16b. Photograph at Big Sandy Gage

Total mercury values obtained during this wet period were commonly in the 100-ng/L range, but got as high as 1900 ng/L in one Santa Maria drainage location. Many of these samples exceeded the chronic standard for support of aquatic and wildlife, 10 ng/L, and the fish consumption standard of 600 ng/L.

D. Alamo Lake Sampling

Data were collected from Alamo Lake during several seasons in order to capture the effects of stratified vs. mixed conditions on mercury concentrations. Total mercury in lake sediments ranged from 20 ng/g to 50 ng/g dry weight, while the highest total mercury water value was 35 ng/L at 20 meters depth under stratified conditions. There were no exceedances of the water column standards in the lake. The highest methyl-mercury concentrations in water as 6 ng/L during the post-flood sample event. The final lake sampling event occurred on August 25, 2005, in which methyl-mercury (meHg) was prevalent in *all* parts of the lake below the thermocline at about 5 m) (Figure 17. MeHg values in bold).

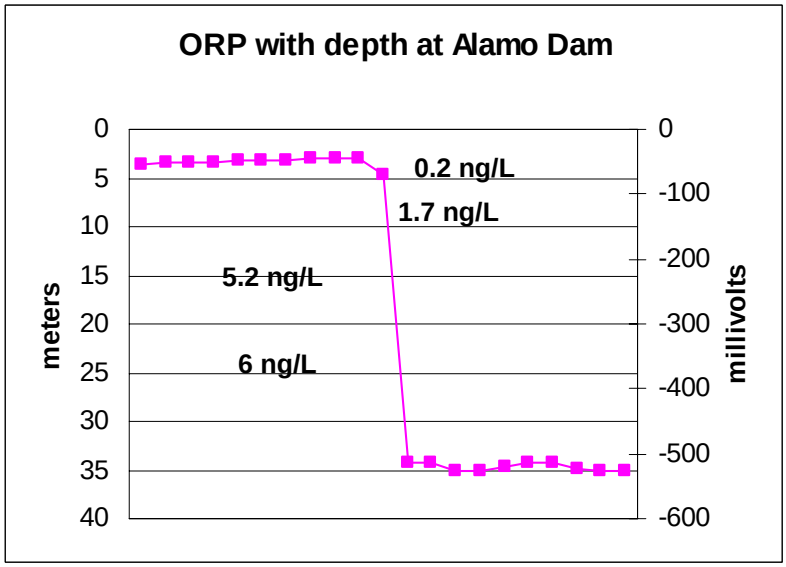


Figure 17. MeHg Results against Depth and ORP, August 25, 2005

E. Fish Tissue Sampling

The fish advisory issued for Alamo Lake applies to Largemouth Bass, Crappie, and Channel Catfish. The TMDL focuses on Largemouth Bass as the top predator. Largemouth bass in Alamo Lake showed no clear relationship between tissue concentration and length or weight (Figure 18). However, tissue concentrations in largemouth bass samples follow an approximately normal distribution (Figure 19). Thus, statistical tests based on a normal distribution assumption are appropriate.

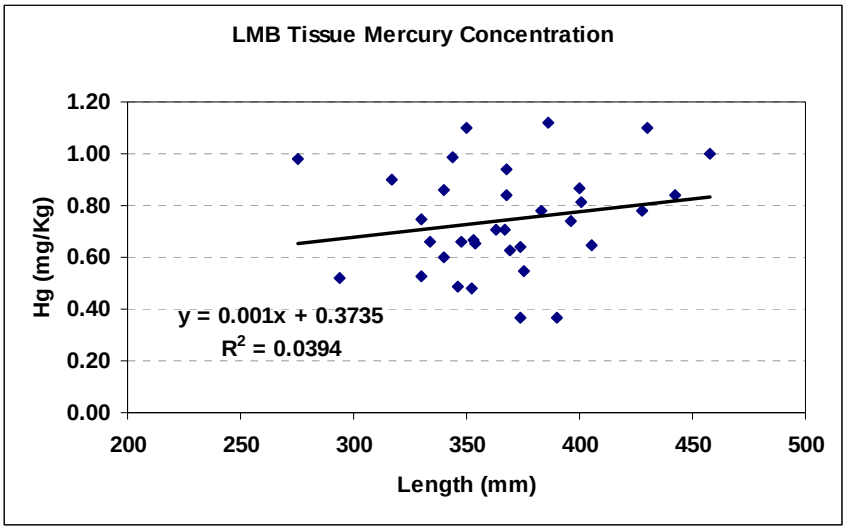


Figure 18. Total Mercury in Relation to Length in Largemouth Bass Tissue

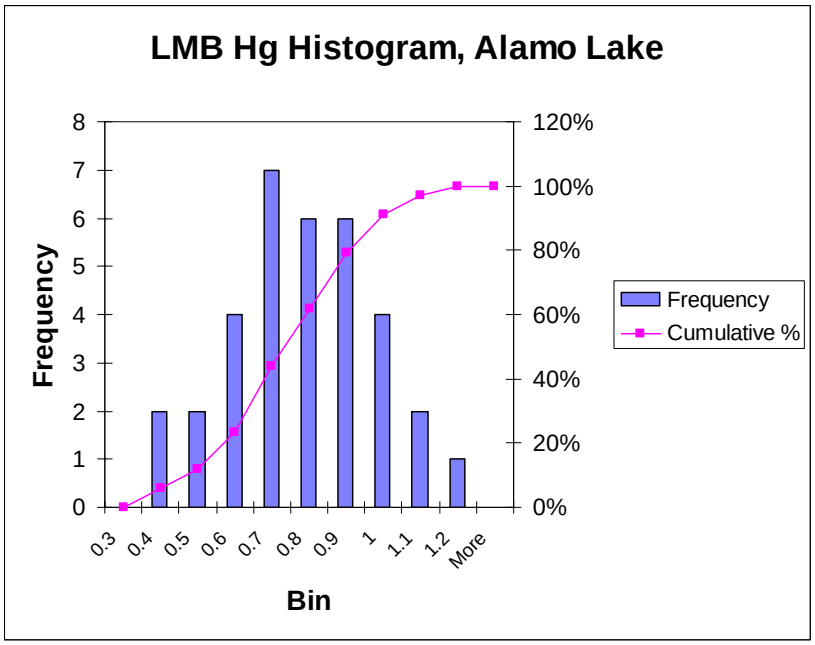


Figure 19. Histogram of Mercury Concentrations in Largemouth Bass, Alamo Lake

IV. TMDL MODELING

A. Conceptual Approach

Mercury impairment in Alamo Lake was based on fish tissue concentrations of mercury. At the time, there were no low-level mercury water samples collected in either the lake or watershed that would inform violation of Arizona's surface water quality criteria for mercury. The modeling challenge involved questions such as: 1) where is the mercury coming from and exactly how is it getting into the lake?; 2) are there areas within the watershed where methylation is occurring?; 3) once in the lake, where is methylation occurring/under what conditions?; 4) assuming both watershed and aerial mercury inputs to the lake, what can be considered 'background'?; and importantly, 5) how is mercury working it's way up the food chain? Answers to each of these puzzling questions should play a role in any strategy developed to break the cycle or minimize accumulation of mercury in fish tissue if a viable sport fishery at Alamo Lake is to be restored.

Tetra Tech Inc. was asked to integrate three components, or compartments, in modeling mercury for this project: 1) possible sources in the watershed and transport via runoff, 2) possible aerial sources and most likely mechanisms of deposition, and 3) factors within the lake system that cause mercury to methylate and move up the food-chain. A TMDL must be quantitative in terms of recommendations for load reductions; each of these compartments requires both sound numeric data and adequate understanding of processes involved. With these challenges and

goals in mind, Tetra Tech Inc. and ADEQ agreed on a combination of mechanistic and empirical modeling that acknowledges data limitations while maintaining the highest possible degree of complexity.

- GIS-based watershed cycling model for sources and routing of mercury (mechanistic) – chose the Watershed Characterization System (WCS, Tetra Tech, 2000)
- Load duration curves for suspended sediment and mercury in runoff (empirical)
- HEC-5 for lake water balance over 12-yr period (mechanistic)
- WASP5/TOXI5 receiving water model package for lake processes (mechanistic)
- Bio-accumulation factors for movement of mercury up the food chain (empirical)

The approach used by Tetra Tech performs two parallel analyses:

- Source Assessment: Compilation and analysis of hydrology and water quality data for assessment of sources of mercury in the watershed and transport processes to Alamo Lake.
- Linkage Analysis: Compilation and analysis of water quality and hydraulic data for development of relationships between flows and mercury loading to the lake, hydraulics, in-lake mercury cycling, and numeric water quality targets for calculation of TMDL's.

A brief description and graphic representation of model components follows. See Tetra Tech, 2005a and 2005b for more detailed discussion.

B. Watershed Loads Using Load Duration Curves

Watershed loading of mercury and sediment was estimated from load-duration curves in concert with the application of the WCS. The load-duration curves convert daily estimates of inflow from the Santa Maria River, Big Sandy River, and Burro Creek into daily estimates of total mercury (THg) load, methyl-mercury (MeHg) load, and total suspended solids (SSC) load. The difference between total Hg and MeHg load was assumed to represent the Hg (II) load. The total solids load predicted by the load-duration analysis was apportioned to a coarse (sand) fraction and a fine (sand/clay) fraction based on observations reported with the tributary monitoring. Four water quality stations in addition to the three gage stations (Figure 20) provided information for analyses of sediment and mercury loading characteristics.

Flow percentiles covered by monitoring included 20%-100% for the Big Sandy and Santa Maria Rivers and 10%-100% for Burro Creek. Because the flow coverage was so extensive, concentration duration curves for mercury and suspended sediment could be projected with a high degree of certainty. As seen in Figures 21 a,b,c, the R^2 values are all above the 75th percentile, and most are higher than the 90th percentile.

