ADEQ
Arizona Department of Environmental Quality

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Alamo Lake TMDL
for
Mercury in Fish Tissue

Bill Williams River Watershed
Mohave, Yavapai, & Yuma Counties

Arizona Department of Environmental Quality

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ACKNOWLEDGEMENTS

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List of Acronyms

303(d)	CWA Section dealing with Impaired Waters
305(b)	CWA Section dealing with Water Quality Assessment
A&W	Aquatic and Wildlife Designation (warm, cold, ephemeral, edw)
A.A.C.	Arizona Administrative Code
A.R.S.	Arizona Revised Statutes
ACOE	U.S. Army Corps of Engineers
ADEQ	Arizona Department of Environmental Quality
AGFD	Arizona Game and Fish Department
AgL	Agriculture Livestock Watering Designated Use
AZMET	Arizona Meteorological Network
AZPDES	Arizona Pollutant Discharge Elimination System
BAF	Biological Accumulation Factor
BASINS	Better Assessment Science Integrating Point & Nonpoint Sources (model)
BCF	Bioconcentration Factor
USBLM	U.S. Bureau of Land Management
C_{avg}	Average Concentration
cfs	Cubic Feet per Second
CMAQ	Community Multi-scale Air Quality
CWA	Clean Water Act
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EPA	U.S. Environmental Protection Agency
FBC	Full Body Contact Designation
USFWS	U.S. Fish and Wildlife Service
GIS	Geographic Information System
Hg	Mercury
Hg(II)	Ionic Mercury
Hg-P	Particulate Mercury
MeHg	Methyl-mercury
Hg^0	Elemental Mercury
HgS	Mercuric Sulfide
HUC	Hydrologic Unit Code
LA	Load Allocation
MDN	Mercury Deposition Network
mg/kg	Milligrams per Kilogram (parts per million)
mg/L	Milligrams per Liter (parts per million)
MILS	Mineral Industry Location System
MOS	Margin of Safety
MSGP	Multi-sector Stormwater General Permit
mv	Millivolts
NB	Natural Background
NEMO	Nonpoint Education for Municipal Officials
ng/g	Nanogram per Gram (parts per billion)

ng/L	Nanogram per Liter (parts per trillion)
NLCD	National Land Cover Data
NOAA	National Oceanic and Atmospheric Administration
NRCS	Natural Resource Conservation Service
ORP	Oxidation-reduction Potential
POR	Period of Record
R^2	Measure of Correlation or Predictability between Variables
RELMAP	Regional Lagrangian Model of Air Pollution
RF	Reduction Factor
RGM	Reactive Gaseous Mercury
SSC	Suspended Sediment Concentration
STATSGO	State Soil Geographic Database
TL-1,2,3,4	Trophic Levels from Phytoplankton (TL-1) to Piscivores (TL-4)
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
*u*g/g	Micrograms per Gram (parts per million)
*u*g/L	Micrograms per Liter (parts per billion)
USDA	U.S. Department of Agriculture
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
USLE	Universal Soil Loss Equation
WASP5	Water Quality Analysis Simulation Program
WCS	Watershed Characterization System
WLA	Wasteload Allocation
WQA	Water Quality Assessment

I.   EXECUTIVE SUMMARY

Alamo Lake is a flood-control reservoir located at the intersection of Mohave, Yavapai, and La Paz counties in western Arizona. Based on a mean value of 0.74 mg/kg total mercury in largemouth bass, as well as mercury levels in catfish and crappie greater than 0.3 mg/kg, the U.S. Environmental Protection Agency (EPA) listed Alamo Lake as impaired for mercury in fish tissue in the fall of 2002. The Arizona Department of Environmental Quality (ADEQ) and the Arizona Game and Fish Department (AGFD) issued a fish consumption advisory in the spring of 2003.   As a result of the 303(d) listing, this Total Maximum Daily Load (TMDL) was calculated using both empirical data and modeling of the lake and its watershed.

Lake data were collected by ADEQ and the U.S. Fish and Wildlife Service (USFWS) between 1990 and 2005 and compiled by ADEQ. Tributary data were collected between 2003 and 2005 by ADEQ. Tetra Tech 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, Inc., and a receiving water model known as WASP5/TOXI5 (Ambrose, et. al., 1993). The U.S. Army Corps of Engineers (ACOE) 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 of the large size of the Alamo Lake watershed, ADEQ decided to establish mercury loading endpoints based on flow and water quality data at three U.S. Geological Survey (USGS) gauges: Big Sandy River near Wikieup, Burro Creek at Highway 93, and Santa Maria River near Bagdad. Several additional sites were also sampled within each sub-watershed in an attempt to isolate possible impacts from historic mining.

To characterize background geologic mercury, 47 soil samples were collected from several locations scattered throughout the three main sub-watersheds as well as the portion of the Bill Williams watershed that drains to the lake. Samples were collected from a minimum of 10 inches below the surface, in order to reach the B or C soil horizon and avoid organic topsoils. Results showed that mercury is naturally present in the watershed in various soil associations, but highest in volcanic rocks and their soil derivatives, as well as in geothermal springs. Geologic sources are significant, particularly at mining sites with exposed waste rock, tailings, or adits. However, modeling shows global aerial sources, particularly from dry deposition, may be contributing up to 87 percent of the total load in some parts of the watershed.

The form of mercury that is toxic to humans and higher trophic level wildlife is the organic form, methyl-mercury. Methylation occurs in the presence of sulfur-reducing micro-organisms where oxygen is lacking. Using the trophic level-weighted geometric means in fish tissue, ADEQ has calculated a reduction of 54 percent in lake water column methyl-mercury is needed to achieve the fish tissue standard of 0.3 mg/kg. Based on this in-lake target, total mercury load from the watershed must be reduced by 61 percent. Background soil mercury and background air deposition taken together, comprise 16 percent to 20 percent of the total mercury load (Tetra Tech, Inc., 2008).

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.   Most of the mercury from the watershed, regardless of initial source, is delivered to Alamo Lake in association with suspended sediment.

Therefore, efforts to mitigate these inputs are likely to require location of specific sources that can be remediated, such as old mines, or areas where sediment runoff can be contained or reduced.   For the lake, maintenance of water elevation, alternative discharge elevation(s), aeration, and pump-back may break stratification and reduce mercury methylation.

This TMDL establishes point and non-point source allocations for the average-year (avg-yr) flow condition and wet-year (wet-yr) flow condition using load duration curves developed by Tetra Tech, Inc., 2006.   WLA loads reflect a combination of permitted concentrations converted to loads under AZPDES# AZ0022268, and concentration-based storm water discharges under the Multi-sector General Permit (MSGP) #AZR05B252, #AZR05B254, and #AZR05B253 for Freeport-McMoRan Copper Mine.   The avg-yr allocations were based on data from 1992 to 2004. Wet-yr allocations were further refined based on data from just the wet season, August to April (1992 to 2004) (Table E-1).   Table E-2 shows the combined TMDL for avg-year and wet-year loads to Alamo Lake.   The TMDL equation is:

$$\text{TMDL (in grams/day)} = \sum \text{Load Allocation (LA)} + \sum \text{Wasteload Allocation (WLA)} + \text{Natural Background (NB)} + \text{Margin of Safety (MOS)}$$

Table E-1. TMDL Equations by Sub-watershed Drainage and Flow Condition

Burro Creek Average Year	TMDL (g/day) = 3.87 (LA) + 0 (WLA)* + 1.05 (NB) + 0.55 (MOS) = 5.47 g/day
Burro Creek Wet Year	TMDL (g/day) = 32.07 (LA) + 2.65 g/day (WLA)* + 9.42 g/day (NB) + 4.90 g/day (MOS) = 49.04 g/day
Big Sandy River Average Year	TMDL (g/day) = 4.15 g/day (LA) + 0 g/day (WLA) + 1.13 g/day (NB) + 0.59 g/day (MOS) = 5.87 g/day
Big Sandy River Wet Year	TMDL (g/day) = 38.48 g/day (LA) + 0 g/day (WLA) + 10.44 g/day (NB) + 5.44 g/day (MOS) = 54.36 g/day
Santa Maria River Average Year	TMDL (g/day) =2.23 g/day (LA) + 0 g/day (WLA)* + 0.60 g/day (NB) + 0.31 g/day (MOS) = 3.14 g/day
Santa Maria River Wet Year	TMDL (g/day) = 10.76 g/day (LA) + 0 g/day (WLA)* + 2.92 g/day (NB) +1.52 g/day (MOS) = 15.20 g/day

* Includes concentration based WLA for Freeport-McMoRan MSGP discharges at 2.4 *u*g/L for each location

Table E-2. TMDL Equations for Alamo Lake by Flow Condition

Alamo Lake Average Year	TMDL= 10.05 (LA) + 0 (WLA)* + 2.73 (NB) + 1.42 (MOS) = 14.2 g/day
Alamo Lake Wet Year	TMDL = 81.32 (LA) + 2.65 (WLA)* + 22.77 (NB) + 11.86 (MOS) = 118.6 g/day

* Includes concentration based WLA for Freeport-McMoRan MSGP discharges at 2.4 *u*g/L for each location

II.   INTRODUCTION AND PROBLEM STATEMENT

A.   Significance of Clean Water Act (CWA) Section 305 (b) and 303 (d)

The CWA requires states to review and revise water quality standards for surface waters 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 and other organisms. 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, and Article 1).

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 CWA, and requires a report to Congress. Waters are classified as "attaining" their uses (full support), "attaining some but not all uses" (partial support), and "inconclusive" where there are insufficient data to assess, and "impaired" according to the number and nature of criteria violations. Based on the 305(b) Report, the state generates a list of impaired waters from a review of the impaired category (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 to be developed. This TMDL is based on a listing of impairment for mercury in fish tissue by EPA in the fall of 2002, and does not include additional listings for dissolved oxygen (DO), pH, and ammonia (in 2010 305b/303d Water Quality Assessment and Listing Report).

B.   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 nation's 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 TMDLs for the pollutants causing impairment with oversight from the EPA. 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. A TMDL allocates pollutant sources in order to meet water quality standards 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. The TMDL must also account for natural background sources, seasonal variation, and provide a margin of safety.

III.   WATERSHED CHARACTERIZATION

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, at 5,373 mi^2, the entire Bill Williams watershed constitutes about 7 percent of the state's land area but less than 0.2 percent of the state's population. The Alamo Lake drainage includes 4,700 mi^2 of the larger Bill Williams watershed.

Land ownership is a combination of Bureau of Land Management (BLM), U.S. Forest Service (USFS), State Trust, and private lands (Figure 1).
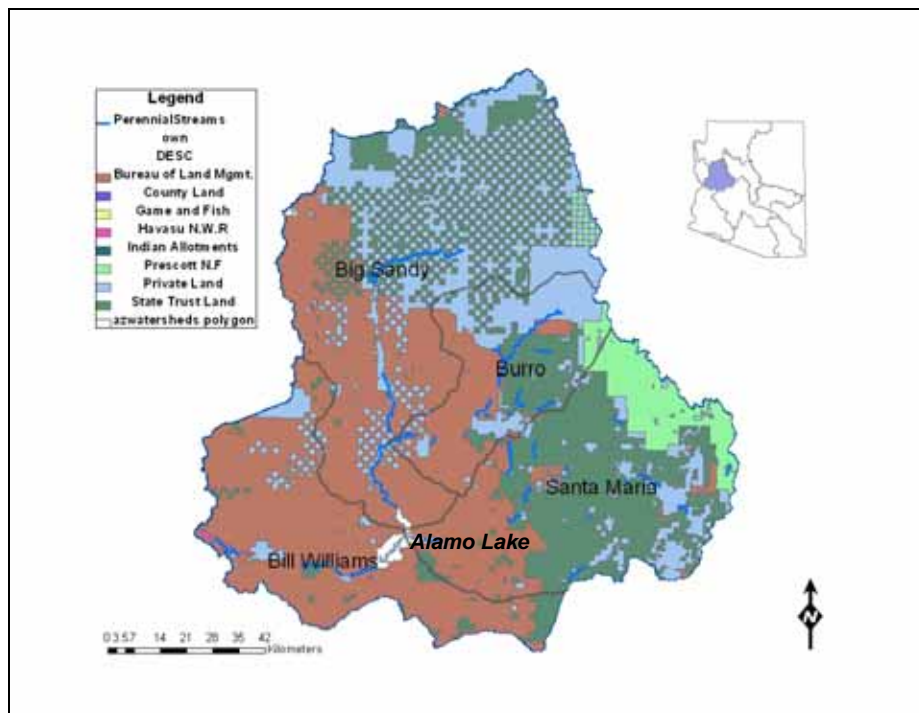
Figure 1. Land Ownership in the Bill Williams Watershed

B.   Lake Overview

Alamo Dam, which created Alamo Lake, was constructed between 1965 and 1968 by the 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 feet above mean sea level. In 1988, to protect threatened and endangered species, the USFWS requested that the lake not be drawn down below 1,100 ft which would more than double the recreational capacity to 2,737 surface acres. Subsequently, 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, and recommended that the lake level be managed 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 flood capacity of the lake is reported as 17,000 surface acres. The lake has become a very popular bass and crappie fishery and contributes to wildlife habitat in the lower Bill Williams River basin.

   C.   Climate

Precipitation data are collected at several stations within and around the Alamo Lake watershed by the National Climatic Data Center (NCDC) and the Arizona Meteorological Network (AZMET). The AZMET stations also provide solar radiation, precipitation, evaporation, temperature, wind, and relative humidity measurements. The locations of 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.
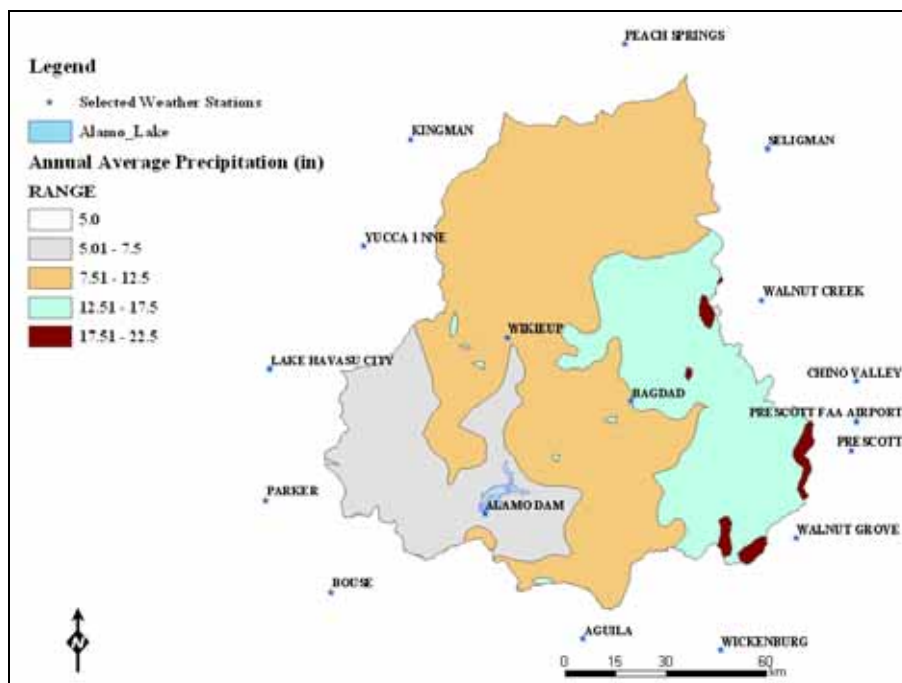
Figure 2. Weather Stations and Rainfall Distribution (Tetra Tech, Inc., 2006)

Monitoring for this TMDL covered both a dry-to-moderate period (fall 2002-spring 2004), and a relatively wet period (summer 2004-winter 2005), as can be seen from graphs of the annual rainfall at the Wikieup and Bagdad locations (Figure 3 and Figure 4, respectively).
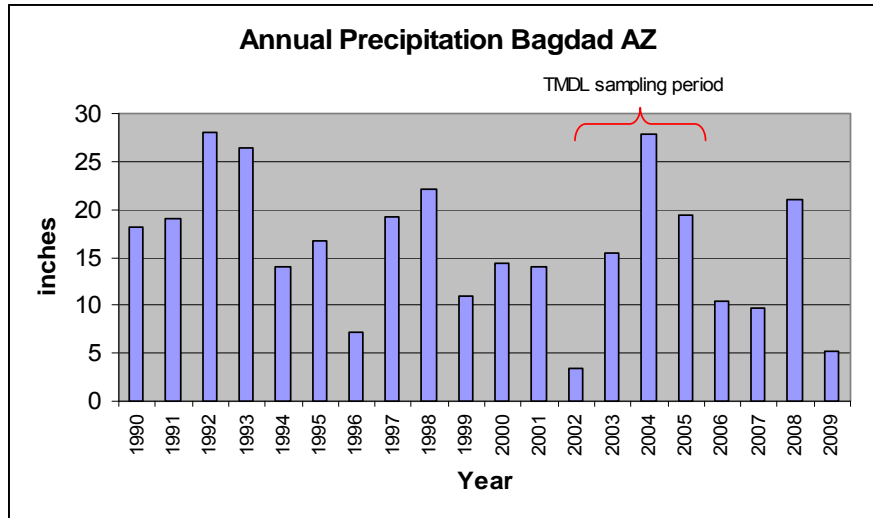
Figure 3. Annual Precipitation for Bagdad, AZ
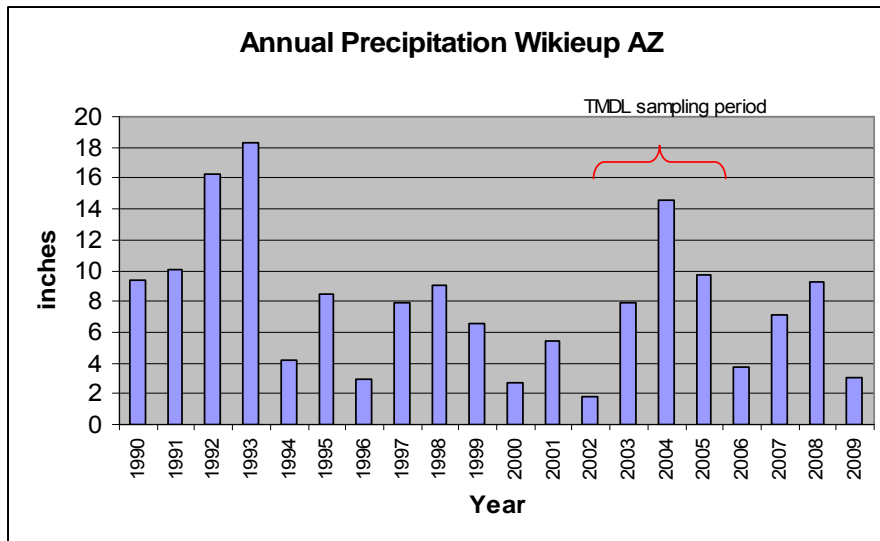
Figure 4. Annual Precipitation for Wikieup, AZ

D.   Hydrology

Approximately 85 percent of the hydrological system is ephemeral to intermittent. 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 overall does not contribute as much flow to the lake as the Big Sandy system. Figure 5 shows historic and current gauge locations; in 2004, ADEQ worked with the USGS to bring the lower Burro Creek gauge, #09424447, back into service The three gauges provided the flow data used to develop load duration curves for mercury and suspended sediment.
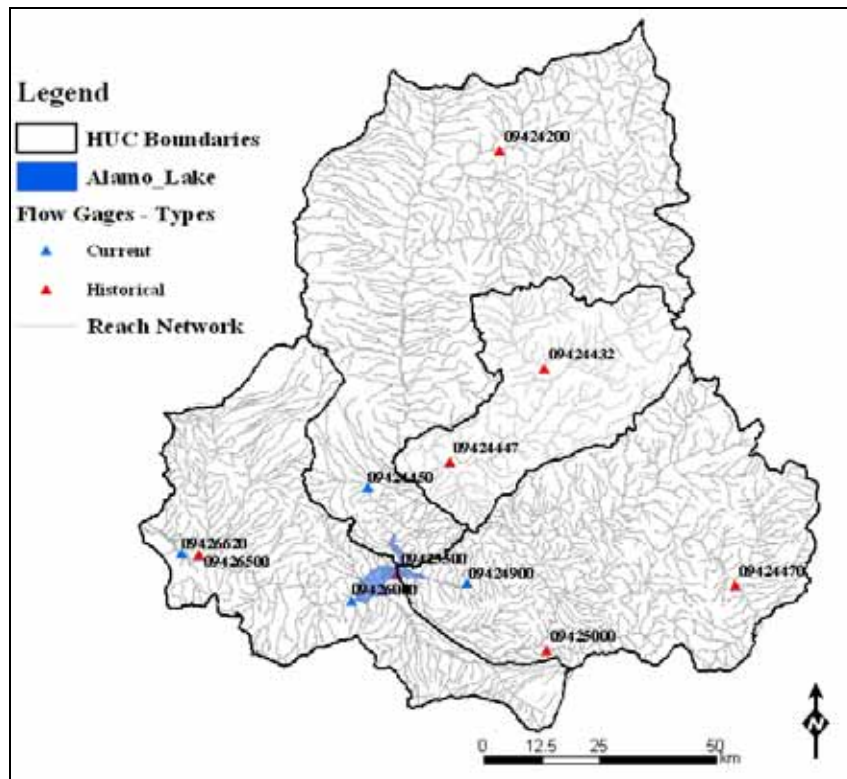
Figure 5. Hydrologic Network and Stream Gauges (Tetra Tech, Inc., 2006)

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 1.   There is a prevalence of high-mercury source rock, a massive sulfide deposit, and hard rock and placer mining in the Alamo Lake watershed.

Table 1. Percentage of Rock Type

Rock Type	Percentage (%)
Alluvium	14
*Basalt	18
*Granitic	31
Metamorphic	3
*Sedimentary	25
*Volcanic	10

* On a national basis, higher levels of mercury are associated with these types

Figure 6 represents the distribution of different rock types in the Alamo Lake watershed. There is a prevalence of high-mercury source rock, a massive sulfide deposit, and hard rock and placer mining in the Alamo Lake watershed.
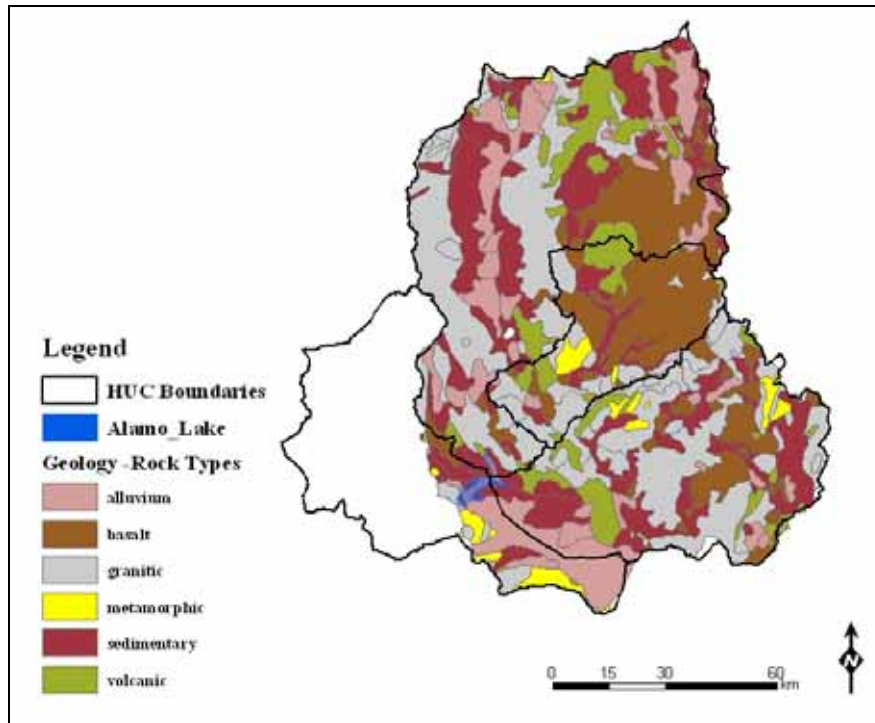
Figure 6. Distribution of Rock Types (Tetra Tech, Inc., 2006)

F.   Land Use

The National Land Cover Data (NLCD) for the Alamo Lake watershed was obtained from the USGS National Seamless Data Distribution System (USGS, 2004b). Table 2 summarizes the land cover data for the Alamo Lake watershed, which is dominated by shrubland (71 percent) and forest (21 percent).   Figure 7 shows the distribution of different land uses.

Table 2. Land Cover 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
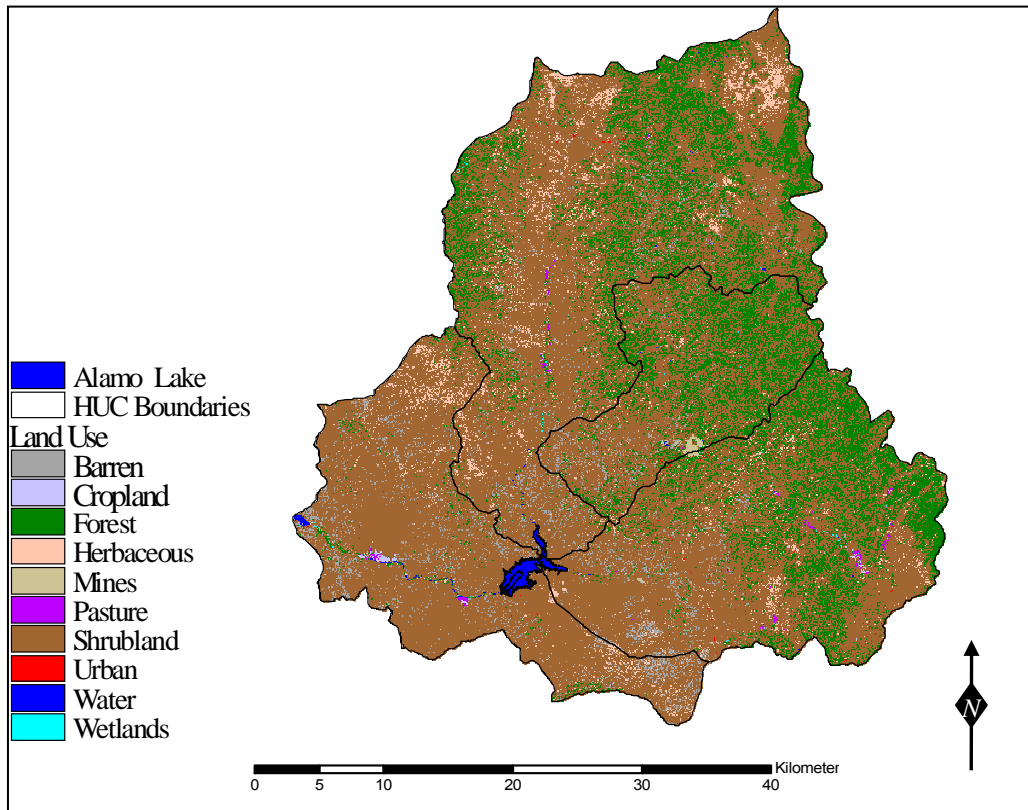
Figure 7. Land Cover Distribution for Alamo Lake Watershed (Tetra Tech, Inc., 2006)

IV. DATA REVIEW

A. Data Collection

Modeling of Alamo Lake included analysis of water quality data collected by USFWS between 1991 and 2004 and ADEQ between 2002 and 2005. Grab samples were collected at several lake locations and six to 12 surface water locations within each Hydrologic Unit Code (HUC) (Figure 8). Lake sampling included a complete suite of water and sediment chemistry (nutrients, general chemistry, total and 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 sites were chosen to capture relatively perennial areas, upstream/downstream of historic mining, and ease of access. Tributary sampling focused on collection of general chemistry, suspended sediment concentration, flow, organic carbon, sulfate, and mercury (total, dissolved, and methyl).
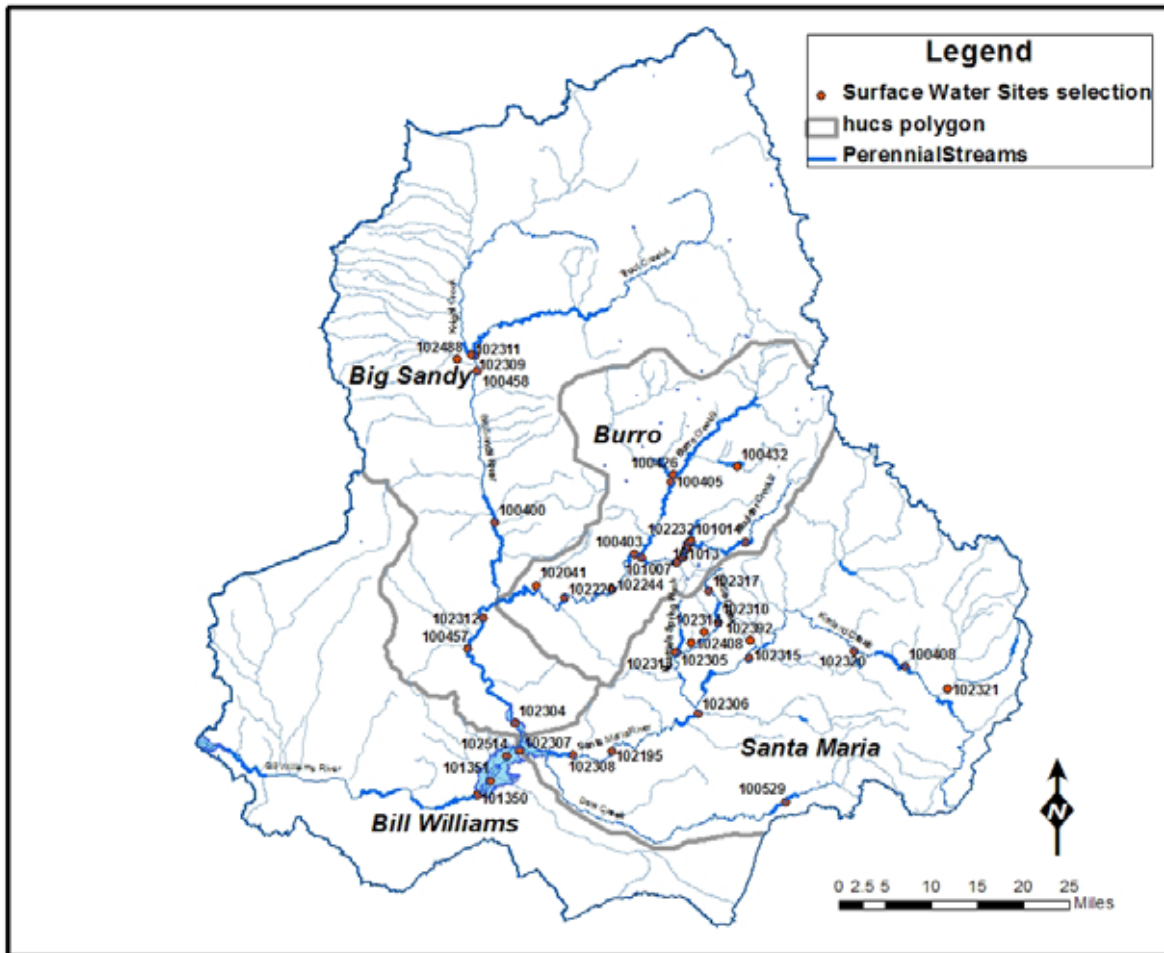
Figure 8. Sampling Locations by ADEQ Number (discussed in Section VI F.)

B.   Watershed Sampling

Because the Alamo Lake watershed is largely ephemeral to intermittent, most streams dry up between spring snowmelt and late summer monsoons, and may dry up again before winter storms. In general, mercury samples collected during snowmelt and in between storm events were not as high as those obtained during fall and winter storm events, in which flow and suspended sediment were also significantly higher.

Generally, results supported the hypothesis that mercury is elevated in soils and sediments within or downstream of historic mining and geological formations containing higher levels of mercury. Initial soil 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 exceptions were results which ranged from 0.22 - 0.46 mg/kg (220-460 ng/g) in soils and tailings within or downstream of historic mine sites, corresponding to the projected ranges from the USGS (2004b).

Starting in August 2004, the Alamo Lake watershed received several large precipitation events, producing some of the highest flows on record. Peak flow at the Big Sandy gage was 24,000 cfs. Data obtained from the primary tributary sites represent an adequate cross-section of flows for projection of sediment and mercury load duration curves.   Suspended sediment concentration was very high in several of these storm events, commonly in the range of 1,000 – 5,000 mg/L, reaching a peak of over 30,000 mg/L. Total mercury values associated with suspended sediment obtained during this wet period were commonly in the 100-ng/L range, with a maximum of 1,900 ng/L in one Santa Maria drainage location. The top 10 values for total mercury in water ranged from 220 ng/L to a high of 143,000 ng/L. Specific locations will be discussed in Section VI of this report.