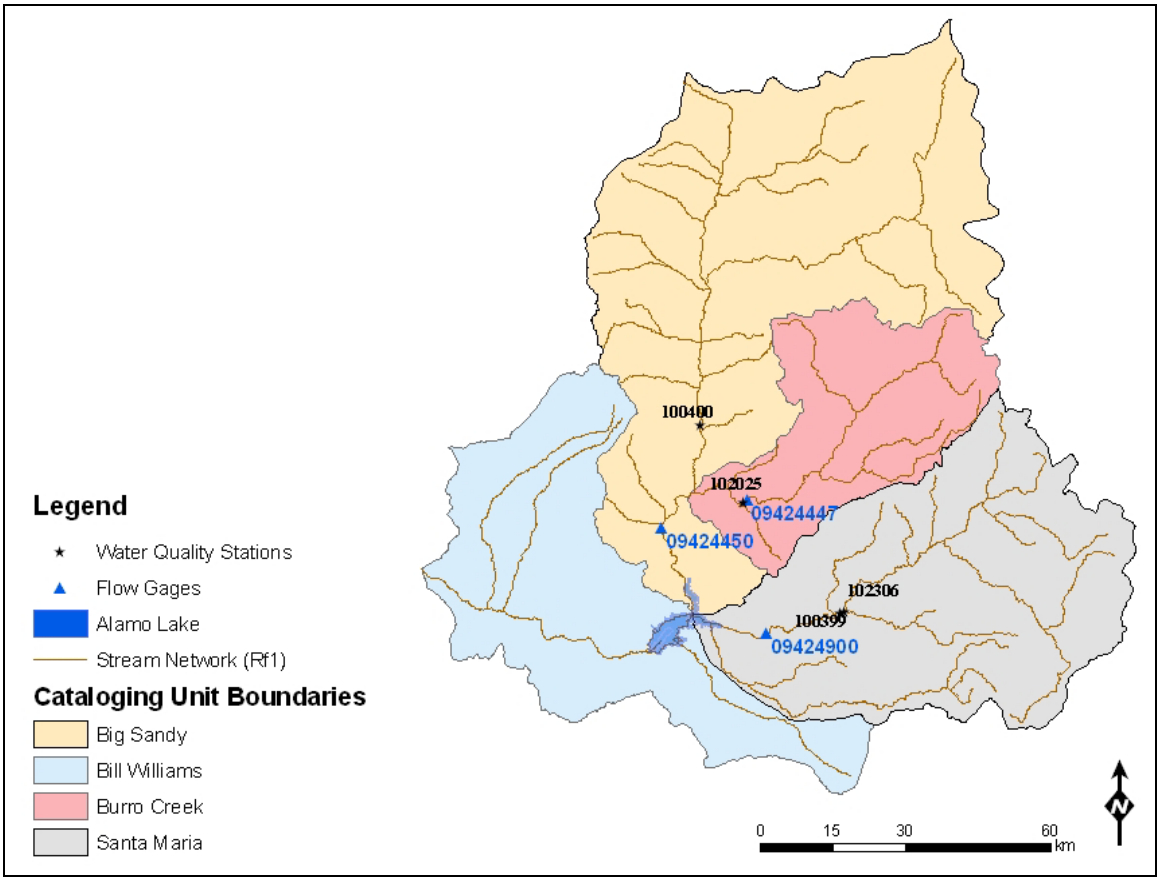
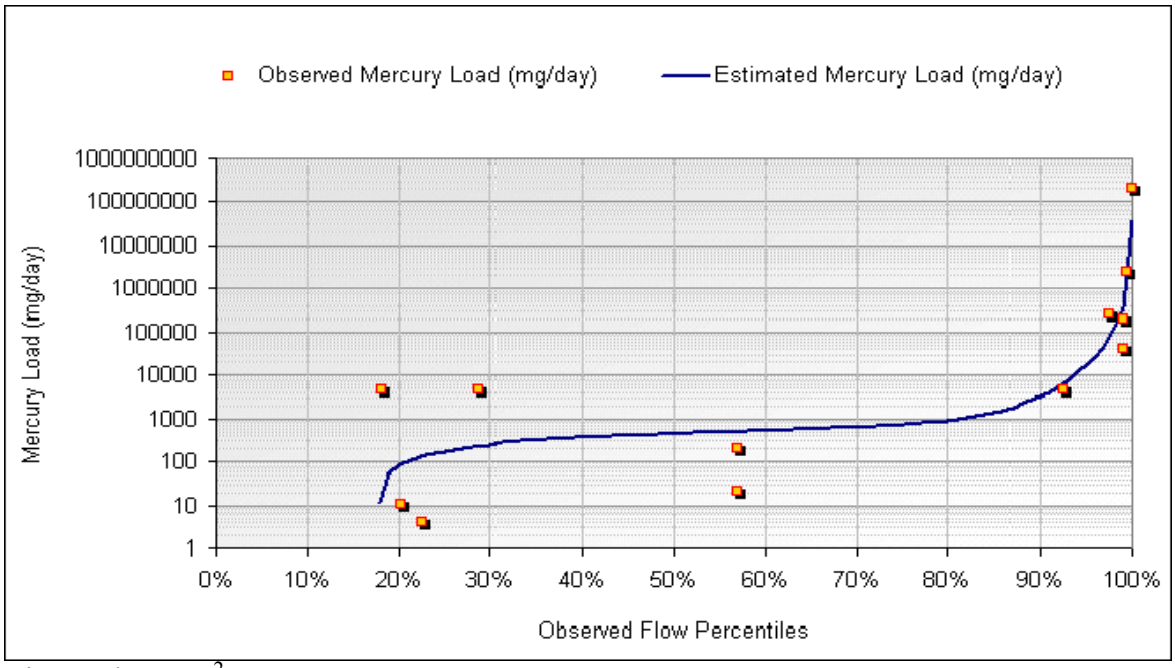
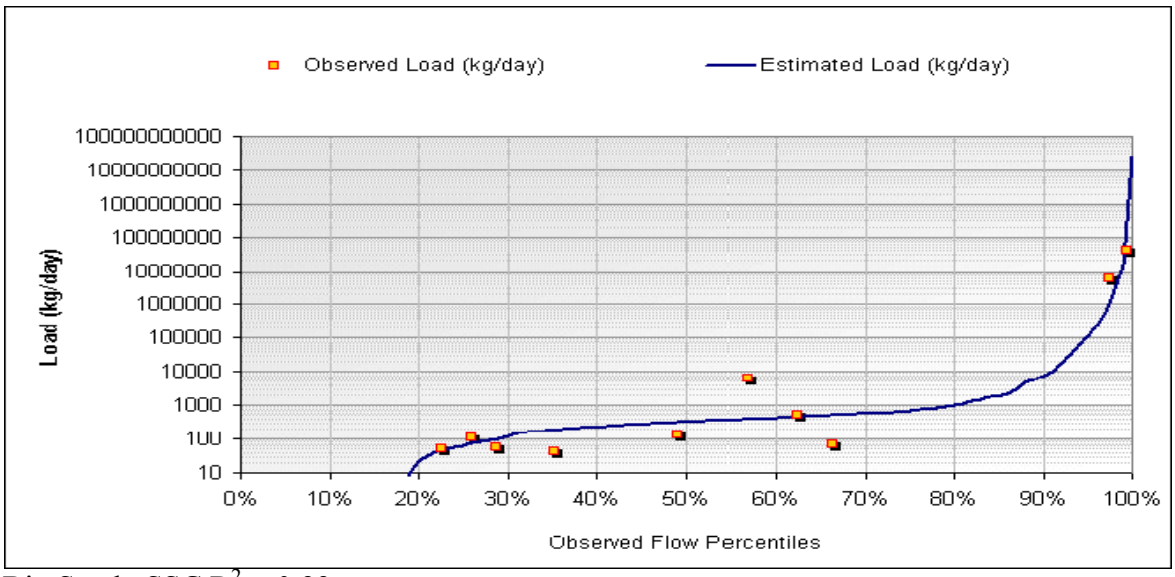


Figure 20. Stations Used for Flow and Load Duration Curves

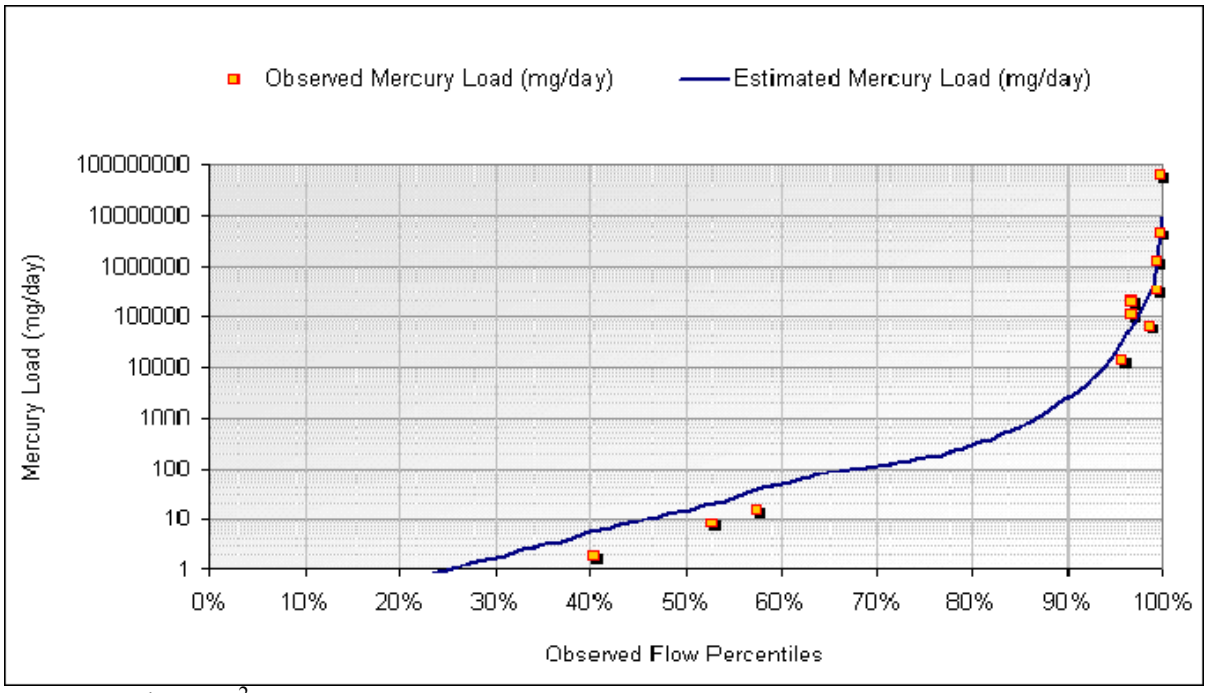


Big Sandy Hg $R^2 = 0.76$

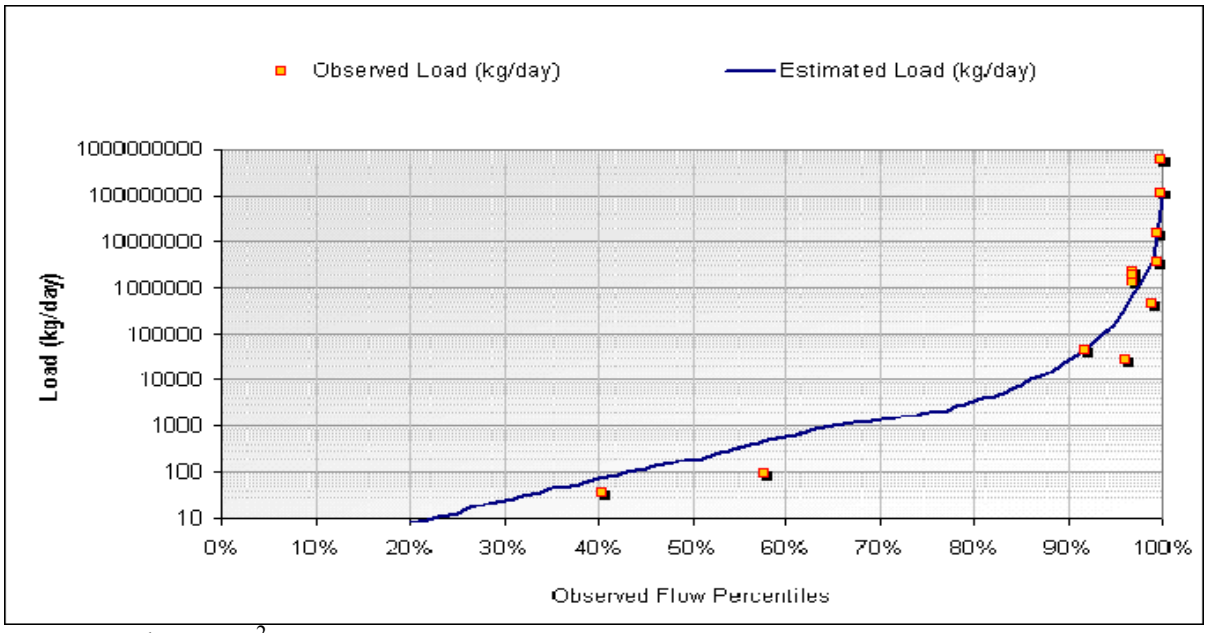


Big Sandy SSC $R^2 = 0.93$

Figure 21a. Load Duration Curves for Mercury (Hg) and Suspended Sediment Concentration (SSC) at Big Sandy River Station