C.   Groundwater and Spring Sampling

ADEQ also sampled a cross-section of geothermal springs and groundwater wells in the Bill Williams and Big Sandy groundwater basins. The 21 ultra-clean mercury samples submitted to Frontier Geosciences Laboratory had a total mercury mean concentration of 10.4 ng/L and a median of 0.95 ng/L, at a detection level of 0.15 ng/L. Results from geothermal springs showed mercury levels elevated four to five times (up to 66 ng/L) above the mean of well samples. These data are included in the TMDL discussion to demonstrate that discharges to surface waters from springs would not cause a violation of surface water quality standards, with the possible exception of geothermal springs. However, the cumulative effect of such discharges would be minimal because springs represent a very small amount of total flow. Consequently, this scenario was not modeled.

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 to 70 ng/g dry weight, while the highest total mercury water column value was 35 ng/L at 20 meters depth under stratified conditions. There were no exceedances of the dissolved mercury water column standard (10 ng/L) in the lake. The highest methyl-mercury concentration in water was 6 ng/L during the post-flood sample event in August 2005. In this sampling event, methyl-mercury increased with depth below the thermocline, which was approximately 6-7 m. The sharp decline in DO to less than 1 mg/L and oxidation reduction

potential (ORP) to -500 mv, illustrate strong reducing conditions ideal for mercury methylation (Figure 8 and Figure 9). Essentially, 66 percent of the lake volume contained 60-95 percent of the methyl-mercury present.
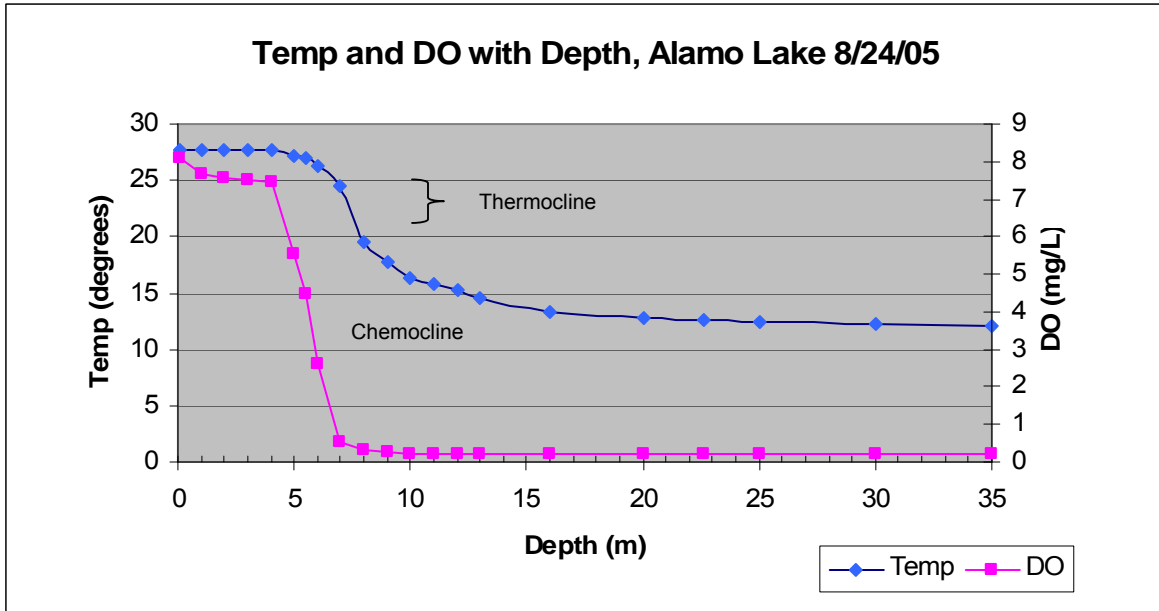
Figure 8. Anoxic Conditions in Alamo Lake below 7 Meters
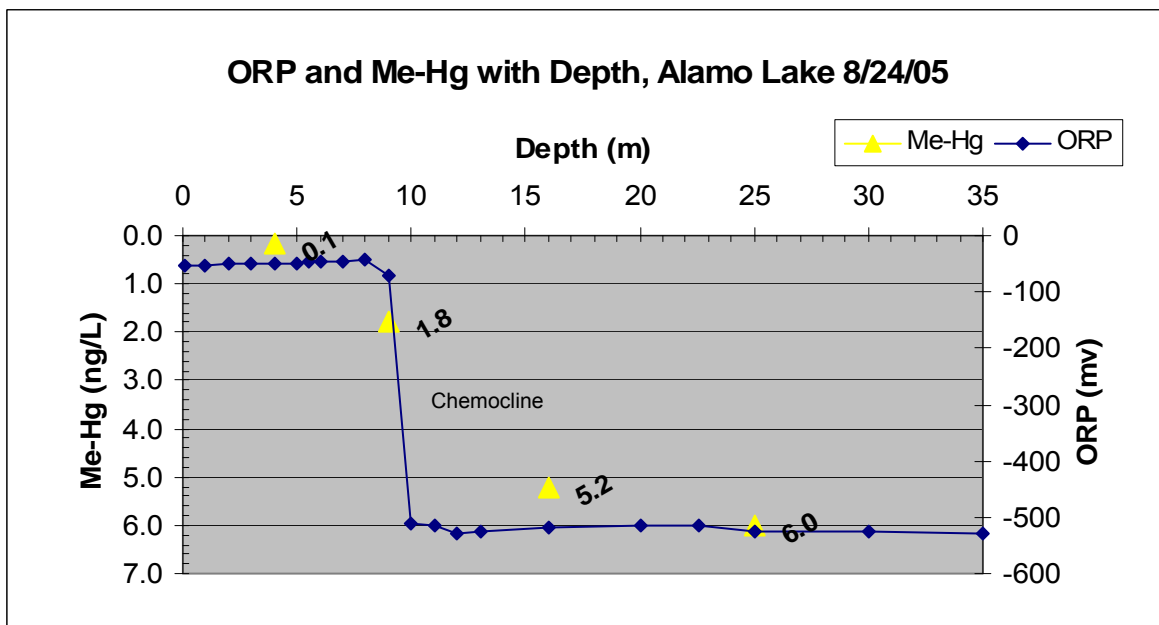
Figure 9. Reducing Conditions and Elevated Methyl-mercury in Alamo Lake

E.   Fish Tissue Sampling

The fish advisory issued for Alamo Lake applies to largemouth bass (geomean mercury concentration of 0.74 mg/kg), crappie (geomean mercury concentration of 0.75 mg/kg), and channel catfish (geomean mercury concentration of 0.42 mg/kg). The top predator in the Alamo system is the largemouth bass. Examination of the largemouth bass tissue data showed no clear relationship between tissue concentration and length (Figure 11), although tissue concentrations follow an approximately normal distribution (Figure 12). The fact that concentrations in fish tissue mercury appear to follow a normal distribution will allow application of least squares regression in predicting the relationship between mercury loading, exposure, and tissue reduction targets.
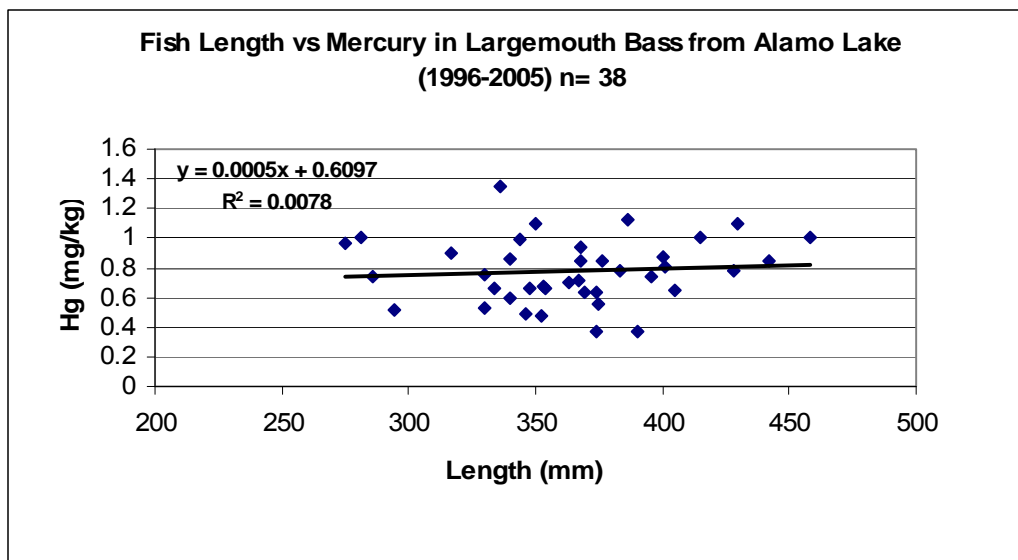
Figure 11. Total Mercury in Relation to Length in Alamo Largemouth Bass
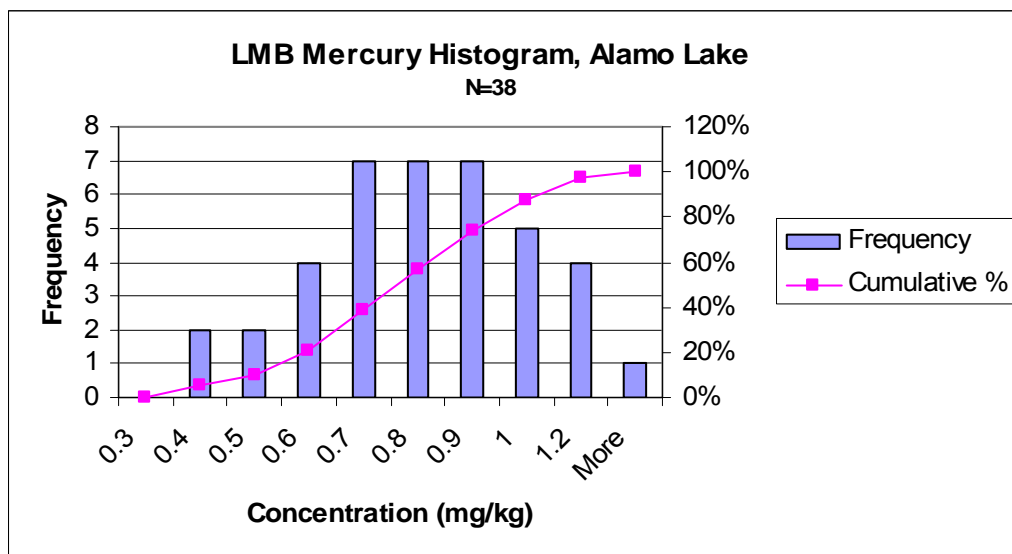
Figure 12. Histogram of Mercury Concentrations in Alamo Largemouth Bass

V.   APPROACH for DETERMINING MERCURY LOADS

A.   Conceptual Approach

Mercury impairment in Alamo Lake was based on mercury fish tissue concentrations. The modeling challenge involved questions such as:
- where is the mercury coming from and exactly how is it getting into the lake?
- are there areas within the watershed where methylation is occurring?
- once in the lake, where is methylation occurring and under what conditions?
- assuming both watershed and aerial mercury inputs to the lake, what can be considered 'background'?
- how is mercury working its way up the food chain?

Answers to each of these 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.

A TMDL must be quantitative in terms of recommendations for load reductions, requiring both sound numeric data and adequate understanding of processes involved. 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. The modeling approach used a combination of the following:

- Watershed Characterization System (WCS, Tetra Tech, Inc., 2000), a GIS-based watershed cycling model for sources and routing of mercury (mechanistic)
- Load duration curves for suspended sediment and mercury in runoff (empirical)
- HEC-5 for lake water balance over 12 year 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, Inc. 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 TMDLs.

A brief description and graphic representation of model components follows. See Tetra Tech, Inc., 2005 and 2006 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 load and suspended sediment concentration (SSC) load. The SSC-related mercury 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 monitoring stations in addition to the three gauge stations (Figure 13) provided information for analyses of sediment and mercury loading characteristics. Flow percentiles covered by sampling are shown in Table 3.

Table 3. Flow Percentiles Captured in Sampling

Sub-watersheds	Mercury Flow percentiles (number of samples)	SSC flow percentiles (number of samples)
Big Sandy River	10-20 (1); 20-30 (3); 50-60 (2); 90-100 (6)	10-20 (1); 20-30 (3); 30-40 (1); 40-50 (1); 50-60 (2); 60-70 (3); 90-100 (4)
Burro Creek	0-10 (1); 40-50 (1); 50-60 (2); 90-100 (8)	0-10 (1); 40-50 (1); 50-60 (2); 90-100 (10)
Santa Maria River	60-70 (4); 70-80 (4); 90-100 (10)	60-70 (3); 70-80 (4); 90-100 (9)

The Burro Creek gauge reflects the most perennial of the three gauge locations. The Big Sandy gauge shows no flow about 20 percent of the time, while the Santa Maria gauge is actually a peak flow gauge, recording flows only in excess of the 70th percentile.
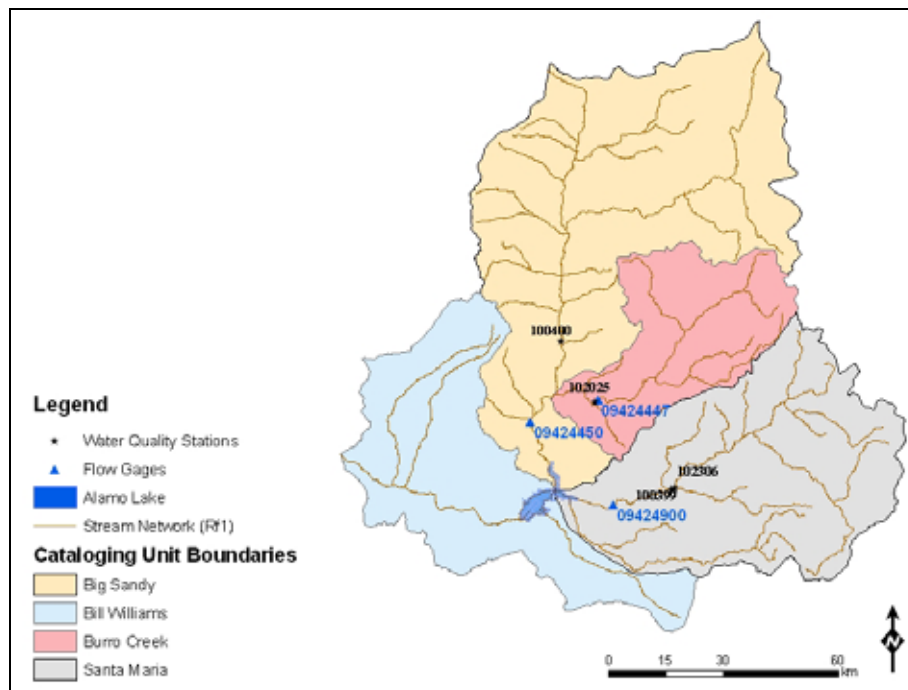
Figure 13. Stations Used for Flow and Load Duration Curves

Because the flow coverage was so extensive, concentration duration curves for mercury and SSC could be projected with a high degree of certainty. As seen in Figures 14, 15, and 16, the R^2 values are all above the 75th percentile, and most are higher than the 90th percentile (Tetra Tech, 2006).

Big Sandy Hg R^2 = 0.76

Big Sandy SSC R^2 = 0.93
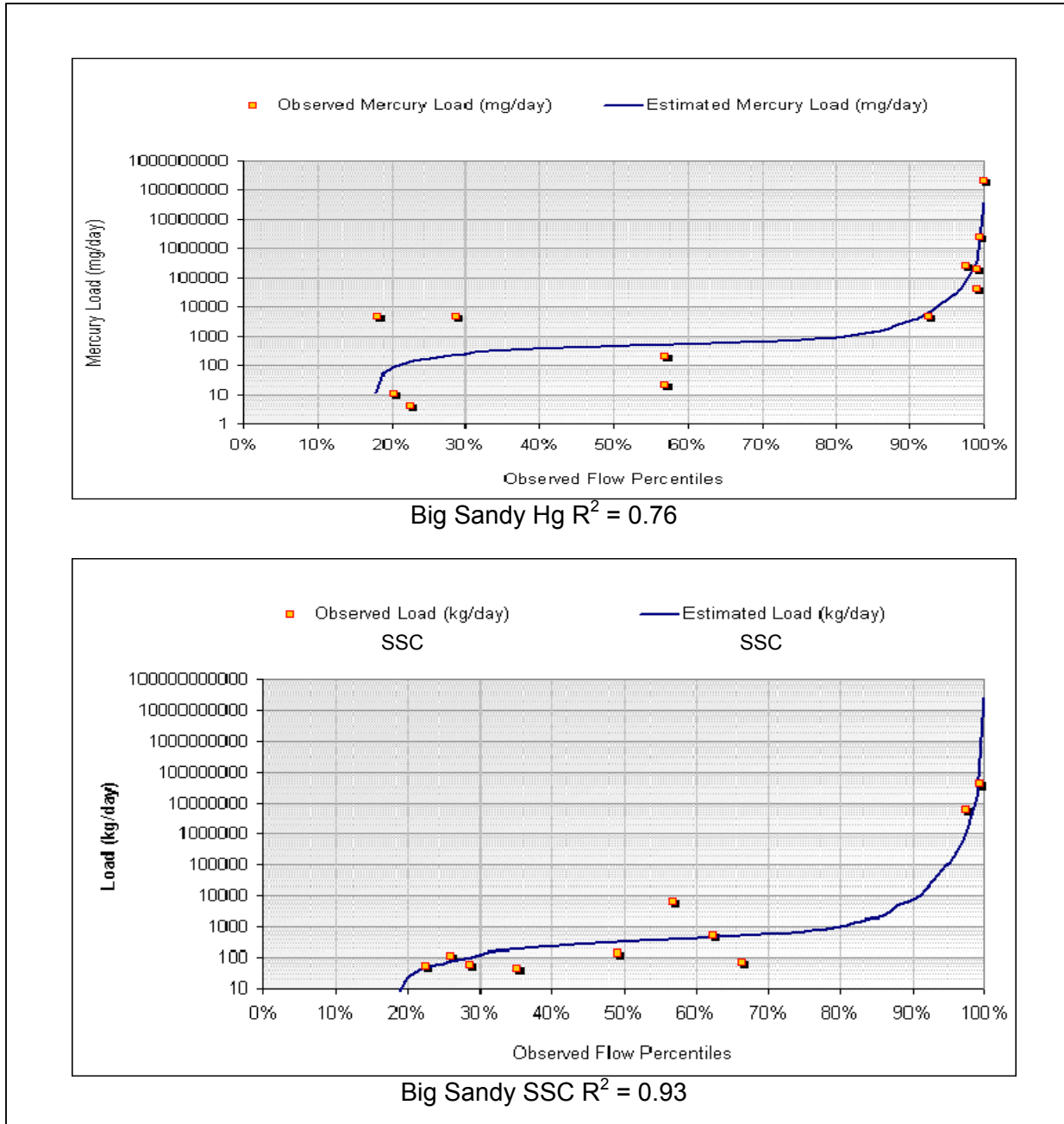
Figure 14. Load Duration Curves for Total Mercury and SSC at Big Sandy River Station (Tetra Tech, Inc., 2006)

Burro Creek Hg R^2 = 0.97

Burro Creek SSC R^2 = 0.94
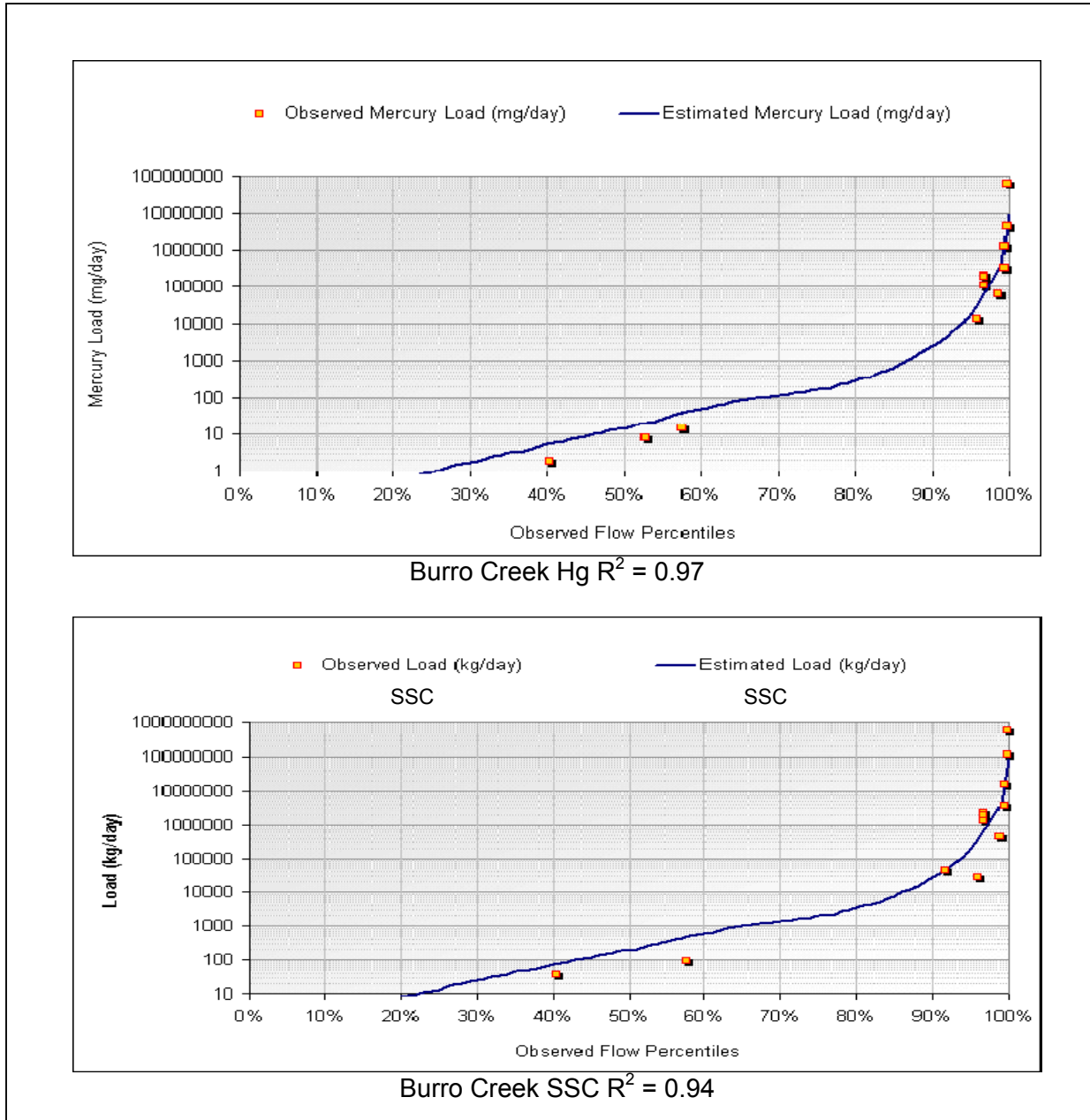
Figure 15. Load Duration Curves for Total Mercury and SSC at Burro Creek Station (Tetra Tech, Inc., 2006)

Santa Maria Hg R^2 = 0.94

Santa Maria SSC R^2 = 0.90
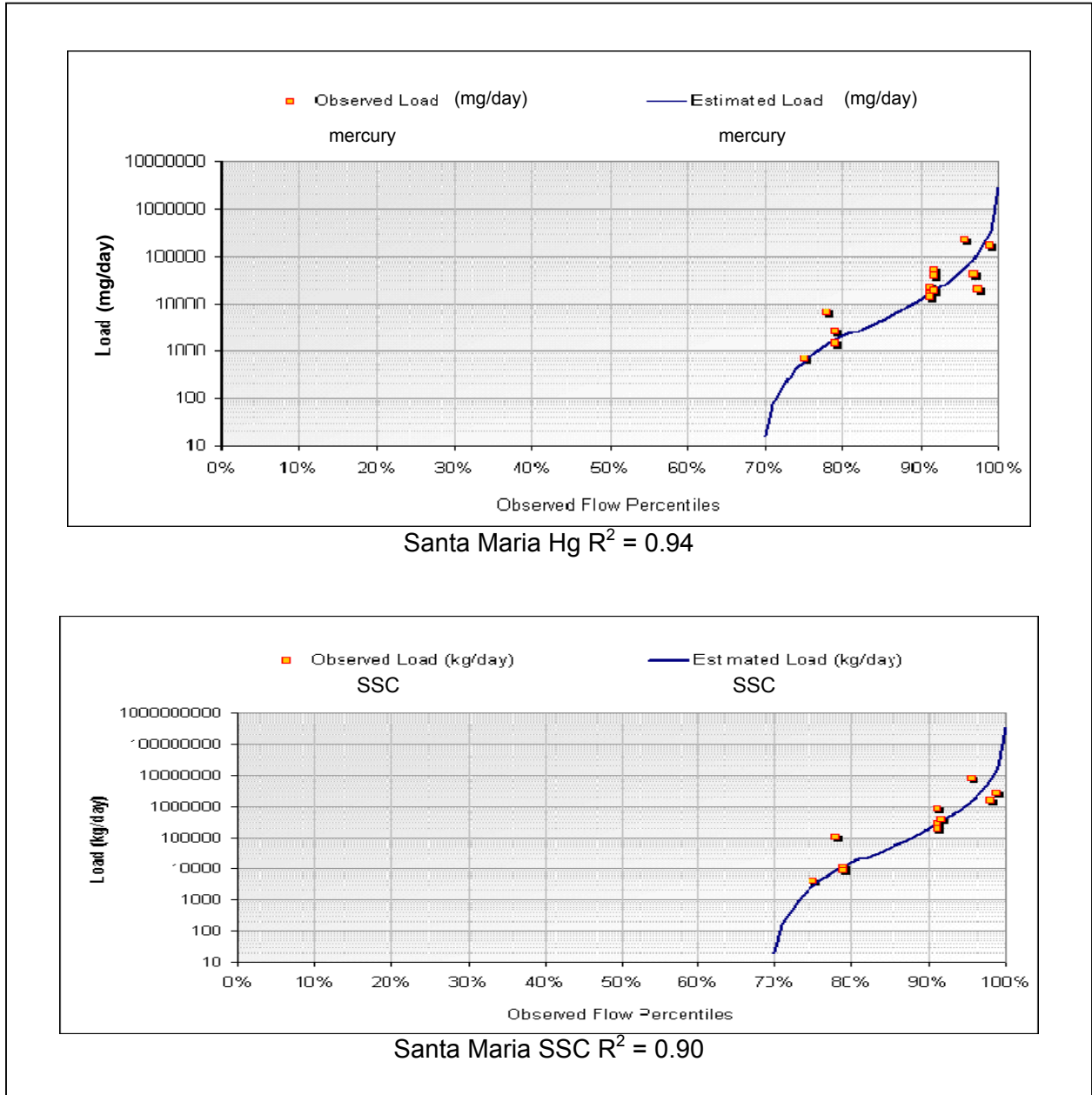
Figure 16. Load Duration Curves for Total Mercury and SSC at Santa Maria (Tetra Tech, Inc., 2006)

In general, both mercury and SSC loads increase with increasing flow. The only exception noted was higher than expected mercury during low flows in the Big Sandy. Data indicate that loading of mercury to Alamo Lake is largely the result of episodic storm inputs. All three tributaries carry a significant SSC load. As mentioned previously, the load duration curves for the Santa Maria gage reflect the fact that it is a peak flow gage.

C.   Watershed Source Identification 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 WCS (Tetra Tech, Inc., 2000). WCS was developed by EPA Region 4 to assist in the development of TMDLs for pollutants such as nutrients, pesticides, sediment, and mercury. It is an ArcView-based program that utilizes spatial and tabular data collected by EPA, USGS, U.S. Department of Agriculture Natural Resources Conservation Service (USDA-NRCS), U.S. Bureau of the Census, and the 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, Inc., 2000). The model uses a soil-mercury mass balance and calculates surface soil mercury 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 17 shows a diagram of the processes simulated by the WCS Mercury Tool.
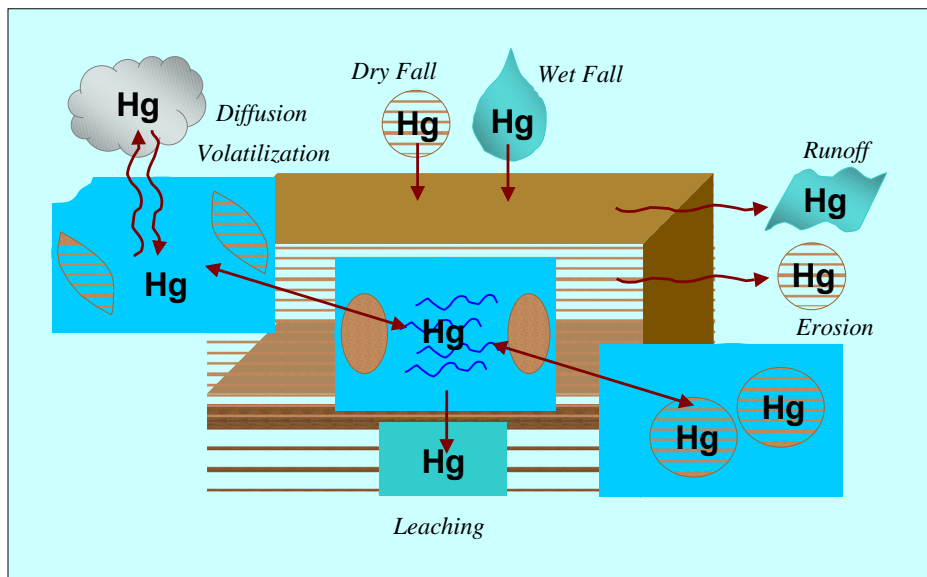
Figure 17. Processes Simulated by WCS (Tetra Tech, Inc., 2006)