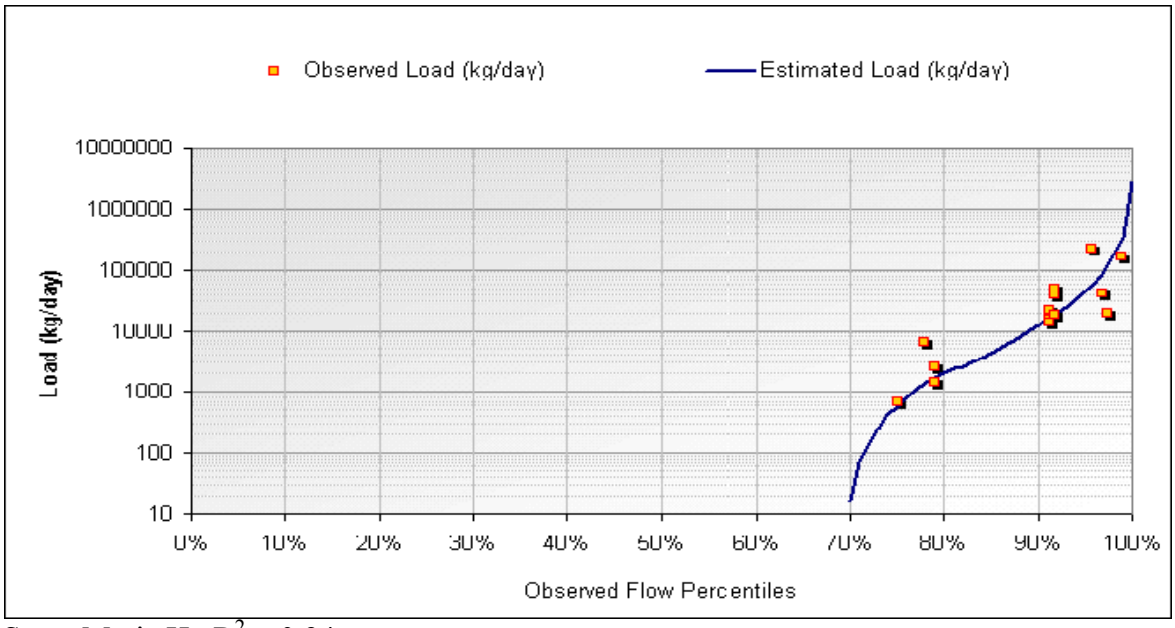


Burro Creek Hg $R^2 = 0.97$

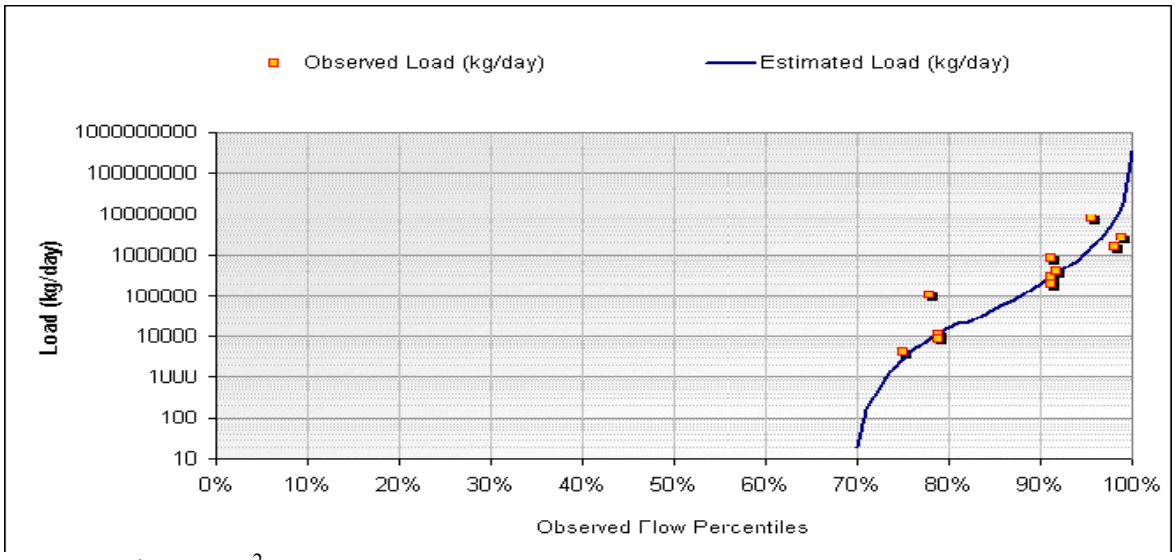


Burro Creek SSC $R^2 = 0.94$

Figure 21b. Load Duration Curves for Mercury (Hg) and Suspended Sediment Concentration at Burro Creek Station



Santa Maria Hg $R^2 = 0.94$



Santa Maria SSC $R^2 = 0.90$

Figure 21c. Load Duration Curves for Mercury (Hg) and Suspended Sediment Concentration (SSC) at Santa Maria (combination of two locations to compensate for peak flow gage)

C. Watershed Source ID and Load Delivery Using the WCS Model

The load duration analyses reported in the previous section provide methods to estimate mercury and sediment loading to the lake. However, to provide an assessment of sources of mercury in the watershed and their relative contribution to the total loading, a separate modeling analysis was performed based on the Watershed Characterization System (WCS) (Tetra Tech, 2000). WCS was developed by the EPA Region 4 to assist in the development of TMDLs for pollutants such as nutrients, pesticides, sediments, and mercury. It is an ArcView-based program that utilizes spatial and tabular data collected by EPA, U.S. Geological Survey (USGS), U.S. Department of Agriculture Natural Resources Conservation Service (USDA-NRCS), U.S. Bureau of the Census, and National Oceanic and Atmospheric Administration (NOAA). This system was modified and adapted for simulation of the Alamo Lake watershed.

The WCS Mercury Tool is based on a soil-mercury mass balance model, IEM v2.05, developed by the EPA Office of Health and Environmental Assessment and the EPA Environmental Research Lab — Athens (Tetra Tech, 2000). The model uses a soil-mercury mass balance and calculates surface soil concentrations in dissolved, sorbed, and gaseous phases. The model accounts for particle-bound contaminant deposition through dry fall (atmosphere), deposition through wet fall (rainfall), and diffusion of vapor phase contaminants into the soil surface. It also accounts for volatilization (diffusion of gas phase out of the soil surface), runoff of dissolved phase from the soil surface, leaching of dissolved phase through the soil horizon, and erosion of particulate phase from the soil surface. Figure 22 shows a diagram of the processes simulated by the WCS Mercury Tool.

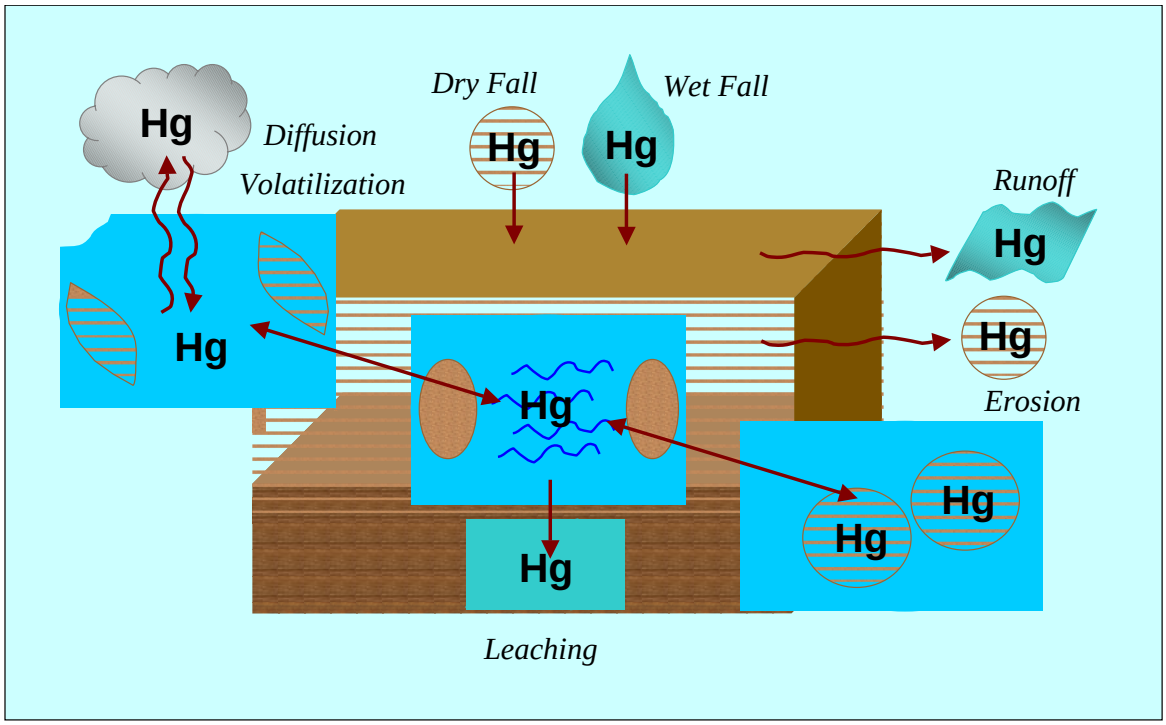


Figure 22. Processes Simulated by WCS

The watershed mercury load is calculated as the total contributed by sediment load due to runoff from both pervious and impervious surfaces, direct atmospheric deposition on water surfaces, and point sources. The model estimates erosion and sediment transport based on the Universal Soil Loss Equation (USLE). To account for losses due to sediment re-deposition, the model calculates the sediment yield from the watershed by applying an area-based sediment delivery ratio. Runoff is calculated using the USDA-NRCS curve number method. Mercury load due to runoff from pervious surfaces is a function of surface runoff and mercury concentration. The annual mercury load from impervious surfaces is a function of the annual mercury deposition.

The three primary HUCs were further broken down into a total of 30 sub-basins for WCS modeling. These sub-basins were assigned the following attributes: area, land uses, vegetative cover, soil types and erodibility factors, hydrologic and climatologic factors, wet and dry atmospheric deposition of mercury, proximity to Mercury Deposition Network (MDN) stations, and distribution of mercury in soils. GIS covers used in this model have been cited previously in Section II with the exception of sub-basins (Figure 23), soil erodibility (Figure 24), and MDN stations (Figure 25).