The watershed mercury load is calculated as the total mercury 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. The 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 and data used in this model have been cited previously in Sections III and IV with the exception of sub-basins (numbered in Figure 18), soil erodibility (Figure 19), and MDN stations (Figure 20).
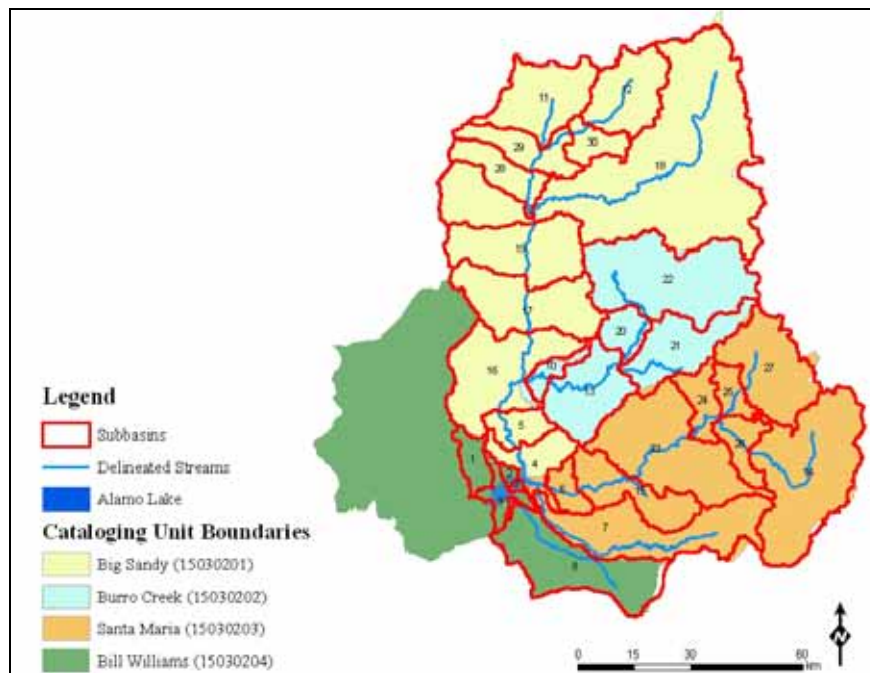
Figure 18. Sub-basins in Alamo Lake Watershed (Tetra Tech, Inc., 2006)
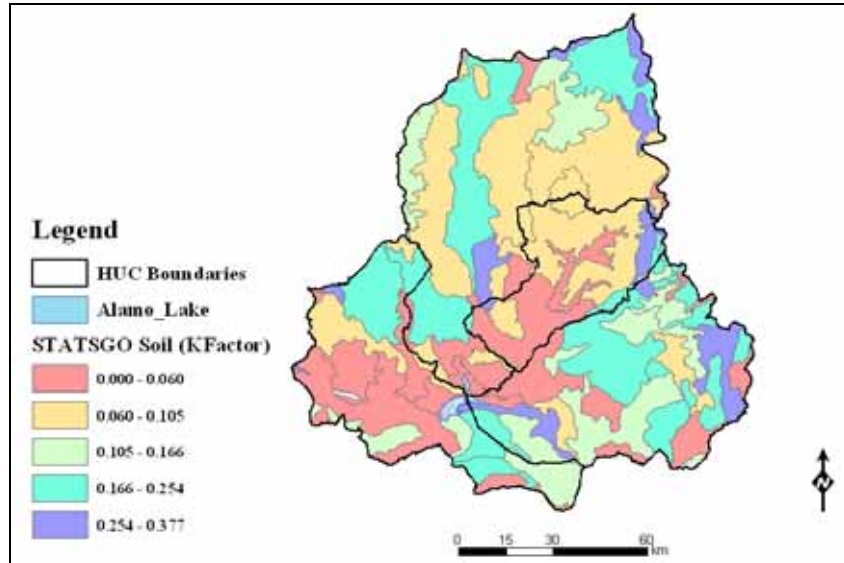
Figure 19.   Soil Erosion Factors (Tetra Tech, Inc., 2006)
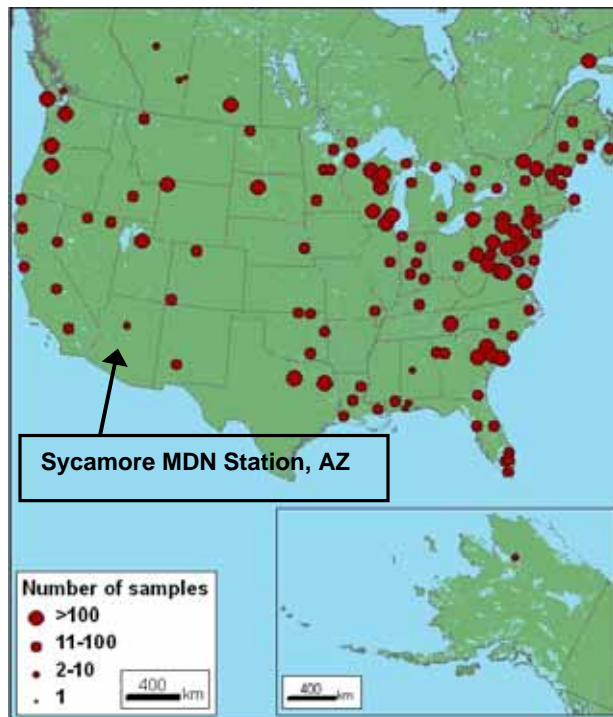
Figure 20. 2010 MDN Stations, showing AZ Station at
Sycamore Canyon established in 2006

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 gauge, Santa Maria at Highway 93, and the Big Sandy
water quality station above Burro Creek at Wikieup.

VI.   MERCURY SOURCE DETERMINATION

A.   Natural vs. Relative Background Mercury Sources

From studying ice cores dating from the year 1700 in Wyoming, Krabbenhoft and Schuster (2002) found that pre-industrial mercury concentrations in ice, resulting from air deposition, fall in a range of 1 to 4 ng/L. Eruptions of Tambora in the year 1815, and Krakatau in 1883, resulted in a temporary increase to 15 ng/L and 27 ng/L, respectively. During the gold rush, 1850-1885, concentrations of total mercury in ice peaked in 1860 and again around 1877 at 18 ng/L. The technology during that time used mercury to extract gold from ore, after which the mercury was burned off as vapor (retort). The modern industrial period, beginning in 1880, shows a steady increase in ice mercury concentration up to a maximum of 20 ng/L by the 1980s, with the eruption of Mount St. Helens spiking concentration to 35 ng/L. Perhaps due to the impacts of the Clean Air Act, concentrations declined sharply from 1987 to the early 1990s, but appear to be climbing again at the top of the core (15 ng/L).

Naturally mercury-enriched substrate is a long-lived source of mercury to the global atmospheric mercury cycle. Gustin, et al, (2000), measured mercury fluxes from three areas of natural enrichment within North America and three areas with low levels of mercury enrichment. Findings showed that the enriched areas were one to five orders of magnitude greater than the value applied to global belts of natural enrichment. Next, the authors scaled emission from one of these areas (New IDRIA Mining District in northern California) to the entire geologic region extending from Canada south into Mexico and running through western North America. The calculations for mercury-enriched areas showed an average total annual flux of about 10 mg/yr, but reached as high as 26 mg/yr (emission rate of 135 ug/sq m). On a statewide basis, within the geologic region that includes Arizona, estimates ranged from a high of 2.1 mg/yr to a low of 0.08 mg/yr.

The authors noted that Arizona did not have many recorded mercury deposits, but that the state has abundant mineralization with which low levels of mercury enrichment are associated. They hypothesized that, with many geothermal areas, precious and base metal deposits and recent volcanic deposits, emissions from these areas could actually be greater than those estimated for the smaller, more enriched sites. In fact, Arizona does have recorded mercury deposits in the form of cinnabar, which was mined for a time in the Dreamy Draw area of the Phoenix Mountains and also in the Mazatzal Mountains between Phoenix and Payson.

A follow-up study by Fischer and Gustin (2001) was conducted on the East Fork of the Upper Carson River drainage basin in Nevada, which contains the open-pit sulfur Leviathan Mine. This study suggested that groundwater recharged during baseflow within enriched areas, contributed almost as much mercury as summer overflow from acid mine drainage holding ponds (12-13 ng/L), as compared with non-discharging areas (2 to 4 ng/L).   Ambient background was considered to be 1 to 3 ng/L. For sediment, Gustin's previous work suggested that a threshold of >0.1 ug/g, or >100 ng/g, could be considered "natural enrichment." In the Carson River Basin study, the range of mercury found in sediments was 40 ng/g to 400 ng/g, suggesting natural enrichment of mercury in association with large sulfur deposits.

B.   Soil Mercury Data for Arizona

As mentioned, the Alamo Lake watershed is comprised of volcanic/basaltic/granitic rocks that make up approximately 59 percent of the total. These rock types are known to be associated with relatively higher amounts of mercury. No comprehensive soil mercury survey exists, but USGS developed distribution maps of several elements including mercury after processing point data collected at 1,323 stations across the conterminous United States (Gustavsson et al., 2001). Weighted-median and Bootstrap procedures were used for interpolation and smoothing. Figure 21 shows the distribution of soil mercury within Arizona based on these data, which likely include aerially deposited mercury as well as geologically derived mercury. A significant portion of the Alamo Lake basin is shown as one of six or seven relatively higher surface soil mercury levels in Arizona.
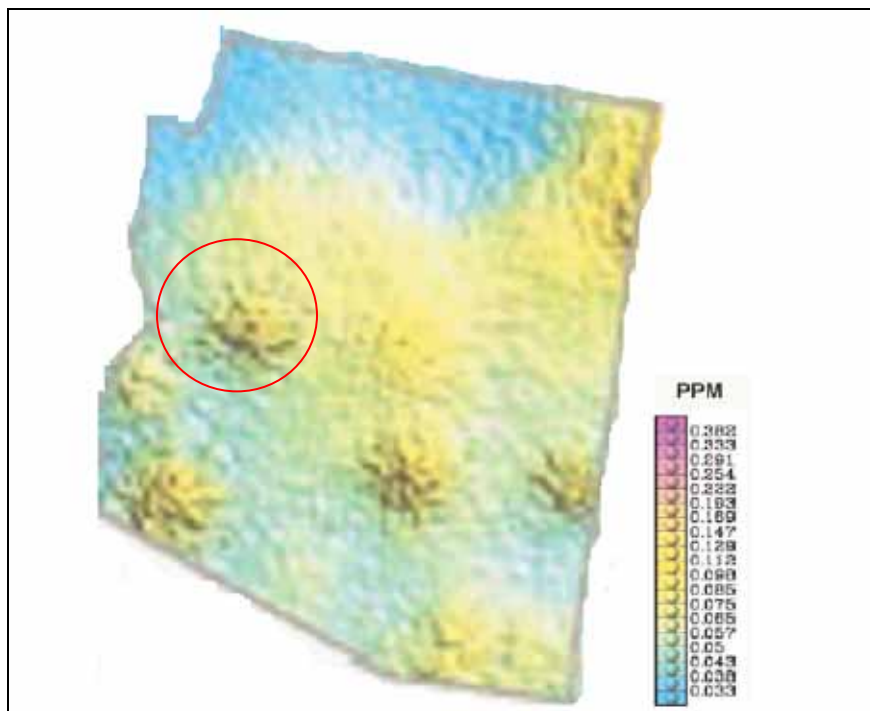
Figure 21. Soil Mercury Values from Gustavsson et al., 2001

Subsurface soil samples are assumed to provide the best estimate of expected natural soil mercury concentrations in the watershed in the absence of atmospheric deposition of mercury and other human influences. Tetra Tech, Inc. observed that, in fact, leaching from the surface will contribute some mercury derived from atmospheric deposition to the lower soil horizons. The contribution, however, is expected to be small given the high soil-water partition coefficients of mercury and low rainfall rates in the arid climate of the Alamo Lake watershed.

To better estimate 'background' geologic mercury in the Alamo Lake watershed, ADEQ chose 47 sites in attempt to represent a cross-section of geology and soil types. Soils were collected using clean hands/dirty hands field technique (EPA Method 1669) from 10-12 inches below the surface, in an attempt to avoid the top organic soil horizon. Soil samples were analyzed for total

mercury using an established low-level detection method (EPA Method 1631e). Table 4 summarizes ADEQ results for soil mercury.

Table 4. Summary of Mercury Concentrations (ng/g or ppb) in Subsurface Soil Samples (Tetra Tech, Inc., 2009)

	Alluvium	Basalt	Granitic	Metamorphic	Sedimentary	Volcanic
Count	5	5	14	3	13	7
Average	8.76	22.95	23.78	21.78	22.54	21.16
Standard Error	2.74	2.59	3.52	8.02	3.09	3.39
Median	11.38	23.40	21.08	16.20	23.00	17.50
Minimum	1.97	14.20	5.27	11.55	7.98	11.20
Maximum	16.20	30.46	52.02	37.60	52.50	33.70

Results varied from 2 to 53 nanogram per gram (ng/g or ppb) or 0.002 to 0.052 milligrams per kilogram (mg/kg or ppm), lower than projected by the Gustavsson bootstrap procedure and Gustin's natural enrichment level of 100 ng/g (0.001 mg/kg). However, it should be noted that soil sample sites were chosen to reflect background, not enrichment.

The average concentrations shown from Table 4 were mapped to the geology of the watershed to show relative native soil mercury concentrations (Tetra Tech, Inc., 2009; Figure 22).
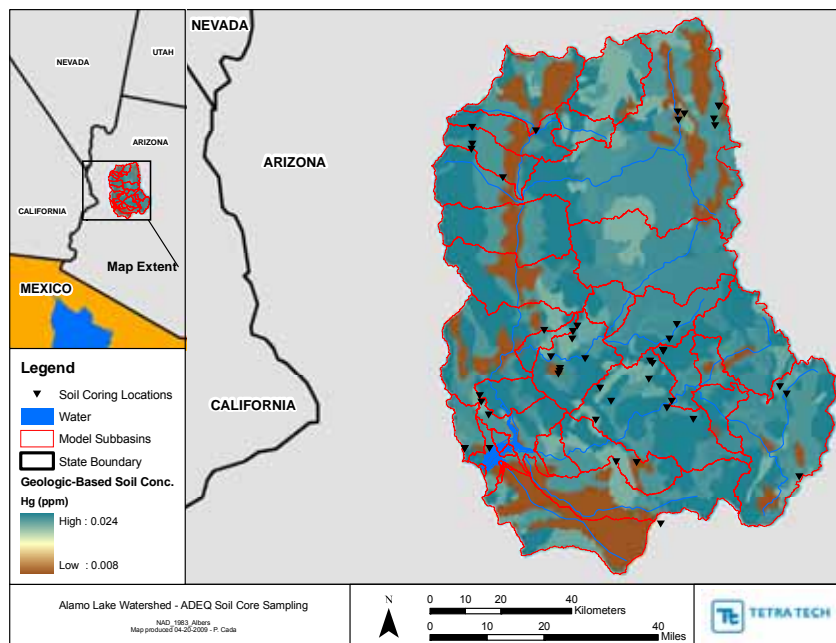
Figure 22. Native Soil Mercury Concentrations in the Alamo Lake Watershed

C.   Mining Sources

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 used hydraulic, drift, and dredging methods were usually a major source of mercury contamination. 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. The locations of historic gold mining within the Alamo Lake watershed are shown in Figure 23 (Mineral Industry Location System database).
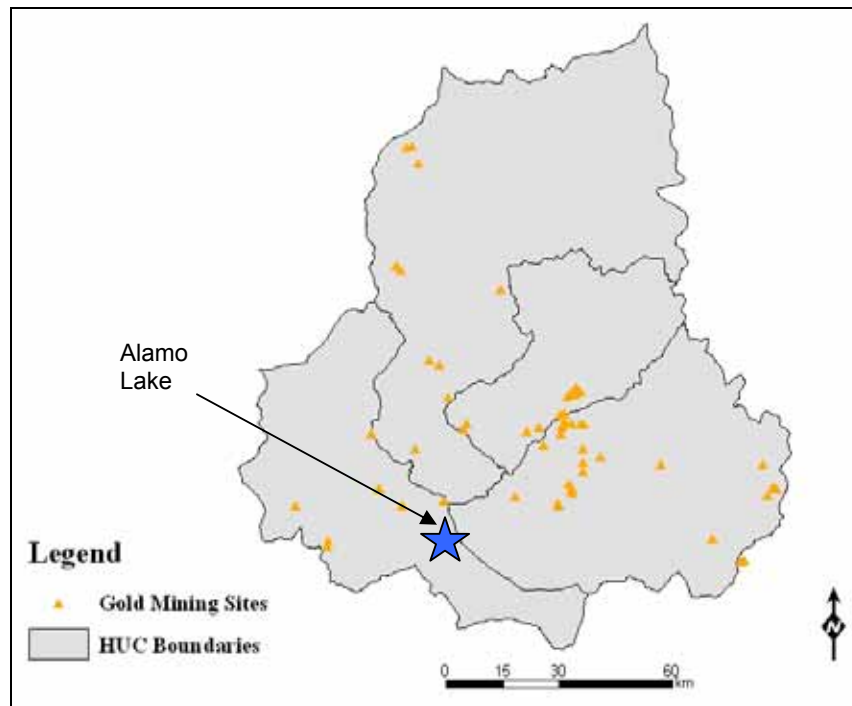
Figure 23. Historic Gold Mining in Alamo Watershed

Other mining activities can result in watershed mercury loads from activity that produces tailing residues of crushed rock. If the parent material contains mercury, the conversion of rock to tailings increases the amount of mercury that is more easily eroded and transported. Figure 24 shows the extent of all mining activities in the watershed.
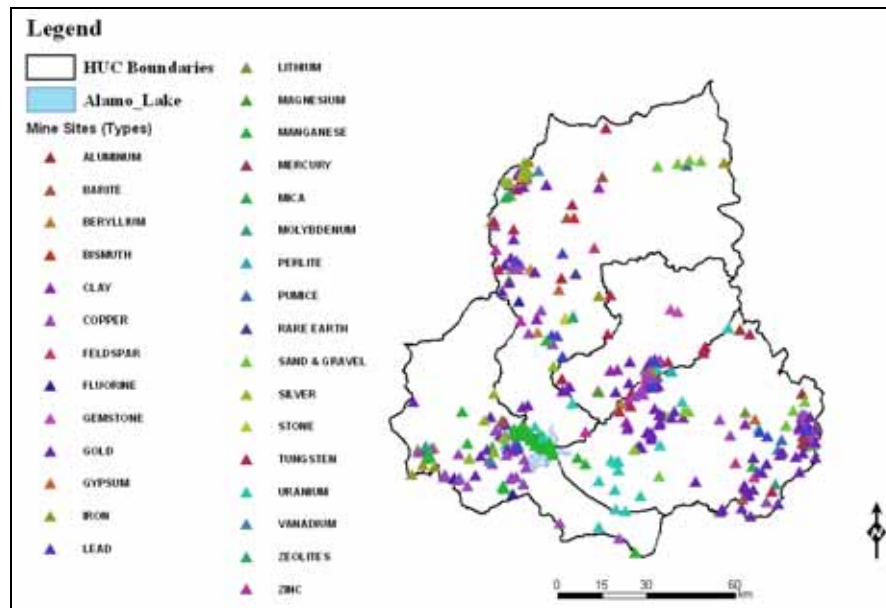
Figure 24. Extent of all Mining Activities in Alamo Lake Watershed

D.   Estimation of the Impacts of Wildfires

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 loading. This increase in mercury load correlated with an increase in the methyl-mercury concentrations within Caballo Reservoir 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 measured by ADEQ, combined with the sediment load predictions by the WCS model. Data regarding the history of forest fires within the Alamo Lake watershed were available from the BLM.   Figure 25 shows the average area within each sub-basin that is affected by the historic forest fires. These 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.