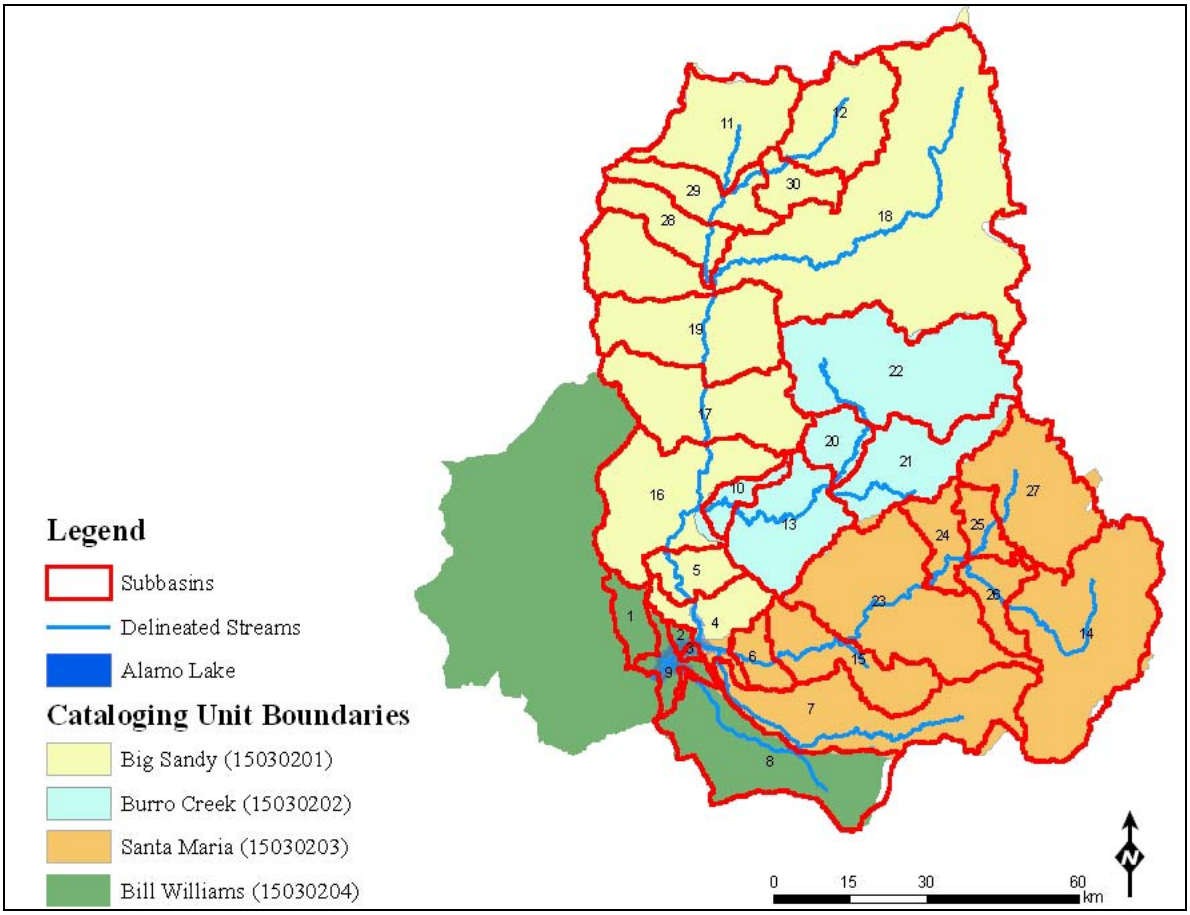


Figure 23. Sub-basins in Alamo Lake Watershed

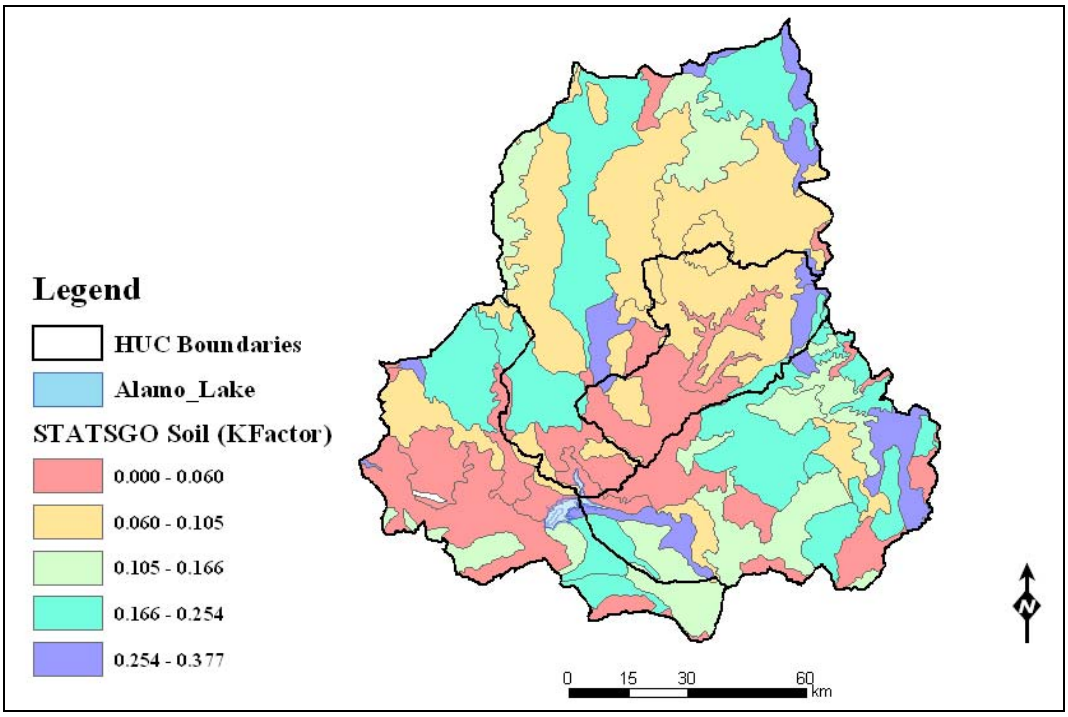


Figure 24. Soil Erosion Factors

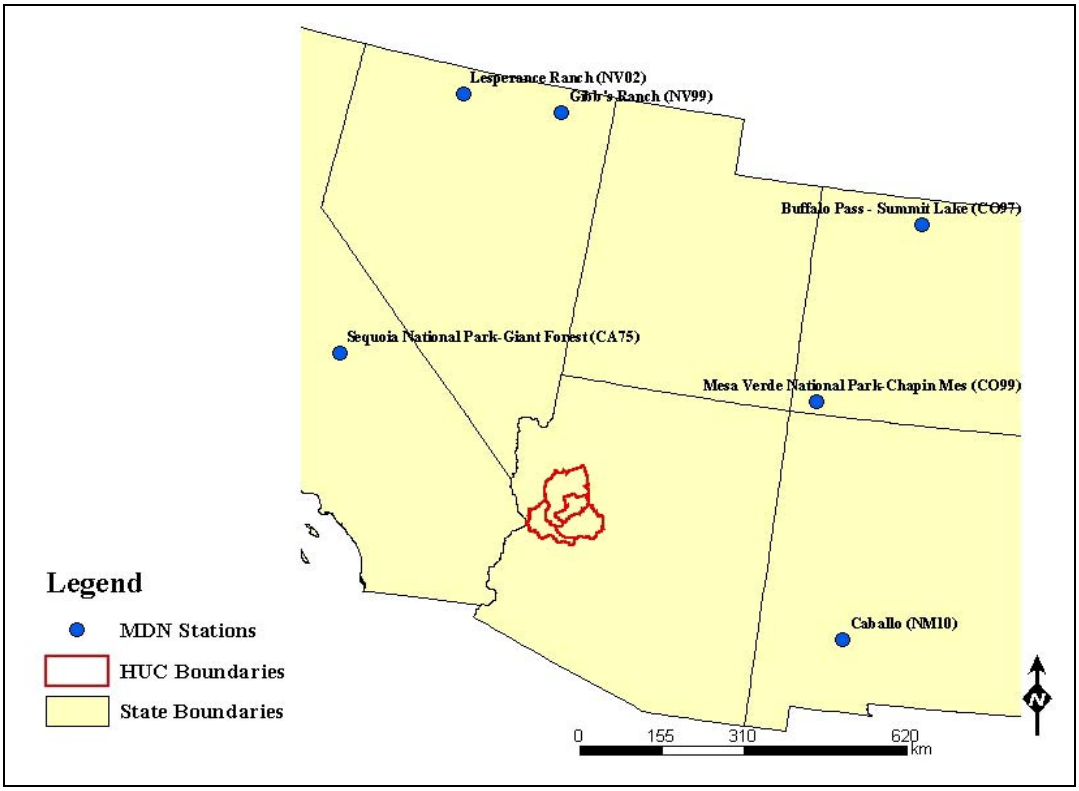


Figure 25. MDN Stations Surrounding Arizona (Note: none in Arizona)

The WCS Mercury Tool was calibrated for hydrology and sediment for the period from 1990 to 1993. This calibration period was selected to include three representative hydrologic periods: normal, dry (below average flow), and wet (above average flow). The locations selected for the calibration included the Burro Creek and Santa Maria gages and the Big Sandy water quality station above Burro Creek.

The number of mining sites in each watershed, based on the Mineral Industry Location System (MILS) database (available with EPA's BASINS dataset), was estimated roughly as 145, 41, and 124, in the Santa Maria, Burro and Big Sandy watersheds, respectively. With more mines, the ratio of loads predicted by the WCS Mercury Tool and load duration analyses (WCS Mercury Tool/load duration) should be reduced, indicating greater under-prediction of loads by the model, and hence a greater impact of mines and other potential unaccounted sources. This same rationale was applied to analysis of potential fire-impact contributions.

V. LINKAGE ANALYSIS using WASP5/TOXI5 & HEC-5

To provide the linkage analysis between external mercury loads to Alamo Lake, internal lake cycling, and the assimilative capacity based on numeric water quality targets, a receiving water model of the lake was developed. The WASP5 toxic chemical model TOXI5 (Ambrose et al., 1993) was implemented to simulate mercury cycling in Alamo Lake. Because WASP5 is well tested and established and has open source code, it is a preferred model for regulatory application. In addition, the WASP5 ASCII output allows custom post-processing of ng/L-scale results.

A general conceptual model of mercury cycling in a lake (showing only the more significant pathways) is shown in Figure 26, based on the representations discussed in Hudson et al. (1994) and Tetra Tech (1999). Note that the linkage between total mercury input and mercury content in fish is mediated through the concentration of MeHg. Mercury methylation can occur both in the lake and in the watershed. Ionic Hg(II) is methylated by a biological process that involves sulfate-reducing bacteria. Rates of biological methylation of mercury can be affected by a number of factors. Demethylation of mercury is also mediated by bacteria. Elemental mercury is only available for methylation following oxidation to the ionic form.

Methylation can occur in water, sediment, and soil solutions, and tends to dominate demethylation under anaerobic conditions. In lakes, methylation occurs mainly at the sediment-water interface and at the oxic-anoxic boundary within the water column. The rate of methylation is affected by the concentration of available Hg(II) (which can be affected by the concentration of certain ions and ligands), the microbial population, pH, temperature, redox potential, and the presence of other chemical processes.

The WASP model application is forced by specification of water inflows, mercury loads, meteorological conditions, and sediment boundary conditions. The model requires a water balance, in this case derived from the US Army Corps of Engineers (USACE) HEC-5 simulation model to test various water management plans for the Alamo Lake and Bill Williams River system (1994).

HEC-5 inflows to Alamo Lake were based on daily average historical flows from various gages within the watershed from October 1, 1928 through September 2004. HEC-5 modeling output

included inflow, outflow, elevation, and storage estimates on a daily time step. Tetra Tech obtained the original USACE application and extended it through 2004. Daily estimates of inflow and outflow were used to apportion water storage into for WASP5 modeling.

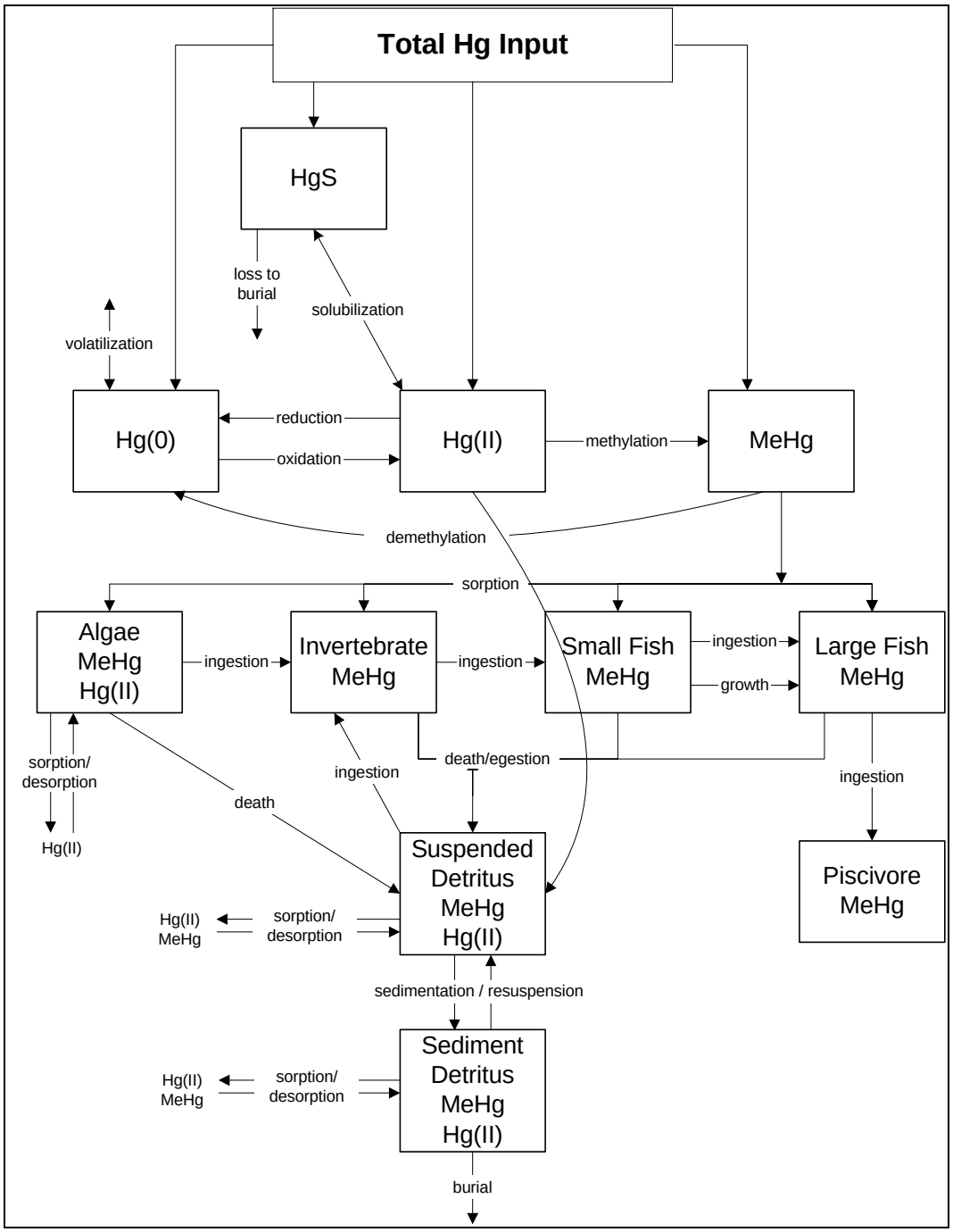


Figure 26. Generalized Lake Mercury Cycle

A. Watershed Loading

Watershed loading of mercury and sediment was estimated from load-duration curves. The load-duration curves convert daily estimates of inflow from the Santa Maria River, Big Sandy River, and Burro Creek into daily estimates of total Hg load and total suspended solids load. To determine the MeHg load, relationships were established based on total Hg and MeHg data collected in each of the watersheds. For corresponding measurements of total and dissolved mercury, equations were developed providing estimation of daily MeHg loads as a function of total Hg loads for each watershed. Figure 27 through Figure 29 show results of these data assessments (locations of monitoring stations correspond to those used for load duration analyses). The difference between total Hg and MeHg load was assumed to represent Hg (II) load indicating no significant load of elemental mercury. The total solids load predicted by the load-duration analysis was apportioned to a coarse (sand) fraction and a fine (sand/clay) fraction based on observations reported with the tributary monitoring: Below flows of 64 cfs in individual tributaries, the sediment load was considered to consist only of fines. At higher flows, the percentage of fine sediment was set to –0.1079 · LN(Flow, cfs) + 1.4481 (Figure 30).