Tetra Tech found a correlation between average size of historical forest fires and the unit area loading estimates of sediment associated mercury. 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.
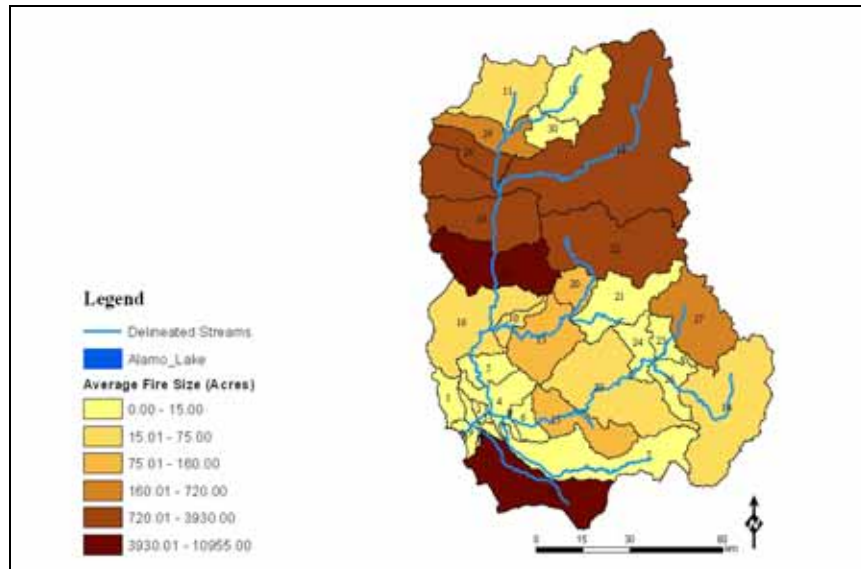
Figure 25. Average Size of Historical Fires (Tetra Tech, Inc., 2005)

E.   Aerial Sources

1. Global Sources of Mercury Emissions

According to the EPA website for mercury emissions, natural sources of mercury, such as volcanic eruptions and emissions from the ocean, have been estimated to contribute about a third of current worldwide mercury air emissions, whereas anthropogenic (human-caused) emissions account for the remaining two-thirds. These estimates are highly uncertain, as land, water, and other surfaces can repeatedly re-emit mercury into the atmosphere after its initial release into the environment. Much of the mercury circulating through today's environment is mercury that was released years ago. Anthropogenic emissions are roughly split between re-emitted emissions from previous human activity and direct emissions from current human activity. Although highly uncertain, recent estimates of annual total global mercury emissions from all sources, natural and anthropogenic, are about 4,400 to 7,500 metric tons emitted per year. Figure 26 shows the worldwide distribution of mercury emissions.
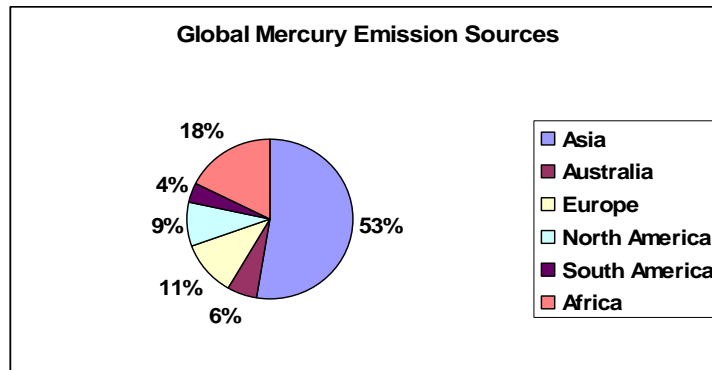
Figure 26. Global Mercury Sources (Pacyna and Munthe, 2004)

In the U.S. and globally, coal combustion is the largest source of anthropogenic mercury emissions (United Nations Environment Programme, 2008). EPA has estimated that about one-third of U.S. emissions are deposited within the contiguous U.S. but the majority enters the global cycle.

2.   Arizona Sources of Mercury Emissions

Beginning in the 1990s, EPA investigated potentially toxic air pollutants with the goal of developing air toxics emissions standards for power plants and utilities under the Clean Air Act (Section 112). The process, though protracted, has resulted in a rule known as the Clean Air Mercury Rule (CAMR). EPA proposed air toxics standards for coal- and oil-fired electric generating units in the spring of 2011. The public comment period has been extended as of this writing and the finalization date is unknown. Data from the emissions inventory were combined with CMAQ modeling for development of the Clean Air Mercury Rule (CAMR). For Arizona utilities, the total mercury emissions for utilities only, from 1999 to 2003, was reported to be 1,256 pounds.

Subsequently, Tetra Tech has summarized the mercury emissions reported in the 2006 Toxic Release Inventory (TRI). Table 5 shows mercury emissions in pounds for all reporting facilities in Arizona, not just utilities, resulting in a total of 1,552 pounds.

Table 5. 2006 TSI Mercury Emissions (Tetra Tech, Inc., 2008)

Facility Name	Total Mercury Air Emissions 2006 (pounds)
Coronado Generating Station	551
Cholla Power Plant	321
Salt River Project Navajo Generating Station	283
Arizona Electric Power Cooperative	129
Tucson Electric Power Co Springerville	122
Phelps Dodge (Freeport-McMoRan) Miami Mine	47
Phoenix Cement	42
Abitibi Consolidated Snowflake Division	34
Asarco LLC Ray Complex & Hayden Smelter/Concentrator	13
Irvington Generating Station	10
Veolia Es Technical Solutions LLC	<1
Arizona Portland Cement Company	<1
Honeywell Air Transport	<1
Phelps Dodge (Freeport-McMoRan) Bagdad Mine	<1
World Resources Company	<1
TOTAL all AZ mercury emissions, including utilities =	1,552 pounds as of 2006

3. Modeled Mercury Deposition in Arizona

Both wet and dry atmospheric deposition can be a major source of mercury to watersheds 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 chlor-alkali plants, (EPA, 1997). There are currently no chlor-alkali plants in Arizona.

EPA has undertaken several modeling studies to develop national estimates of mercury deposition rates. The 1997 EPA Mercury Report to Congress used the 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; EPA, 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 with a reference to 2002 meteorological data. Figures 27 and 28 show the atmospheric deposition rates based on CMAQ modeling results for the 2002 base case (note: numbers correspond to sub-watershed modeled by Tetra Tech). CMAQ is believed to provide a more accurate estimate of total mercury deposition, particularly in the arid Southwest.
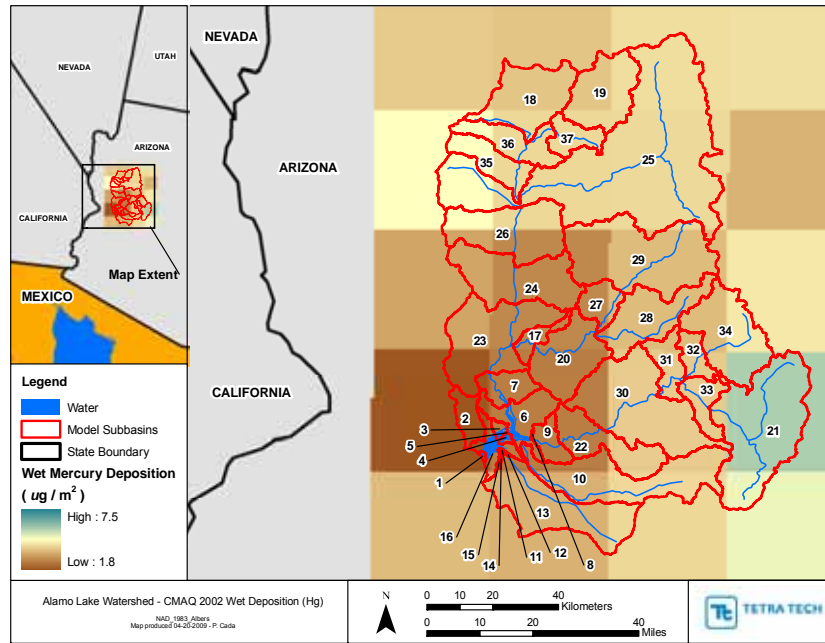
Figure 27. Wet Deposition in Alamo Lake Airshed (Tetra Tech, Inc., 2008;
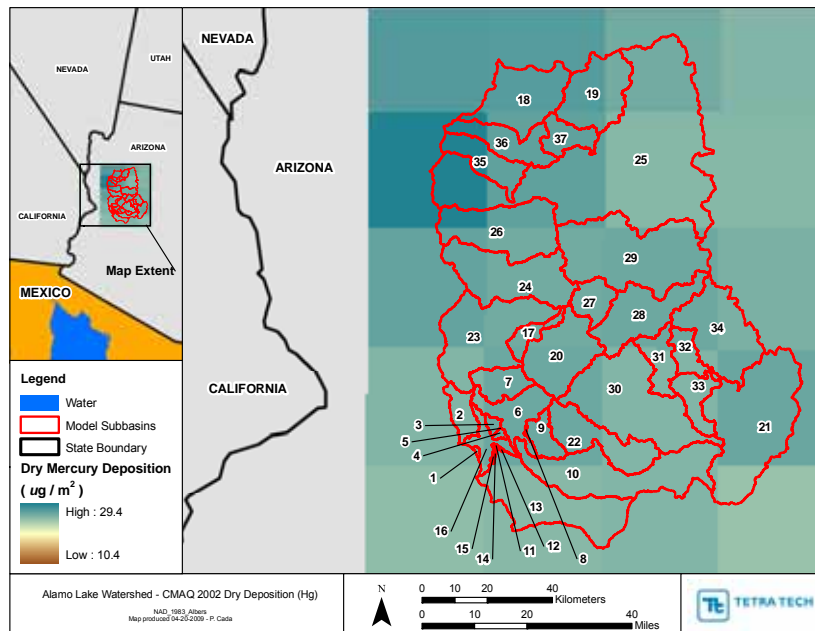
Figure 28. Dry Deposition in Alamo Lake Airshed (Tetra Tech, Inc., 2008)

As part of the CMAQ analysis, Tetra Tech analyzed dry deposition data collected by a mobile Tekran mercury analyzer. Tekran data were collected at four locations in Arizona from December 2005 to April 2007, as well as data collected between January 2006 and December 2007 at Arizona's Sycamore MDN wet deposition station near Williams, Arizona. The average wet deposition concentration of total mercury at the Sycamore MDN station was found to be 34.1 ng/L; the volume-weighted concentration over the monitoring period was 21.5 ng/L. The rate of deposition at the MDN station was 211.0 $ng/m^2/wk$, or 11.0 $g/m^2/yr$.

Estimating dry deposition rates is difficult because the dynamics of two of the three mercury species, reactive gaseous mercury (RGM), and particulate mercury (Hg-P), are highly variable. Elemental mercury (Hg^0), is the dominant species in terms of ambient concentration, but is re-emitted most readily. Net deposition rates are much higher for the other two forms (Lindberg et al, 1992, as cited in Tetra Tech, Inc., 2008), and require consideration of local and seasonal meteorological conditions, proximity of potential sources, and foliar uptake and leaf loss rates.

Table 6 shows resulting dry deposition mercury loading at each of the four stations (Tetra Tech, Inc., 2008). CMAQ modeling of the Alamo Lake watershed yielded a range of 3 to 8 ug/m^2 for wet deposition of mercury and 10 to 19 ug/m^2 for dry deposition of mercury (Tetra Tech, 2008), suggesting that total dry deposition loading may be two to three times greater than total wet deposition loading in Arizona and similarly arid regions of the Southwest.

Table 6. Dry Deposition Mercury Loading (g/km^2/yr) at Arizona Tekran Monitoring Stations (Tetra Tech, 2008)

Dry Deposition by Component	Lake Pleasant	Lyman Lake	Parker Canyon Lake	Sycamore Canyon (MDN location)
RGM	15.98	15.09	23.92	16.96
Hg-P	0.10	0.13	0.20	0.08
Total dry deposition to water surfaces and land (settling only)	16.08	15.22	24.12	17.04
Hg^0 Foliar Accumulation*	8.25	6.68	7.07	6.96
Total dry deposition to land surfaces (settling and foliar accumulation)	24.33	21.90	31.20	24.00

* Tetra Tech noted that whether single species or mixed vegetation was modeled, there was less than a 4 percent difference

4. WCS: Deposition Impacts on Soil Mercury

The WCS Mercury Tool incorporates EPA's IEM-2M methodology (Indirect Exposure Methodology used in USEPA, 1997) to compute long-term changes in soil mercury concentrations in response to atmospheric deposition. However, because the equilibration of soil mercury with atmospheric deposition is a slow process, running the model for a period of a few years does not result in re-equilibration of initial soil concentrations with current atmospheric deposition rates. Thus an external analysis is needed to evaluate likely soil surface concentrations.

Unfortunately, the history of atmospheric mercury deposition in the Alamo Lake watershed is not well known, so Tetra Tech applied the IEM-2M approach, starting at native subsoil concentrations. They assumed constant deposition at the rates predicted in the CMAQ 2002 model run (2008), thought to best characterize dry deposition. Long-term runs of IEM-2M then suggest that soil concentrations are likely to have increased significantly above native background levels as a result of atmospheric deposition. The 50-year time frame was selected to provide a sensitivity analysis to the effects of ongoing deposition, as seen in Figure 29.
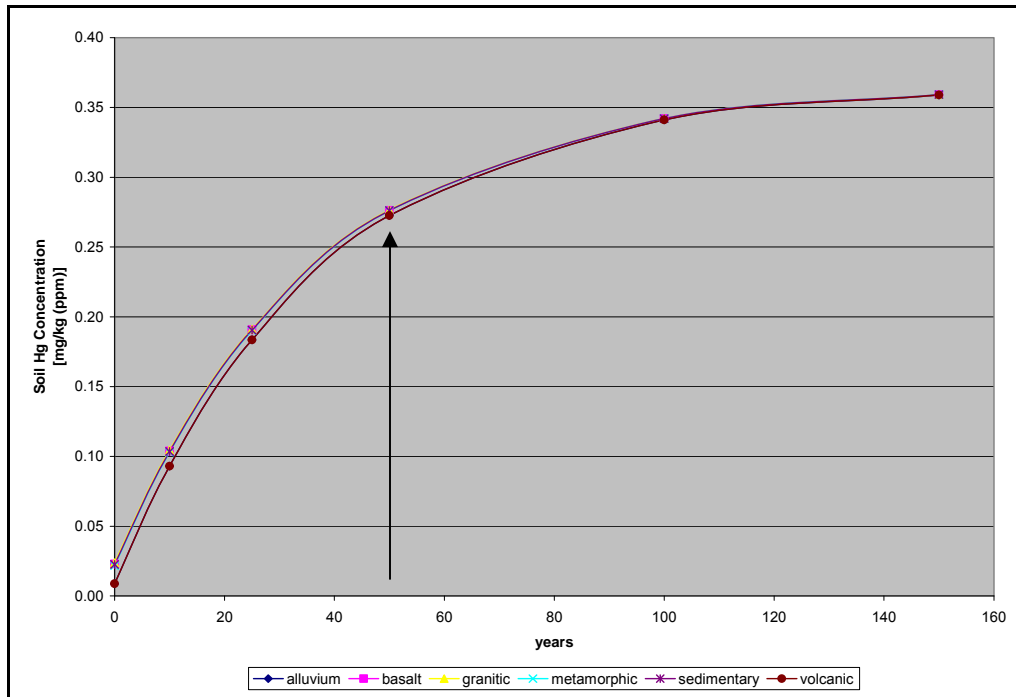
Figure 29. IEM-2M Projections for Increase in Surface Soil Mercury

After 50 years, the graph indicates that surface soil mercury concentrations would be 10 times greater than sub-surface native concentrations, an approximately uniform surface soil concentrations of 0.276 ppm (276 ppb ng/g), of total mercury across the watershed. After 100 years, surface concentrations would be an additional 7-8 percent higher.

Two different soil conditions were simulated: "native" conditions, directly based on the subsurface soil measurements, and "equilibrated" conditions, based on the 50-year IEM-2M analysis of equilibration between native soil and CMAQ 2002 atmospheric deposition. Results by major watershed are summarized in Table 7 and compared to both the load duration and WCS results provided in Tetra Tech, 2006. Reflecting the updated spatial patterns of soil concentrations, the two new WCS estimates bracket the one developed previously, though minor shifts can be seen in the relative importance of the different sub-watersheds. Nevertheless, the relationship of WCS projections to estimates from the load duration equations remains weak (Tetra Tech, Inc., 2008). Based on the updated model, natural background (soil-based) mercury accounts for a relatively small percentage (10 -14 percent) of the total mercury load in normal or wet years.

Table 7. Comparison of Mercury Loading Results by Watershed

Watershed	Condition	Total Hg Loading (g/year)				
		Load-Duration Equations (Tetra Tech, 2006)	WCS Model (Tetra Tech, 2006)	WCS Model, Native Soils (Tetra Tech, 2008)	WCS Model, Equilibrated Soils (Tetra Tech, 2008)	Native
Santa Maria Watershed	Dry	296	895	3.81	15.3	25%
	Normal	5,188	900	188	1,614	12%
	Wet	14,224	6,262	1,212	11,485	11%
Burro Watershed	Dry	3,872	105	18	122	15%
	Normal	6,881	3,334	604	4,734	13%
	Wet	45,900	37,047	8,323	80,603	10%
Big Sandy Watershed	Dry	342	4	2	5.	33%
	Normal	528	98	39	281	14%
	Wet	50,879	27,166	7,939	83,496	10%
Total to Alamo Lake	Dry	4,510	119	24	142	17%
	Normal	12,598	4,332	831	6,628	13%
	Wet	111,003	70,475	17,475	175,584	10%

In comparison to load duration calculations, WCS underestimated sampled mercury levels under normal conditions and overestimated mercury levels under wet conditions. Several reasons for the discrepancy in predicting mercury loading include: 1) naturally elevated geologic formations, 2) scores of uncharacterized abandoned mine sites, 3) uncertainty in aerial deposition and reemission in the xeric southwest, and 4) the cumulative impact of fire in the watershed.

F.   Statistical Analysis of Mercury Data Using Outlier Detection

Tetra Tech used an empirical visualization technique for evaluation of outliers through the use of box plots. A box plot consists of a central box (showing the interquartile range with a line at the median), whisker lines that extend to 1.5 times the interquartile range, and individual points

beyond that range. Points within three times the interquartile range are shown by "ж", points more than four times the interquartile range from the median (extreme outliers) are shown by circles. Figures 30 and 31 (respectively) display the results for mercury concentration on suspended sediment concentration and total mercury in water, separated by HUC. The top three sites in Table 8 have outliers in both water and sediment categories. The six-digit numbers are ADEQ sample site identifiers.
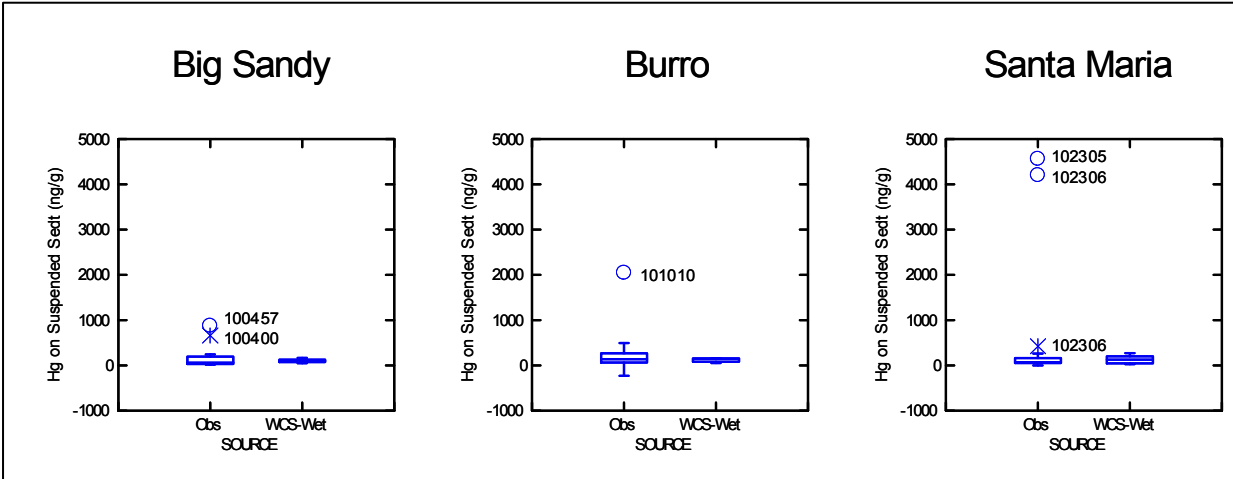
Figure 30. Box and Whisker Plots of Mercury associated with Sediment
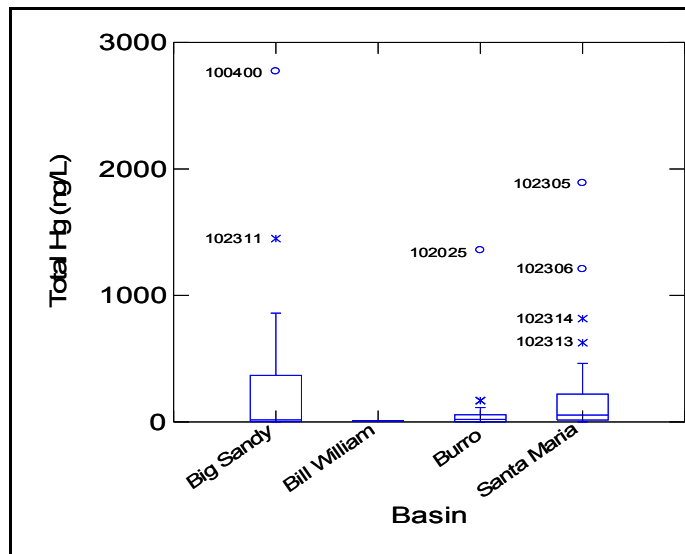
Figure 31. Box and Whisker Plots of Total Mercury in Water

Table 8. Sample Sites with Mercury Outliers

Total Mercury in water	Mercury on sediment
102305 Mountain Spring Wash above Highway 97	102305 Mountain Spring Wash above Highway 97
102306 Santa Maria River at Highway 93	102306 Santa Maria River at Highway 93
100400 Big Sandy River at Highway 93 bridge	100400 Big Sandy River at Highway 93 bridge
102025 Burro Creek at old Highway 93 Bridge	101010 Boulder Creek below Hillside tailings
102306 Santa Maria River at Highway 93	100457 Big Sandy River near Wikieup, AZ
102311 Knight Creek above Big Sandy	
102313 Bridle Creek below Mountain Springs Wash	
102014 Cowboy Wash above Highway 97	

The analysis of outliers suggests some sites that warrant further investigation, but not a single dominant source of mercury load. Instead, the data available at this time suggest that there are likely multiple small sources of elevated mercury loadings throughout the Alamo Lake watershed (Figure 32).
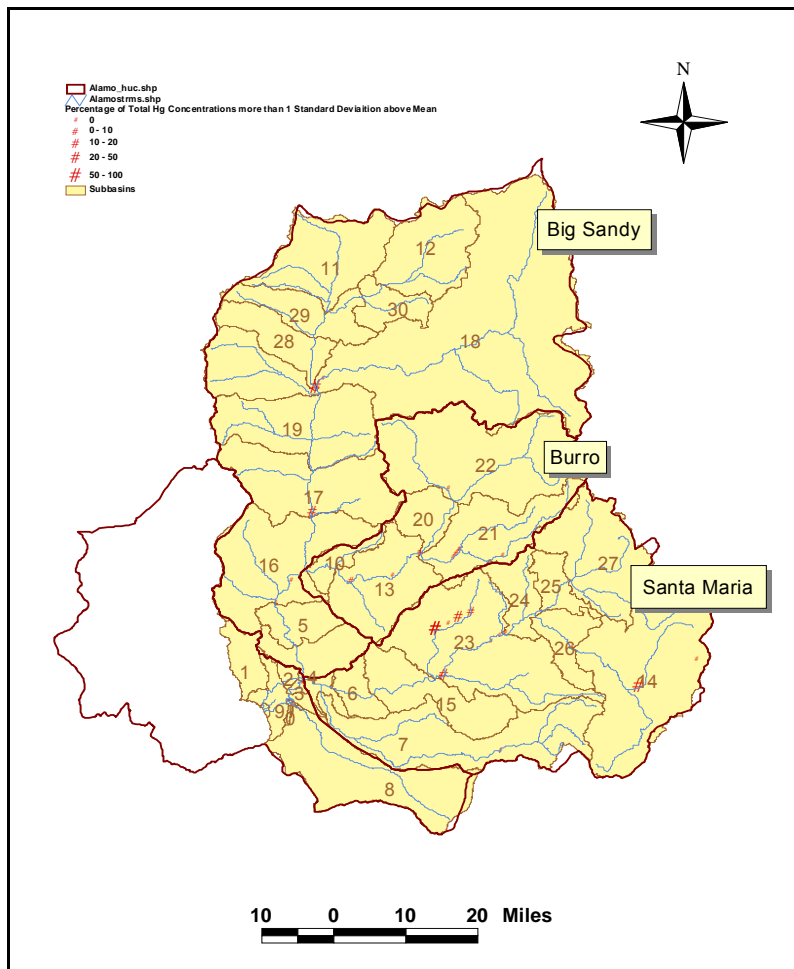
Figure 32. Percentage of Total Hg Observations > 1 Standard Deviation above the Mean

The maximum total mercury results, ranked by site, support the outlier analysis. Table 9 lists the TMDL sampling sites with the highest total mercury values in water, with each site's highest SSC values. Boulder Creek below Hillside Mine is in a class by itself, reflecting erosion from three large tailings piles adjacent to the creek.

Table 9. Top Ten Total Mercury Results in Water; Highest SSC Results per site

Outlier Sites	Site ID	T-Hg Rank	Max T-Hg (ng/L)	Max SSC_C * (mg/L)	Max SSC_F * (mg/L)
•	Boulder below Hillside	1	143,000	30,700	49,900
•	Big Sandy at Highway 93	2	2,772	6,900	4,000
•	Knight above Big Sandy	3	1,941	46,000	2,700
•	Mountain Spring Wash above Highway 97	4	1,889	5,990	7,700
•	Burro at Highway 93	5	1,359	3,500	9,690
•	Santa Maria at Highway 93	6	1,209	17,000	12,400
•	Bridle below Mountain Spring Wash	7	626	3,780	8,460
	Skull Valley Wash	8	464	2,800	3,200
	Bridle above Highway 97	9	233	8,600	2,390
	Santa Maria above Highway 96	10	220	8,200	4,990

•   Outlier sites from box plot analysis
* SSC_C = course fraction suspended sediment concentration; SSC_F = fine fraction suspended sediment

VII.   LINKAGE 1: WATERSHED LOAD and LAKE RESPONSE

To provide the linkage analysis between external mercury loads to Alamo Lake, internal lake cycling, and the assimilative capacity based on numeric water quality and fish tissue targets, a receiving water model of the lake was developed by Tetra Tech (2006).   The WASP5 toxic chemical model TOXI5 module (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 TMDL application.

A general conceptual model of mercury cycling in a lake (showing only the more significant pathways) is shown in Figure 33, 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 methyl-mercury. Mercury methylation can occur both in the lake and in the watershed. Ionic mercury is methylated by a biological process that involves sulfur-reducing bacteria. Rates of biological methylation of mercury can be affected by a number of factors, as discussed below. 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, lake or stream sediment, and saturated soils where oxygen is low and reducing bacteria are present.   Methylation 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 site-specific kinetic processes.

Functions in the WASP model application are 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 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 gauges 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 that application through 2004. Daily estimates of inflow and outflow were used to apportion water storage for WASP5 modeling.
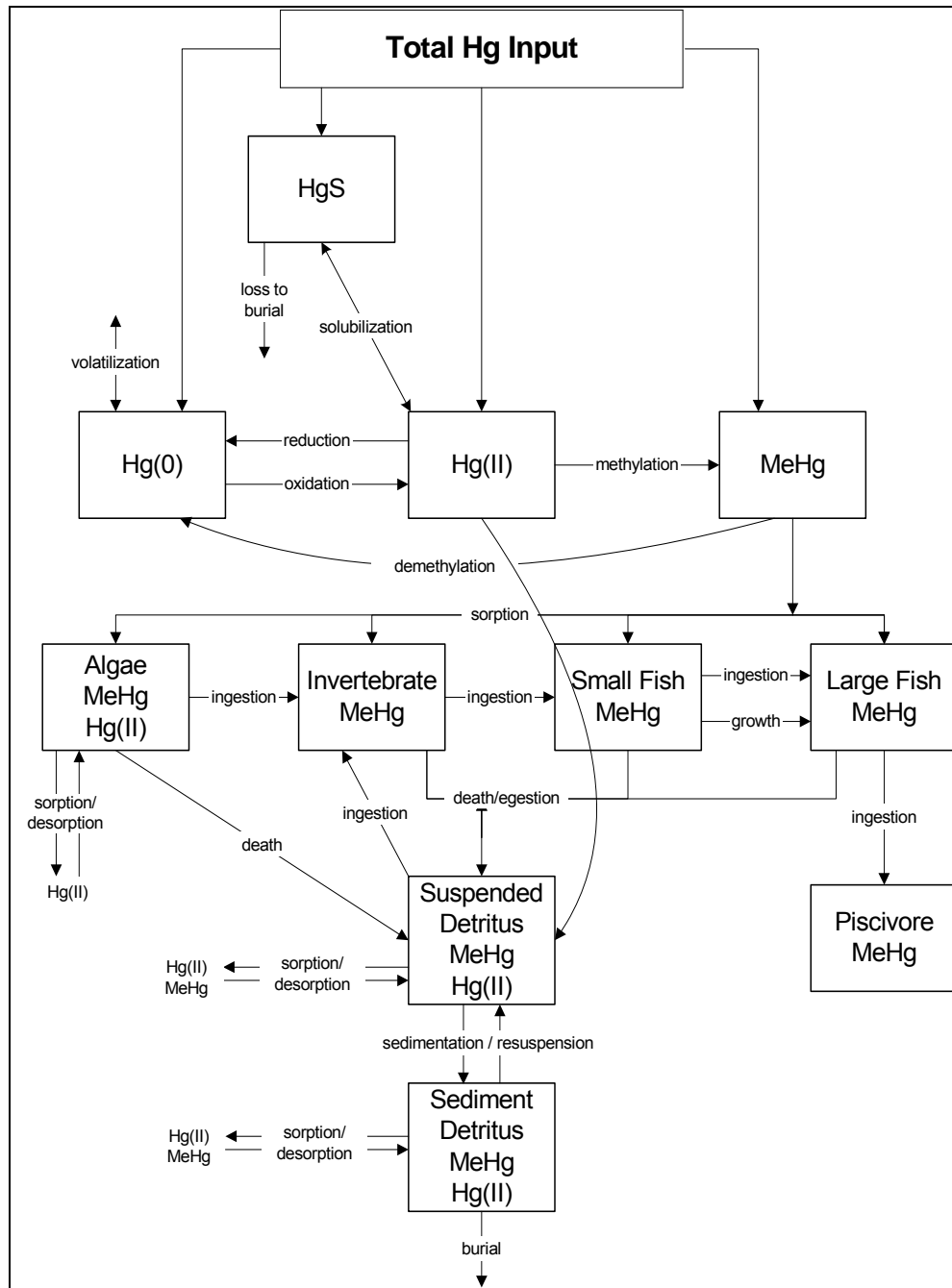
Figure 33. Generalized Lake Mercury Cycle from Hudson et al. (1994)

A.   Review of Method Used for Watershed Loading

As discussed in Section V, watershed loading of mercury and sediment was estimated from load duration curves developed from empirical data (Tetra Tech, 2006). 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 load and suspended sediment concentration (SSC) load. To determine the methyl-mercury load, relationships were established based on total mercury and methyl-mercury data collected in each of the watersheds. For corresponding measurements of total and dissolved mercury, equations were developed providing estimation of daily methyl-mercury loads as a function of total mercury loads for each watershed (Section 3.2.2.2, Modeling Report, Tetra Tech, 2006).   The difference between total mercury and methyl-mercury load was assumed to represent ionic mercury load indicating no significant load of elemental mercury. The SSC 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.