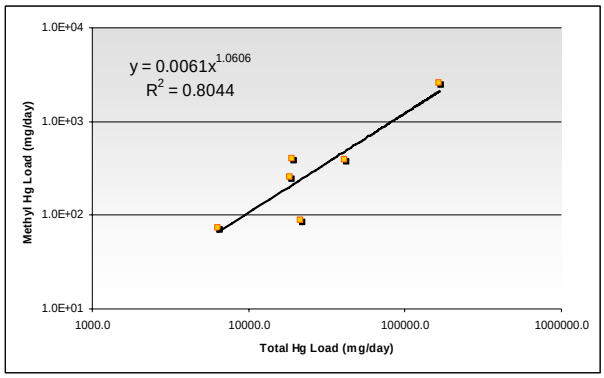


Figure 27. MeHg vs. Total Hg Load Relationship for Santa Maria River

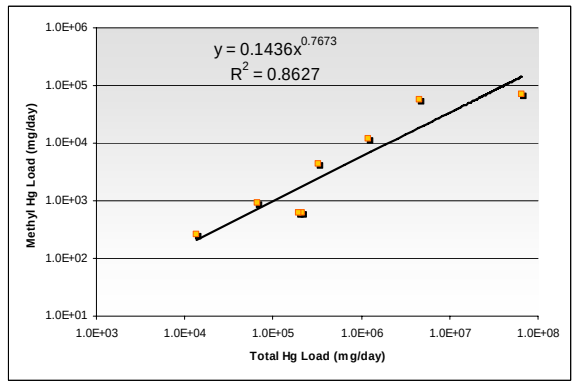


Figure 28. MeHg vs. Total Hg Load Relationship for Burro Creek

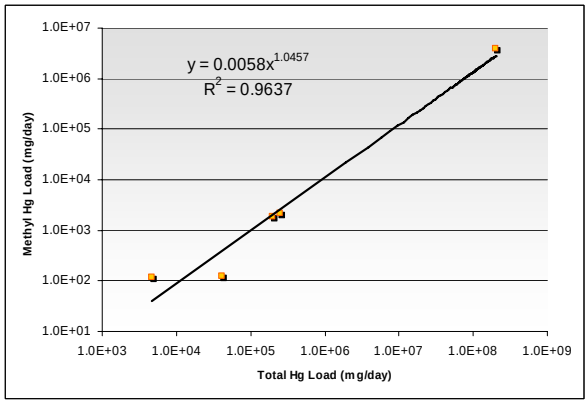


Figure 29. MeHg vs. Total Hg Load Relationship for Big Sandy River

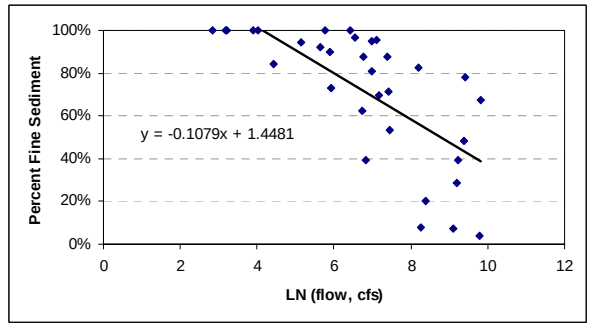


Figure 30. Analysis of Tributary Sediment Size Data

Dissolved organic carbon (DOC) concentrations are important to the simulation of mercury sorption and settling. Constant values of DOC were specified to WASP/TOXI by model segment, based on the average of observed data. DOC was set to 8.6, 7.9, and 7.8 mg/L in segments 1, 2, and 3 respectively. The actual observed range in the water column was 5.7 to 10.1 mg/L. Sediment DOC was set to 12 mg/L.

B. Loading to Alamo Lake

Loading to Alamo Lake is represented by three water segments and three sediment segments (Figure 31). The surface water segments participate in atmospheric exchanges and either subsurface water or shallow sediment exchanges depending on the type of segment beneath. The upstream portion of Alamo Lake is represented by a single water segment underlain by a shallow sediment segment. The downstream portion of the lake is represented by a surface water and a subsurface water segment because the deeper waters in this section are subject to thermal stratification. The shallow sediment segments represent the "active" sediment layer in which exchanges with the water column and biological mercury transformations take place and have an assumed depth of 10 cm. The surficial sediment layers are in turn underlain by a common deep sediment layer, which allows for sequestration and deep burial.

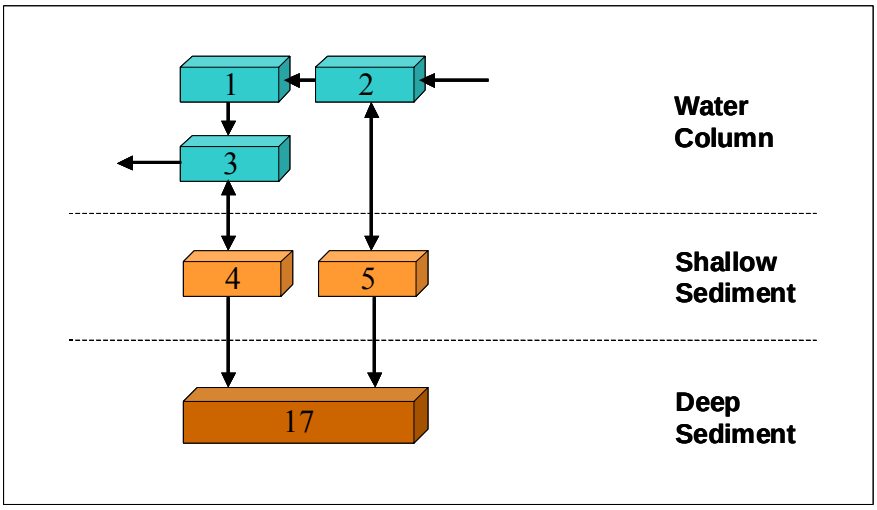


Figure 31. Linkage of WASP Model Compartments

The TOXI-WASP application can represent three species of mercury (elemental, ionic, and methyl) in compartments associated with surface water, subsurface water, and sediment (Figure 32). The model provides a full description of transformations between mercury species and exchanges between compartments and with the atmosphere.

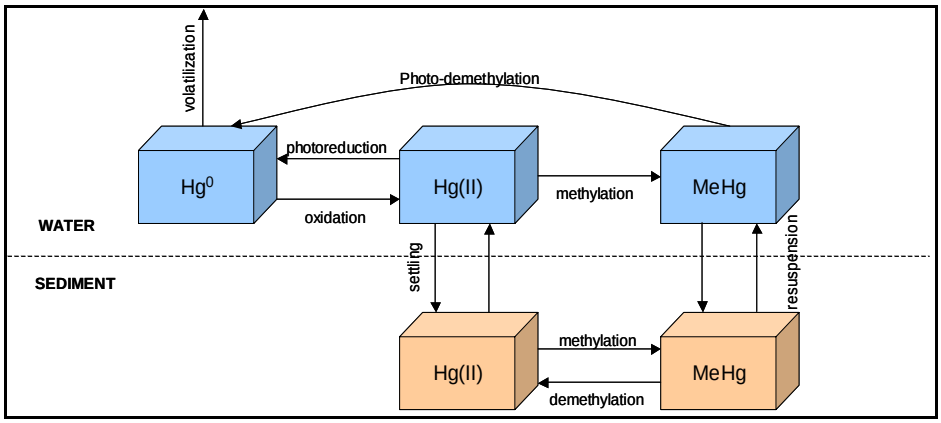


Figure 32. Model Representation of Mercury Transformation Kinetics

The equilibrium concentrations observed in the water column are primarily a function of the loading rate, as modified by the sediment recycle and loss rates. Initial rates of sediment settling in the water column were based on Stokes law considerations and set to 20 m/d for the coarse fragment and 0.2 m/d for the fine fragment.

Some evidence on rates of deep burial are provided by the NAU coring study (Gremillion and Toney, 2005), which showed long-term burial rates of about 12.2 cm/yr. This estimate should, however, be taken as an approximate upper bound, because the cores were purposely sited in areas of consistent high deposition: "Coring locations were chosen to retrieve the thickest, undisturbed, sequential sediment package from each site."

Calibration of the model thus focused on rates of settling, resuspension, and deep burial of the finer sediment fraction with which mercury is primarily associated. Calibration to observed data used the Parameter ESTimation (PEST) numerical optimization software (Watermark Numerical Computing, 2002), which attempts to minimize the squared error between observations and simulated values by adjusting user specified parameters in the model.

Using WASP, Table 4 compares the magnitude of mercury species concentrations and percent of (apparent) dissolved mercury species in the water and sediment with the average of 2002-2004 observations for Alamo Lake. In general, a reasonable fit has been obtained to concentrations and speciation in both the water and sediment.

Table 4. Comparison of Simulated and Observed Mercury Concentrations

Compartment	Component	Simulated	Observed (Average)
Water Column	Total Hg (ng/L)	1.64	1.52
	MeHg (ng/L)	0.24	0.35
	Total Hg, Dissolved (ng/L)	0.47	0.53
	MeHg, Dissolved (ng/L)	0.07	ND
Surface Sediment (Solid Phase)	Total Hg (ng/g)	29.39	41.92
	MeHg (ng/g)	1.81	0.62

The concentration fit is summarized graphically in Figure 33. With the exception of the single observation of MeHg in sediment, the average-condition fit is quite close, as would be expected from the numerical optimization of parameters. Note: Large blue diamonds are average predictions from WASP-TOXI model; small green triangles are observations from 2003-2004.

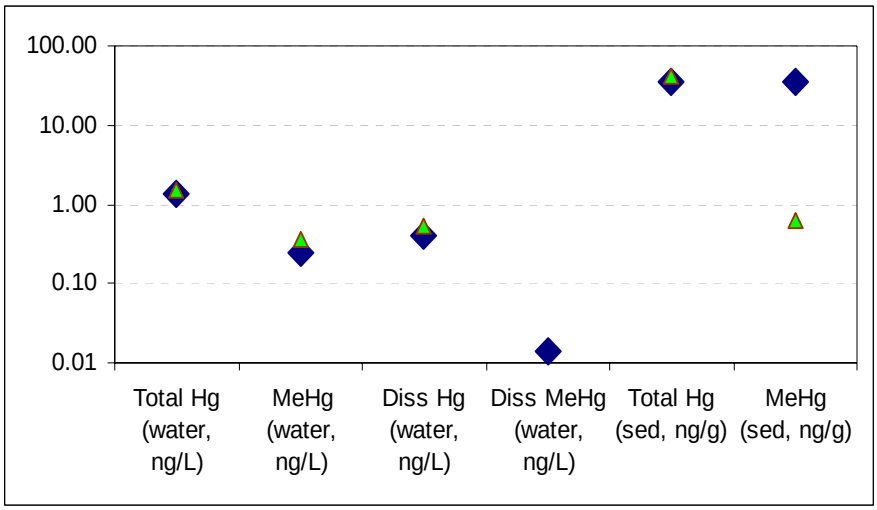


Figure 33. Simulated and Observed Avg Hg Concentrations

Figure 34 shows the trajectory of the model over time during the 12 3/4 years of simulation for Segment 1, the downstream segment of Alamo Lake. Hg(II) is not shown, because it closely parallels total mercury, of which it is the dominant component. The graph shows a pattern of occasional pulse-loading of mercury from the watershed during infrequent large washoff events. Such loads are followed by more gradual peaks in Hg(0) and MeHg as the incoming mercury load is processed in the water column and sediment.

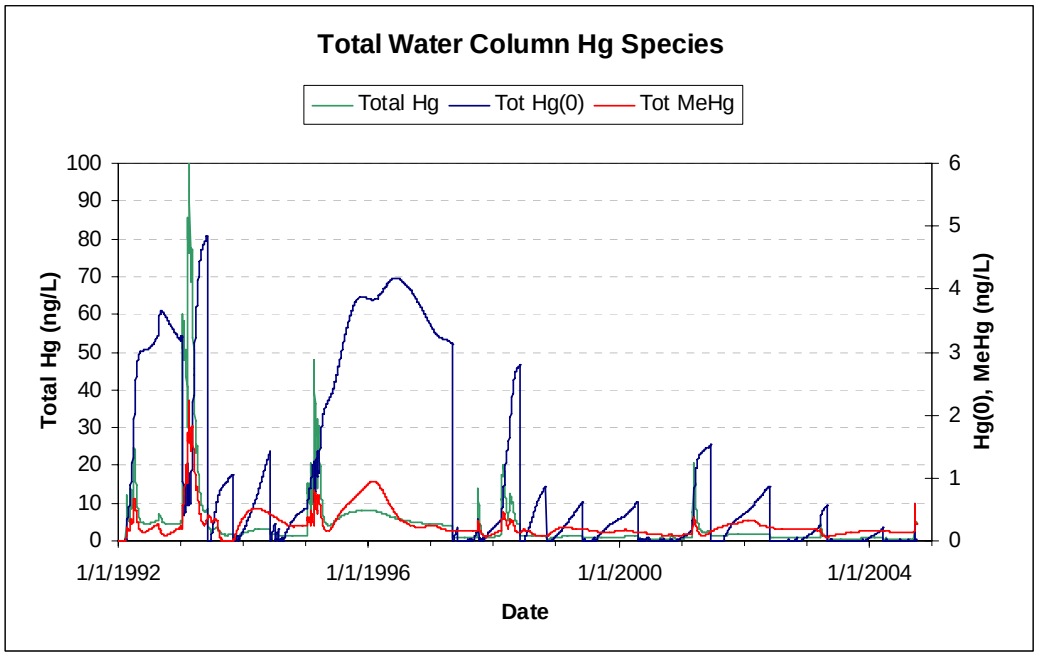


Figure 34. 12-yr Model Trajectory for Hg

C. *Lake Sampling Results and Resetting of Mercury Exposure Concentrations by High Flow Events*

An important insight from the lake modeling is that mercury concentrations in Alamo Lake are periodically reset by large influent loads. This conclusion of the model can be validated through examination of the most recent monitoring data.

During the winter of 2004-2005, Alamo Lake experienced several large inflow events that raised lake levels dramatically (by nearly 40 feet of stage). Flows in the Santa Maria River at Bagdad reached 4,690 cfs on Feb. 12, 2005 – the highest inflow rate since 1995. Additional, but smaller increased flows occurred around Aug. 14, 2005 (628 cfs at Bagdad). Unfortunately, USACOE stage-storage records for 2005 (necessary for running the lake model) are largely missing for Alamo, and the lake model has not been run through 2005. However, the implication of the model is that elevated total mercury concentrations in Alamo likely persisted throughout the summer of 2005, coupled with increasing MeHg concentrations.

ADEQ conducted a thorough set of lake water quality observations on August 24, 2005. Results are summarized in Table 5.

Table 5. Results of Alamo Lake Sampling, August 24, 2005

Station	Depth (m)	Total Hg	Dissolved Hg	MeHg
BWALA-A (near dam)	4	1.07 ng/L	0.64 ng/L	0.14 ng/L
	9	4.72 ng/L	2.20 ng/L	1.78 ng/L
	15	6.00 ng/L	4.31 ng/L	5.21 ng/L
	25	6.40 ng/L	5.37 ng/L	5.99 ng/L
	Sediment	76.64 ng/g	-	0.94 ng/g
BWALA-C (mid-lake)	3	1.18 ng/L	0.74 ng/L	0.17 ng/L
	8	3.61 ng/L	1.37 ng/L	1.18 ng/L
	15	6.02 ng/L	5.57 ng/L	5.84 ng/L
	Sediment	58.64 ng/g	-	0.44 ng/g
BWALA-B (upper lake)	2	1.24 ng/L	1.03 ng/L	0.15 ng/L
	7	1.86 ng/L	0.59 ng/L	0.14 ng/L
	10	6.73 ng/L	2.05 ng/L	4.08 ng/L
	Sediment	62.98 ng/g	-	0.32 ng/g

Examination of these sample results qualitatively confirms the model predictions regarding lake mercury status. Most notably, both total mercury and MeHg concentrations in subsurface waters were significantly elevated in August 2005 relative to concentrations observed in the relatively low flow periods of 2003-2004.

Plots of total and MeHg concentrations with depth for station BWALA-A (near dam) in 2005 are shown in Figure 35 along with the results of the Sept. 2003 samples. Not only were the mercury levels elevated in 2005, but the fraction of mercury in the bioaccumulatable methylated form was also high. Indeed, the observed MeHg concentrations in August 2005 were higher than any previously monitored in Alamo Lake – but consistent with model predictions for MeHg concentrations after earlier large inflow events, such as occurred in the early to mid-1990s..

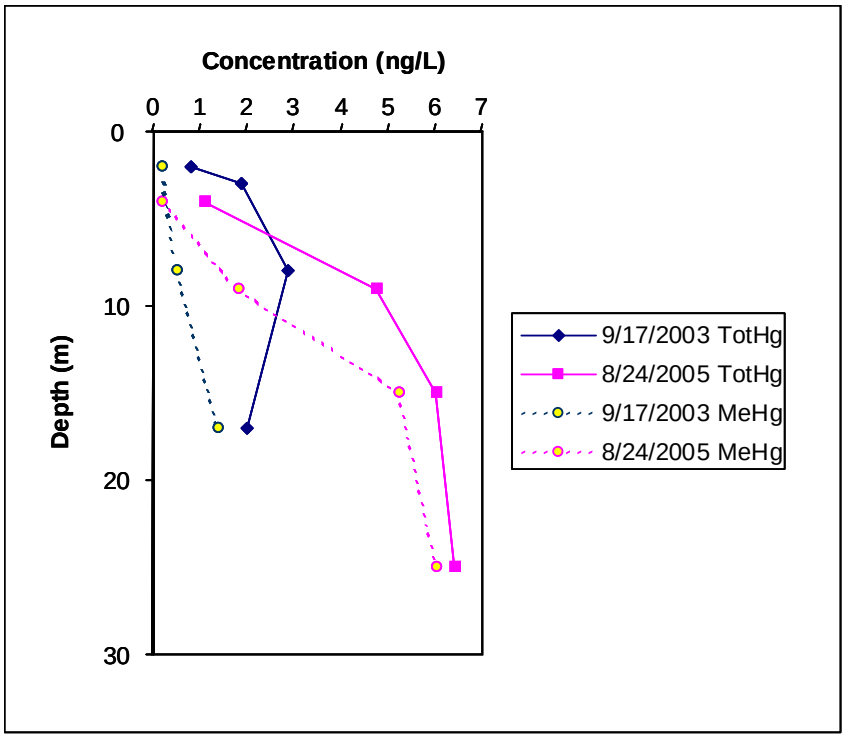


Figure 35. Comparision of 2005 and 2003 Mercury Samples at Station BWALA-A (Alamo Lake near Dam)

Similar, but less dramatic increases in MeHg concentrations are also evident at the mid-lake and upper lake stations. The 2005 sediment concentration at BWALA-A of 76.64 ng/g is higher than concentrations ranging from 21 to 50 ng/g reported in March 2003, February 2004 and September 2004.

The recent elevated concentrations of MeHg will in turn lead to increased rates of bioaccumulation of mercury in fish and make recovery of fish tissue concentrations to acceptable levels more difficult. Major inflow events can bring significant amounts of mercury into Alamo Lake from the watershed. Corresponding increases in lake stage, inundating previously exposed shoreline areas, likely increase the concentration of sulfates in the lake, which provide a substrate for production of MeHg once lake bottom waters become hypoxic. Controlling the rapid increases in lake stage might reduce the rate of MeHg formulation (by limiting sulfate availability), but would reduce the reservoir's water storage purpose, which is largely provided by infrequent high-runoff events. Therefore, achieving acceptable fish tissue concentrations in the lake will likely require reduction in the mercury load delivered to the lake from its watershed.

D. Linkage of mercury loading to fish impairment

Linking fish tissue impairment to mercury loads requires tools that describe the transformations of mercury in the lake and its bioaccumulation in the food chain. Typically, almost all of the mercury body burden found in fish (greater than 95 percent) is in the form of monomethyl mercury (MeHg). Loading from the land surface and atmosphere, however, is primarily in the

form of elemental mercury (Hg(0)) and ionic mercury (Hg(II) or its compounds such as cinnabar (HgS). Mercury bioaccumulation problems require two components: a source of mercury and a mechanism to methylate the mercury into its bioaccumulatable form. The presence of elemental and ionic mercury alone would not result in bioaccumulation. For this reason, the tissue concentrations of mercury in biota are often found to be at best weakly related to total mercury load on a cross-sectional (inter-waterbody) basis.

The calibrated model was used to test the sensitivity of the system to reductions in mercury loads. This was accomplished by running the model with reduced input loads over the hydrology of the 12+ year simulation. This enables examination of the extent of load reduction required to achieve a specified level of MeHg exposure concentrations in the lake.

Fish bioaccumulate mercury over their life spans. Therefore, the most relevant target for evaluating load reductions is the average MeHg concentration in lake water over time. The concentrations in the water column at equilibrium are a function of the influent loads and the net impacts of kinetics. Further, Alamo Lake experiences significant sequestration of mercury due to burial in the sediment. As the kinetic parameters are not changed for the scenarios, the response to reduced loading at equilibrium should be approximately linear. A variety of scenarios were run with watershed loads set to a fixed fraction of the estimated existing load, with no alteration to the existing atmospheric load. Results are shown in Figure 36. As expected, the response is nearly linear. Note: The Normalized Average Concentration is the predicted average MeHg concentration over the 1992-2004 period of simulation divided by the simulated average concentration at existing loading rates.

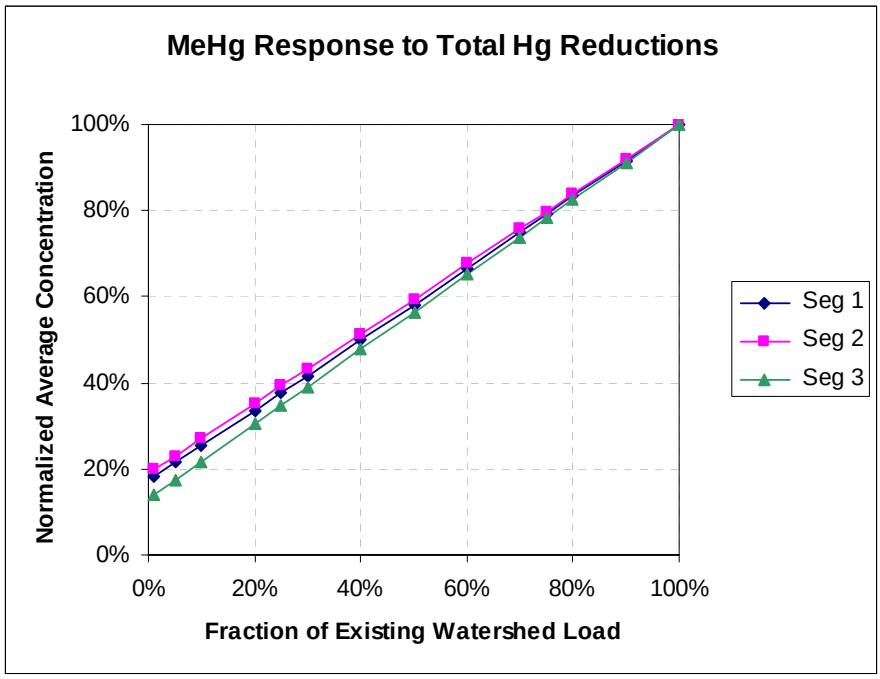


Figure 36. Response of Average MeHg Concentrations in the Water Column of Alamo Lake to Reductions in Watershed Load

A complete removal of watershed loads is predicted to result in MeHg concentrations in the lake that range from 14 to 20 percent of the simulated average concentration over the period of simulation due to the influence of atmospheric loads. As a result, for example, obtaining a 50 percent reduction in average exposure concentrations would require an approximately 56 percent reduction in watershed loads.

E. Derivation of Bioaccumulation Factors

Sufficient data on population dynamics, feeding preferences, and mercury concentrations in lower trophic levels are not available at this time to develop a mechanistic simulation of the bioaccumulation of mercury in Alamo Lake. However, simpler methods (such as regression models and bioaccumulation factors) can be used to predict approximate values of tissue mercury concentrations in various trophic levels.

For piscivorous fish at Trophic Level 4 (TL4) - including largemouth bass, the species of most concern in Alamo Lake – the tissue concentration typically increases with age and length. As a result, simple bioaccumulation factors (BAFs) that do not account for length/age effects are of limited use. Brumbaugh et al. (2001) summarized data from across the United States and developed the following equation for length-normalized concentration of mercury in largemouth bass as a function of MeHg concentration in water (R^2 = 50.75%):

$$Ln\left[Hg - fish/len\right](mg/kg/m) = 0.3999 \cdot Ln\left[MeHg - water\right](ng/L) + 1.3184$$

For Alamo Lake, the model simulated average MeHg concentration in surface water for 2002-2004 is 0.20 ng/L. Application of the Brumbaugh equation yields a value of 1.963 for Ln[Hg-fish/len] (mg/kg/m). The mean length of largemouth bass sampled from Alamo is 367.176 mm, and the predicted concentration at the mean length is 0.721 mg/kg. This agrees almost exactly with the median of the observed tissue concentration in largemouth bass of 0.725 mg/kg. (The mean of the data is also 0.725 mg/kg.)

Similar equations are not available for other trophic levels, but these are less affected by length-dependence. USEPA (1997a and 1997b; vol. 6 and vol.3, Appendix D) summarized information on mercury bioaccumulation factors, with a focus on TL3 and TL4 fish. These are the source for the majority of the BAFs used in the SERAFM risk assessment model (Knightes and Ambrose, 2005). A more detailed survey of BAFs was conducted in conjunction with the 2001 criterion document for methylmercury (USEPA, 2001, Appendix A). The BAFs present in that document are for total methylmercury in biota as a function of dissolved methylmercury in water. However, the majority of the data are summarized from information on total mercury with the assumptions that dissolved methylmercury is 61.3 percent of total methylmercury, methylmercury is 18 percent of the total body burden at TL 1, 44 percent at TL 2, and essentially 100 percent of the body burden at higher trophic levels.

For Alamo Lake, measurements in biota are for total mercury, requiring a correction at lower trophic levels. Further, model predictions of total methylmercury are expected to be more accurate than predictions of dissolved methylmercury. Therefore, BAFs for TL 2 (zooplankton and benthos) and TL 3 (forage fish) were converted to a basis in which total Hg in biota is

predicted from total MeHg in water, using the median dissolved MeHg BAF value as a starting point. USEPA (2001) reports considerable difference between BAFs for lentic and lotic systems for TL 3, but not for lower trophic levels. Therefore, for TL 3 the lentic (lake) value is used in the calculation.

For TL 2, concentrations in benthos are expected to be higher than those in zooplankton due to direct uptake from sediment. Therefore, the BAF for benthos is increased relative to the general TL 2 BAF by the factor of 1.54, as is done in Knightes and Ambrose (2005).

For TL 1 plankton, the uptake process differs from that in high trophic levels, and a majority of the mercury present in TL 1 biota is typically present in non-methylated forms. In addition, plankton BAFs are generally calculated on a dry weight basis. Available data are primarily for total mercury, and the values cited in USEPA (2001) are in many cases calculated based on a translator assumption that dissolved MeHg is 3.2% of total Hg in the water column. It therefore makes sense to re-express the BAF (or bioconcentration factor, BCF) given in USEPA (2001) on a total mercury basis (dry weight).

In Alamo Lake, the calibrated model results for 2002-2004 yield average surface water exposure concentrations of 1.61 ng/L total Hg and 0.20 ng/L MeHg. The median BAF values and resulting predicted tissue concentrations resulting from a water column MeHg concentration of 20 ng/L are shown in Table 6 for Trophic Levels 1 through 3. The table also shows results obtained from limited sampling of plankton (TL 1) and benthos (TL 2) by ADEQ in September 2004.

Table 6. MeHg BAFs and Predicted Tissue Concentrations for Lower Trophic Level Biota in Alamo Lake

Trophic Level	Median BAF ([mg/kg]/[ng/L)]	Predicted Total Hg Concentration (mg/kg)	Observed Total Hg Concentration (mg/kg)
TL 1: Phytoplankton	$5.87 \cdot 10^3$ (total Hg)	0.00944 (dry weight)	0.0054 (dry weight)
TL 1: Zooplankton	$1.67 \cdot 10^5$ (total MeHg)	0.0334 (wet weight)	NA
TL 2: Benthos	$2.5 \cdot 10^5$ (total MeHg)	0.0515 (wet weight)	0.0525 (wet weight)
TL 3: Forage Fish	$6.84 \cdot 10^5$ (total MeHg)	0.137 (wet weight)	NA

The limited observed data are generally consistent with the estimates of tissue mercury concentrations obtained from BAFs in Table 5. Further, the ratio of the mean TL 4 concentration (0.725) to the estimated TL 3 concentration of 0.137 is 5.3, consistent with the median predator-prey factor of 5 reported by USEPA (1997b). Although reported BAFs/BCFs for mercury are highly variable and subject to uncertainty due to the effects of age and influences of other

environmental factors such as dissolved organic carbon concentration, this analysis does suggest that conditions observed in Alamo Lake are consistent with those in other lakes in which the mercury tissue concentration in TL 4 sport fish is ultimately driven by MeHg concentration in surface water.

VI. MODELING CONCLUSIONS

A. Watershed and Aerial Loading

- Watershed loading of total mercury is tied to suspended sediment loading delivered in episodic runoff events.

- Modeling a total reduction in watershed mercury loads predicts a residual atmospheric mercury load of approximately 15 – 20 percent.

B. Lake Loading

- The calibrated water quality model is in general agreement with available data from Alamo Lake.

- Inputs of mercury from the watershed is episodic and a significant proportion is sequestered and buried in the deep sediments.

- The conditions following influx of a major runoff event are ripe for mercury methylation, due to the presence of dissolved carbon, a drop in pH, and sulfur-reducing bacteria under reducing conditions.

- Modeling changes in inflow/outflow to/from Alamo Lake results in relatively minor changes MeHg concentrations; in the near-dam surface segment they decrease by about 9% on average, but are not always lower, particularly after large inflow events (Figure 37). MeHg in the upstream segment decreases by about 3% on average, while the concentration in the bottom water increases by about 3%. The analysis is approximate without a high-resolution hydrodynamic model that can evaluate the effects of changing discharge location on lake stratification patterns.

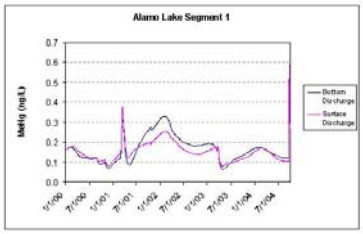


Figure 37. Modeled changes to inflow/outflow

- Exposure of fish to methyl-mercury occurs largely within the water column; therefore, the most relevant target for evaluating load reductions is the average MeHg concentration in lake water over time

VII. TMDL and ALLOCATIONS

A. TMDL Calculation

A TMDL is the total amount of a pollutant that can be assimilated by the receiving water while still achieving water quality standards. TMDLs can be expressed in terms of mass per time or by other appropriate measures. TMDLs are comprised of the sum of individual wasteload allocations (WLAs) for point sources, load allocations (LAs) for nonpoint sources, and natural background levels. In addition, the TMDL must include a margin of safety (MOS), either implicitly or explicitly, that accounts for the uncertainty in the relationship between pollutant loads and the quality of the receiving water body. Conceptually, this definition is denoted by the equation:

$$\text{TMDL} = \sum \text{WLAs} + \sum \text{LAs} + \text{MOS} \qquad (13)$$

B. Numeric Targets

TMDLs are developed to meet applicable water quality standards. These may include numeric water quality standards, narrative standards for the support of designated uses, and other associated indicators of support of beneficial uses. A numeric target identifies the specific goals or endpoints for the TMDL that equate to attainment of the water quality standard. The numeric target may be equivalent to a numeric water quality standard (where one exists), or it may represent a quantitative interpretation of a narrative standard. This section reviews the applicable water quality standards and identifies an appropriate numeric indicator and associated numeric target level for the calculation of the Alamo Lake mercury TMDL.

Arizona has adopted water quality standards for mercury that apply to a number of the designated uses specified for Alamo Lake (Arizona Administrative Code, R-18-11, Appendix A). The standards for the protection of aquatic life and wildlife are expressed in terms of the dissolved, rather than total recoverable mercury concentration, as recommended by EPA (FR 60(86): 22229-22237, May 4, 1995).

Numeric water quality criteria for mercury applicable to human and agricultural uses are expressed in terms of total recoverable mercury. These water quality standards are summarized in Table 7. None of the mercury criteria are hardness-dependent.

Table 7. Arizona Numeric Water Quality Standards for Mercury

Designated Use	Criterion (µg/l)	Chemical Form
Aquatic and Wildlife (Warmwater) (A&Ww)	acute: 2.4 chronic: 0.01	dissolved dissolved
Full Body Contact (FBC)	42.0	total recoverable
Fish Consumption (FC)	0.6*	total recoverable
Agricultural Irrigation (AgI)	No numeric criterion	
Agricultural Livestock Watering (AgL)	10.0	total recoverable
Fish Tissue	0.3*(mg/kg)	Methyl-mercury

* Fish tissue standard is proposed to replace the FC standard in the FY'06 Triennial Review

The most stringent applicable current standard for total recoverable mercury is 0.6 µg/L (FC). The dissolved standards for protection of aquatic life and wildlife include both an acute standard, applicable to short-term exposures, with compliance determined from grab samples, and a chronic standard, applicable to longer-term exposures, with compliance determined from the arithmetic mean of consecutive daily samples collected over a 4-day period (Arizona Administrative Code, R-18-11-120.C). Therefore, the most stringent water column standard is 0.01 ug/L or 10 ng/L. Since Alamo Lake has not exceeded any mercury standard other than fish tissue, additional more stringent water column targets must be established to ensure attainment of appropriate fish tissue targets.

C. Narrative Standards

The state narrative language for toxics is expressed in part as follows (Arizona Administrative Code, R-18-11-108(A)):

A surface water shall be free from pollutants in amounts or combinations that:

1. Settle to form bottom deposits that inhibit or prohibit the habitation, growth, or propagation of aquatic life or that impair recreational uses; …
5. Are toxic to humans, animals, plants, or other organisms; …

These two clauses may be taken to generally prohibit loading of mercury to the lake in amounts that result in fish tissue contamination levels sufficient to impair recreational uses or present a risk to human health.

D. Fish Consumption Advisory as Impairment

To protect human health against long-term chronic effects of fish consumption, ADEQ has historically used an advisory listing criterion for fish tissue concentration of 0.6 mg/kg total Hg

in fillets. In the current Triennial Review, ADEQ is proposing to adopt the EPA target of 0.3 mg/kg MeHg and will apply this latter criterion to the Alamo TMDL.

As discussed, Largemouth Bass in Alamo Lake show no clear relationship between tissue concentration and length or weight (in the size classes that have been sampled); thus the TMDL will evaluate against the average concentration in all largemouth bass samples rather than targeting a specific length or weight.

E. TMDL Target

TMDL reduction targets for Alamo Lake must be designed to achieve acceptable fish tissue concentrations, as well as water quality criteria. However, water quality observations of mercury in Alamo Lake have not exceeded the ambient criteria. The maximum observed concentration in lake water is 6.9 ng/L total Hg., which is less than the dissolved chronic criterion. Therefore, the fish tissue concentration criterion is the most restrictive for Alamo Lake. The applicable numeric target for TMDL development is a fish tissue concentration of 0.3 mg/kg MeHg. The species of primary interest for determining targets is largemouth bass, as this is a top predator species, is the primary sport fish in the lake, tends to have high concentrations as a piscivore, and has been frequently sampled. In addition to the TL-4 (Bass) target, this TMDL establishes an associated target for protection of prey fish (TL-3) and corresponding wildlife that may be impacted through consumption of these fish.

F. Margin of Safety

As a chronic health target, it is appropriate to evaluate attainment of the fish tissue criterion against average concentrations in fish of consumable size – plus a Margin of Safety (MOS). A small MOS is already built in because the revised fish consumption criterion is based on MeHg, whereas ADEQ evaluates attainment against observed total Hg in fish. Typically, 90 percent or more of the Hg burden in fish tissue is present as MeHg. In addition, the risk calculation on which the human health criterion is based uses conservative assumptions that provide a MOS.
An appropriate method to establish reduction targets is to calculate an upper confidence limit (UCL) on the observed mean, then evaluate the percentage reduction needed to meet the target level of 0.3 mg/kg. The UCL may be estimated as:

$$UCL_{1-\alpha} = \bar{x} + t_{1-\alpha,\, n-1} \, s/\sqrt{n} \qquad (14)$$

and the needed reduction is $1 - 0.3/UCL_{1-\alpha}$.

The observed fish tissue data from 1996 are similar to those from 2001-2002 and can be combined. The combined largemouth bass data have a mean of 0.74 mg/kg total Hg and a standard deviation of 0.20 on a sample size of 34. The choice of a confidence level for the analysis is part of the Margin of Safety. The reduction target depends on the confidence limit chosen. Some examples are provided in Table 8.

Table 8. Example Confidence Levels and Required Load Reductions to Meet the Numeric Target

Confidence Level on Mean	t score	Upper Confidence Limit (mg/kg)	Reduction Required
50%	0	0.744	59.7%
66%	0.416142	0.758	60.4%
80%	0.852649	0.773	61.2%
95%	1.69236	0.802	62.6%
99%	2.444795	0.828	63.8%

Note that increasing the confidence limit on the mean incurs only a small "cost" in terms of greater reductions because the standard error on the mean is small. A 95 percent confidence level on the mean was assumed for application in TMDL calculation. This assumption, in combination with the other conservative assumptions described herein, results in a Margin of Safety that is considered implicit for TMDL calculation. Therefore, an explicit numeric value for the Margin of Safety was not quantified.

G. Critical Condition

The critical condition for TMDL calculation was determined to be an average of three historical years representative of different hydrologic regimes when sources and methods of transport of mercury through the watershed vary. Since the cumulative, long-term bioaccumulation is the concern, it is appropriate to evaluate over the range of typical annual regimes, rather than worst case conditions. Assessment of hydrologic periods was based on analyses of USGS flow records for Big Sandy River (USGS 09424450), Burro Creek (USGS 09424447), and Santa Maria River (USGS 09424900). Selected periods were identified for Big Sandy River, Burro Creek, and Santa Maria River as follows:

- Year 1993 was observed as an El Niño associated with a very high annual average flow for all watersheds
- Year 1990 was observed to be a dry year for all watersheds.
- The flow pattern during years 1991 and 1992 was classified as normal for both Big Sandy and Santa Maria, while flow at Burro Creek was classified normal during the year 1992.

H. TMDL Allocations

Based on this modeling for this and other Arizona mercury TMDLs, it is reasonable to assume that fish tissue concentrations will decline approximately linearly with reductions in water

column MeHg concentrations. Thus, the reduction target in fish can be interpreted as a reduction target in water column MeHg concentration. This assumption has been corroborated through modeling.

As discussed, the TMDL should be based on reductions necessary to achieve the TL-4 fish tissue criterion of 0.3 mg/kg MeHg.. At the 95 percent confidence level, *a reduction of 62.6 percent in average water column concentration in the lake is needed* (concentrations 37.4 percent of current average). Based on interpolation of data shown previously in Figure 34, *the model predicts that watershed loads would need to be reduced to 22.71 percent of current loads (77.29 percent reduction)* to achieve this goal in Segment 2 of the lake.

I. Wasteload Allocations (WLAs)

No wasteload allocations (WLAs) were made for Alamo Lake since no NPDES permitted specific point sources were identified within the watershed.

J. Load Allocations (LAs)

As discussed above, a 77.29 percent load reduction in watershed load is required to meet numeric targets and hence the TMDL. The total reduction could be obtained in many ways, however given the current state of information load allocations (LAs) were developed that assign equal reductions to each of the major tributaries. To assess the required watershed load reduction to meet the TMDL, the average load of the critical years identified in Section G above was used. Table 9 lists the required LAs to meet the TMDL. Without WLAs specified, the LAs designated for each watershed include the entire TMDL.

Table 9. Watershed Total Mercury Load Allocations

Watershed	Existing Load (g/year)	Percent Reduction	TMDL (g/year)	LA (g/year)
Santa Maria River	11,212	77.29%	2,546	2,546
Burro Creek	18,870	77.29%	4,285	4,285
Big Sandy River	17,250	77.29%	3,917	3,917

Alamo Lake Hg TMDL = WLA(0) + LA(Santa Maria) + LA(Burro Creek) + LA(Big Sandy River) + MOS

Translating into a daily load, the Alamo Lake mercury TMDL is as follows:

TMDL = 0 (WLA)+ 7.0 g/day (LA for Santa Maria River) + 11.7 g/day (LA for Burro Creek) + 10.7 g/day (LA for Big Sandy) + Implicit MOS

This TMDL will meet the existing water quality standards for Aquatic and Wildlife protection in Alamo Lake: acute standard of 2.4 ug/L (2,400 ng/L) dissolved mercury and chronic standard of 0.01 ug/L (10 ng/L), as well as the existing Fish Consumption standard of 0.6 ug/L (600 ng/L) total mercury. In addition to existing water quality standards, through bioconcentration calculations, this TMDL establishes three additional targets: 1) 0.11 mg/kg MeHg in TL-3 fish, 2) 1.24 ng/L total Hg in water, and 3) 0.15 ng/L MeHg in water. These targets have been established based on the relationship of linearity between increasing methyl-mercury in water and impairments to the food chain. In summary, while in support of existing mercury standards, this TMDL also establishes new targets for the following:

1) **Protection of human health (fish consumption) – two numeric targets [0.3 mg/kg MeHg for TL-4 fish, and 0.11 mg/kg MeHg for TL-3 fish]**
2) **Protection of aquatic life – two intermediate control targets [1.24 ng/L T-Hg and 0.15 ng/L MeHg - in water]**
3) **of wildlife – Protection four numeric targets [[0.3 mg/kg MeHg for TL-4 fish, and 0.11 mg/kg MeHg for TL-3 fish] and [1.24 ng/L T-Hg and 0.15 ng/L MeHg - in water]**

VIII. PRIORITIES for TMDL IMPLEMENTATION

1) Load allocations were quantified based on total loads predicted for each watershed, and did not consider individual sources within each watershed that contribute to those loads. Modeling analysis was performed to provide assessment of sources that can be used for guidance in TMDL implementation. Diistribution of LAs among watershed sources (e.g., mines, watershed runoff) are based on results of the analysis reported in TT's Modeling Report. However, further study is recommended to provide additional information for assessment of mining loads and background loads from runoff, atmospheric deposition, etc.
2) Future monitoring Alamo Lake and it's watershed must include consideration of loading targets, source identification, source reduction, air deposition, and in-lake tracking of water column and fish tissue targets.
3) Lake management to control cycling of mercury can have additional impacts on the overall assimilative capacity of the lake, and hence require external load reductions to meet the TMDL. Assessment of the benefits received from alternative

management scenarios for the lake requires further study. The WASP model developed for the current study may be used to provide this assessment. Specifically recommended: additional sediment cores, flow-through modeling using a dynamic model, evaluation of maintaining consistent water level and dam release options including pump-back system to break stratification.

4) Additional considerations: monitor Bill Williams River water quality, fish tissue, and sediment; if warranted, monitor Lower Lake Havasu and CAP to determine mercury impacts and imparment

IX. PROPOSED ACTIONS FOR IMPLEMENTATION

- ADEQ will work with USCOE, USFWS, and AGFD to integrate continued monitoring and modeling objectives
- ADEQ will work with AGFD and ASPS to ensure Fish Advisory posting is prominent and updated as needed
- ADEQ will work with BLM to schedule and implement an intensive survey of abandoned mines in the Alamo Lake watershed
- ADEQ will develop and implement a plan for conducting air deposition monitoring
- ADEQ will work with stakeholders to identify mercury sources and to assist in funding remediation efforts

REFERENCES

Ambrose, R., I. Tsiros, and T. Wool. 2003. Predicting Envinronmental Concentrations of Airborne Pollutants in Terrestrial Receptors: The Case of Mercury. Proceedings of the 8th International Conference on Environmental Science and Technology, Lemnos Island, Greece.

Burke, J., M. Hoyer, G. Keeler, and T. Scherbatskoy. 1995. Wet deposition of mercury and ambient mercury concentrations at a site in the Lake Champlain basin. Water, Air, and Soil Pollution 80:353-362.

Byun, D.W. and J.K.S. Ching, eds. 1999. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System. EPA/600/R-99/030. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

EPRI. 2000. An Assessment of Mercury Emissions from U.S. Coal-Fired Power Plants. Report TR-1000608. Electric Power Research Institute, Palo Alto, CA.

Glass G., J. Sorensen, K. Schmidt, G. Rapp, D. Yap, and D. Fraser. 1991. Mercury deposition and sources for the Upper Great Lakes region. Water, Air, and Soil Pollution, 56: 235-249.

Gremillion, P.T. and J.L. Toney. 2005. Metals Deposition in Northern Arizona Reservoirs, Draft Final Report. Submitted to Arizona Department of Environmental Quality by Northern Arizona University, Flagstaff, AZ. March 24, 2005.

Gustavsson, N., B. Bølviken, D.B. Smith, and R.C. Severson. 2001. Geochemical landscapes of the conterminous United States – New map presentations for 22 elements. USGS Professional Paper 1648. USGS. Denver, Co.: US Geological Survey.

Haith, D. A., R. Mandel, and R. S. Wu. 1992. Generalized Watershed Loading Functions Version 2.0 User's Manual, Cornell University, Ithaca, New York.

Keeler, G.J,, M.E. Hoyer, and C.H. Lamborg. 1994. Measurements of atmospheric mercury in the Great Lakes Basin. In Mercury Pollution: Integration and Synthesis, ed. C.J. Watras and J.W. Huckabee, pp. 231-241, Lewis Publishers, Chelsea, MI.

Nater E. and D. Grigal. 1992. Regional trends in mercury distribution across the Great Lakes states, north central USA. Nature 358: 139-141.

Popp, C.J., D.K. Brandvold, K. Kirk, L.A. Brandvold, V. McLemore, S. Hansen, R. Radtke, and P. Kyle. 1996. Reconnaissance and Investigation of Trace Metal Sources, Sinks, and Transport in the Upper Pecos River Basin, New Mexico. Cooperative Agreement No. 3-FC-40-13830. New Mexico Institute of Mining and Technology, U.S. Department of the Interior and U.S. Bureau of Reclamation.

Seigneur, C., K. Vijayraghavan, K. Lohman, P. Karamchandani, and C. Scott. 2004. Global source attribution for mercury deposition in the United States. Environmental Science and Technology, 38: 555-569.

Soil Conservation Service. 1986. Urban Hydrology for Small Watersheds, U.S. Dept. of Agriculture, Soil Conservation Service, Engineering Division, Technical Release 55

Tetra Tech. 2000. Watershed Characterization System User's Guide, Version 1.1. Prepared for U.S. Environmental Protection Agency, Region 4. Tetra Tech, Inc., Fairfax, VA.

Tetra Tech. 2001. Technical Support for Developing a Total Maximum Daily Load for Mercury in McPhee and Narraguinnep Reservoirs, Colorado. Report to USEPA, Region 8. Tetra Tech, Inc., Research Triangle Park, NC.

University of Arizona. 2005. Arizona Plant Climatic Zones. Cooperative Extension, College of Agriculture and Life Sciences, The University of Arizona. Available at http://ag.arizona.edu/pubs/garden/az1169/ Accessed 20 January 2005.

USACE. 1994. Proposed Water Management Plan for Alamo Lake and the Bill Williams River, Final Report and Recommendations of the Bill Williams River Corridor Technical Committee, Volume 1, November 1994.

USACE. 1998. Technical Considerations for Alamo Lake Operation. US Army Corps of Engineers, Hydrologic Engineering Center, April 1998.

USEPA. 1997. Mercury Study Report to Congress. Office of Air Quality Planning & Standards and Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC.

USEPA. 2001. Frequently Asked Questions about Atmospheric Deposition. EPA-453-R-01-009. Office of Wetlands, Oceans, and Watersheds, U.S. Environmental Protection Agency, Washington, DC.

USEPA. 2003. Total Maximum Load Development for Total Mercury in the St. Mary's Watershed. USEPA Region 4, Atlanta, GA.

USEPA. 2004. Index of /waterscience/ftp/basins/. Washington D.C.: US Environmental Protection Agency. Available at: http://www.epa.gov/ waterscience/ftp/basins/ Accessed 20 September 2004.

USGS. 2004. The National Map Seamless Data Distribution System Viewer. Reston, Va.: US Geological Survey. Available at: http://seamless.usgs.gov/viewer.htm. Accessed 22 September 2004.

Watermark Numerical Computing. 2002. PEST, Model-Independent Parameter Estimation. Watermark Numerical Computing.

Watras, C.J., N.S. Bloom, R.J.M. Hudson, S. Gherini, R. Munson, S.A. Claas, K.A. Morrison, J. Hurley, J.G. Wiener, W.F. Fitzgerald, R. Mason, G. Vandal, D. Powell, R. Rada, L. Rislov, M. Winfrey, J. Elder, D. Krabbenhoft, A.W. Andren, C. Babiarz, D.B. Porcella, and J.W. Huckabee. 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes. In Mercury Pollution: Integration and Synthesis, ed. C.J. Watras and J.W. Huckabee. Lewis Publishers, Chelsea, MI.

Wischmeier, W. H. and D. D. Smith. 1978. Predicting Rainfall Erosion Losses – A Guide to Conservation Planning. USDA Agriculture Handbook No. 537, U.S. Government Printing Office, Washington, D.C.

Wu, J.I. and E.J. Mahaffey. 1977. Mercury in Soils Geochemistry on Massive Sulfide Deposits in Arizona.

References

Brumbaugh, W.G., D.P. Krabbenhoft, D.R. Helsel, J.G. Wiener, and K.R. Echols. 2001. A National Pilot Study of Mercury Contamination of Aquatic Ecosystems along Multiple Gradients: Bioaccumulation in Fish. Biological Sciences Report USGS/BRD/BSR-2001-0009. U.S. Geological Survey, Reston, VA.

Knightes, C.D. and R.B. Ambrose, Jr. 2005. Development of a Methodology to Assist Ecological Risk Assessors in Evaluating Wildlife Exposure Risk Associated with Mercury-Contaminated Sediment in Lake and River Systems, Par 1: Essential Data Requirements, Part 2: Microsoft Excel Spreadsheet Model (SERAFM). Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA.

USEPA. 1997a. Mercury Study Report to Congress, Volume III: Fate and Transport of Mercury in the Environment. EPA-452/R-97-005. Office of Air Quality Planning and Standards an Office of Research and Development, U.S. Mercury Study Report to Congress, Volume III: Fate and Transport of Mercury in the Environment. EPA-452/R-97-005. Office of Air Quality Planning and Standards an Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC.

USEPA. 1997b. Mercury Study Report to Congress, Volume VI: An Ecological Assessment for Anthropogenic Mercury Emissions in the United States. EPA-452/R-97-008. Office of Air Quality Planning and Standards an Office of Research and Development, U.S. Mercury Study Report to Congress, Volume III: Fate and Transport of Mercury in the Environment. EPA-452/R-97-005. Office of Air Quality Planning and Standards an Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC.

USEPA. 2001. Water Quality Criterion for the Protection of Human Health: Methylmercury, Final. EPA-823-R-01-001. Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency, Washington, DC.