B.   Methodology for Loading to Alamo Lake

Loading to Alamo Lake is represented by three water segments and three sediment segments (Figure 34).   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 (2) underlain by a shallow sediment segment (5). The downstream portion of the lake is represented by two water layers, surface (1) and subsurface (3) segments, because the deeper waters in this section are subject to thermal stratification and oxygen depletion. The shallow sediment segments (4 and 5) 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 centimeters. The surficial sediment layers are in turn underlain by a common deep sediment layer (17), which allows for sequestration and deep burial.
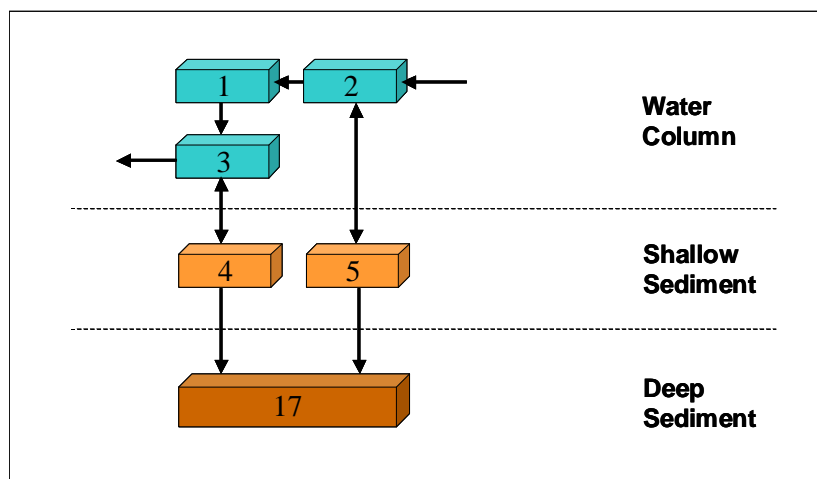
Figure 34. Linkage of WASP Model Compartments (Tetra Tech, 2006)

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 35).   The model provides a full description of transformations between mercury species and exchanges between compartments and with the atmosphere.

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 lake segments 1, 2, and 3 respectively.   The actual observed range in the water column was 5.7 to 10.1 milligrams per liter (mg/L). Shallow surface sediment DOC was set to 12 mg/L.
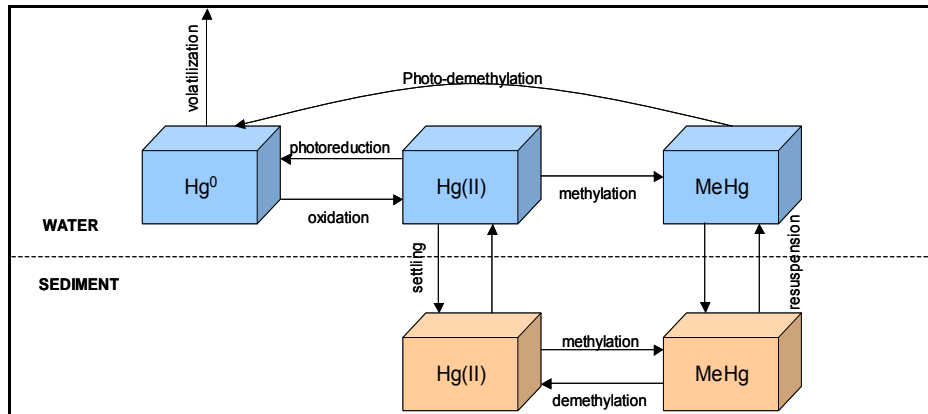
Figure 35. Model Representation of Mercury Transformation Kinetics
Tetra Tech, 2006)

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 throughout the water column were based on Stokes law considerations and set to 20 meters per day (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 centimeters per year (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. Model projections and supporting observations of sediment versus water mercury levels are in agreement.   While sediment mercury is suspended, it remains active in the transformation process, whereas, when sediment drops out of the water column, it appears to become sequestered and buried over time.

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 WASP5/TOXI5 results, Table 10 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.   With the exception of methyl-mercury in sediment, the average-condition fit is quite close, as would be expected from the numerical optimization of parameters.

Table 10. 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	NA
Surface Sediment (Solid Phase)	Total Hg (ng/g)	29.39	41.92
	MeHg (ng/g)	1.81	0.62

Figure 36 shows the trajectory of the model over time during the 12 3/4 years of simulation for Segment 1, the downstream surface 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 runoff events. Such loads are followed by more gradual peaks in elemental and methyl-mercury as the incoming mercury load is processed in the water column. Figure 37 shows that the dynamic for buildup of sediment methymercury increases over time, but plateaus at a concentration of about 4.25 ng/g as additional sediments enter the lake and the process restarts.
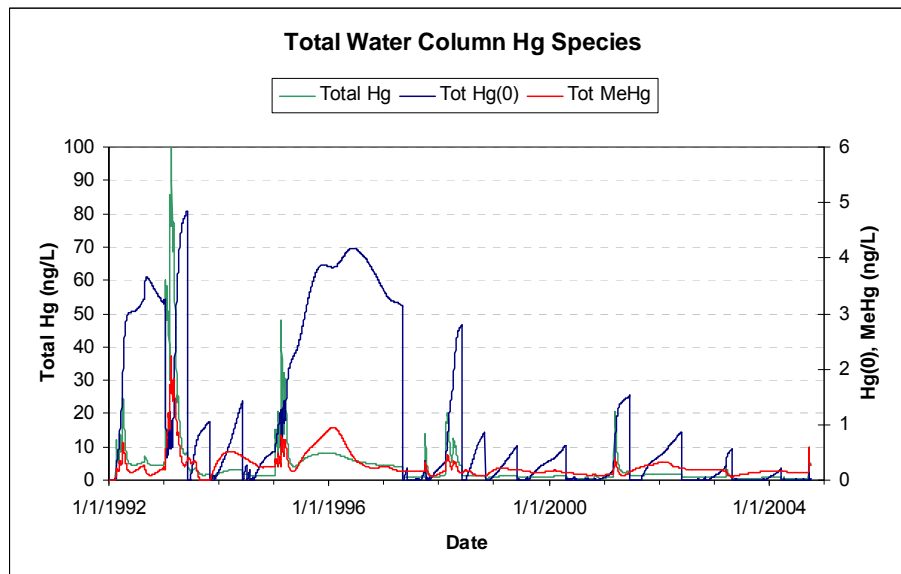
Figure 36. 12-yr Model Trajectory for Mercury in Segment 1
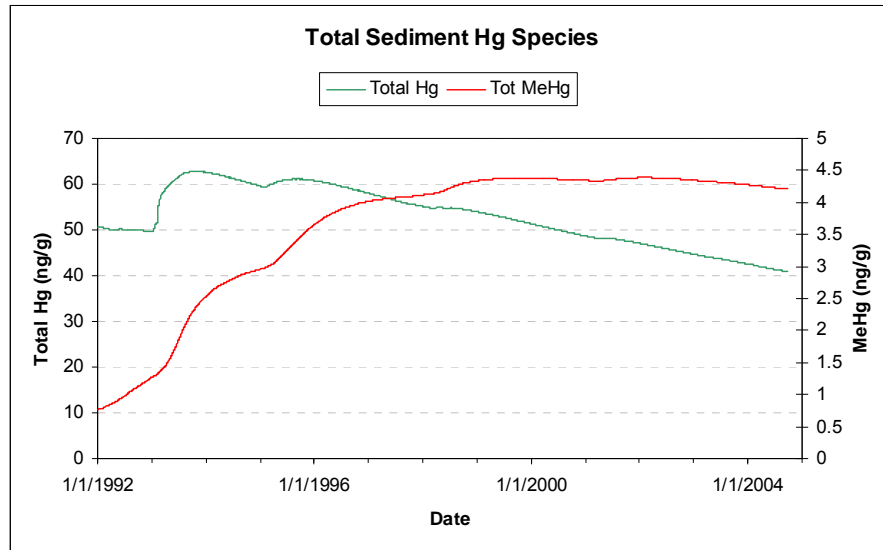
Figure 37.   WASP Model Trajectory for Mercury in Surface Sediment, Segment 4 (shallow sediment by dam)

C.   Lake Sampling Results; Resetting 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. Flows in the Santa Maria River near 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 near Bagdad). The implication of the model is that elevated total mercury concentrations in Alamo likely persisted throughout the summer of 2005, coupled with increasing methyl-mercury concentrations.

Sample results from Alamo Lake in August 2005 quantitatively confirm the model predictions regarding lake mercury status.   Most notably, both total mercury and methyl-mercury 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 methyl-mercury concentrations with depth for sample site BWALA-A (near dam) in 2005 are shown in Figure 38 along with the results from the September 2003 event at the same site.
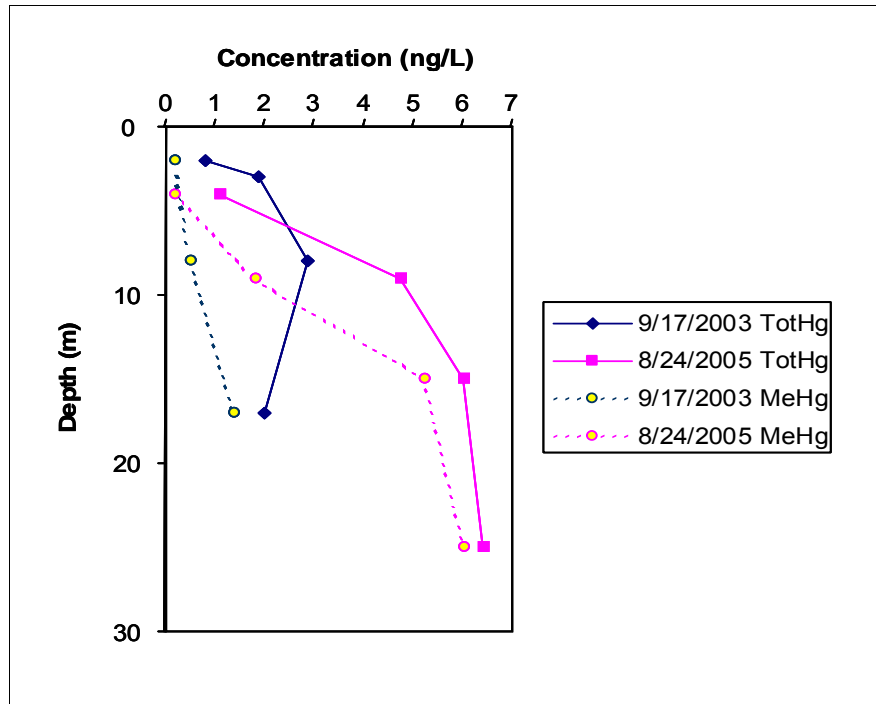
Figure 38. Comparison of 2005 and 2003 Mercury Samples at
Station BWALA-A (Alamo Lake near Dam)

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 methyl-mercury concentrations in August 2005 were higher than any previously monitored in Alamo Lake – but consistent with model predictions for methyl-mercury concentrations after earlier large inflow events, such as occurred in the early to mid-1990s. Similar, but less dramatic increases in methyl-mercury concentrations are also evident at the mid-lake and upper-lake stations.

Interestingly, although the concentration of total mercury in sediment at BWALA-A in 2005 was higher than previous years (76.64 ng/g as opposed to 40-50 ng/g), corresponding concentration of methyl-mercury in sediment was not elevated, confirming the modeled dynamic seen in Figure 37.

Elevated concentrations of methyl-mercury in the water column 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 increases the concentration of sulfates in the lake, which provide a substrate for production of methyl-mercury through sulfur-reducing bacteria. Controlling the rapid increases in lake stage might reduce the rate of methyl-mercury 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.

VIII.   LINKAGE 2: LAKE LOADING & FISH IMPAIRMENT

A.   Relationship of Total Mercury to Methyl-mercury Loading

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 total monomethyl mercury. 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 requires 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 12-plus year simulation period. This enables examination of the extent of load reduction in fish tissue required to achieve a specified level of methyl-mercury concentrations in the lake. As fish bioaccumulate mercury over their life spans, the most relevant target for evaluating load reductions (aside from fish tissue) is the average methyl-mercury 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 in-lake kinetics. 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 39. As expected, the response is linear, but differs slightly by lake segment (Segment 1 surface by dam; Segment 2 surface by inflow; Segment 3 deep by dam).

A complete removal of watershed loads is predicted to result in methyl-mercury 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 direct atmospheric loads to the lake. Reading the graph in Figure 39, for example, if a 50 percent reduction in average exposure concentrations of methyl-mercury were needed, that would require an approximately 59 percent reduction in watershed loads.
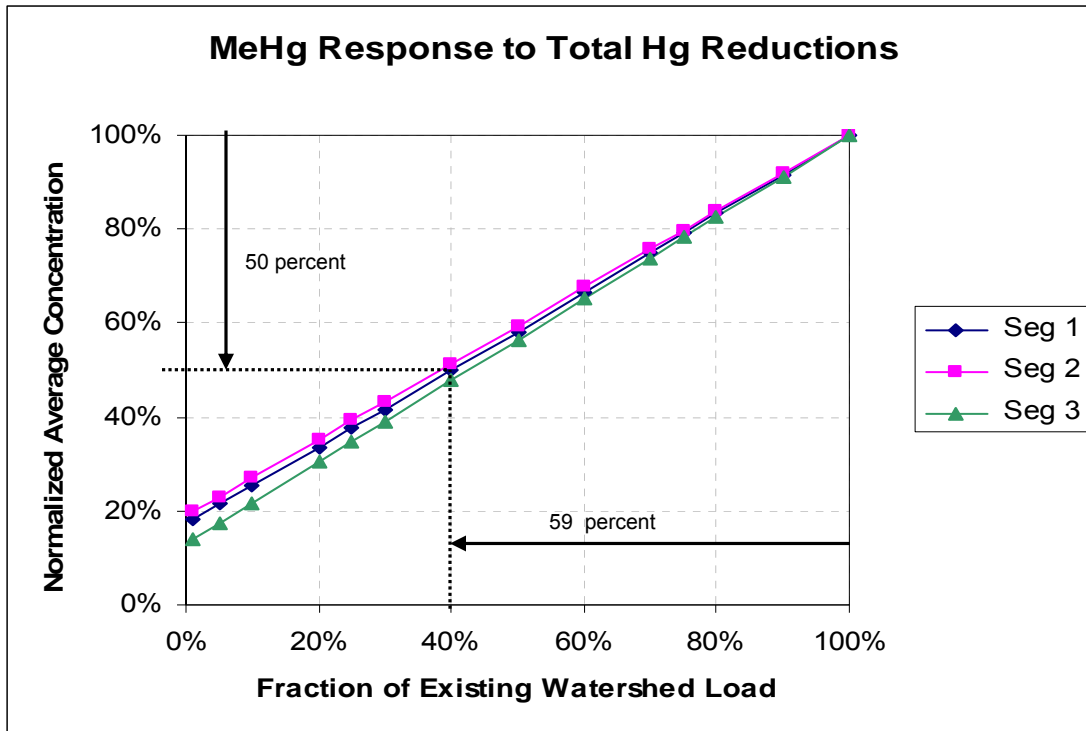
Figure 39. Response of Average Methyl-mercury Concentrations in the Water
Column of Alamo Lake to Reductions in Watershed Load

Summarizing, 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 percent. Most atmospheric deposition occurs as dry deposition. The calibrated water quality model is in general agreement with available data from Alamo Lake. Input 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 ideal for mercury methylation, due to the presence of dissolved organic carbon, a drop in pH, and presence of sulfur-reducing bacteria under anoxic, reducing conditions.

B.   Modeling Changes in Inflow/Outflow

Modeling changes in inflow/outflow to/from Alamo Lake results in relatively minor changes to methyl-mercury concentrations; in the near-dam surface segment they decrease by about 9 percent on average, but are not always lower, particularly after large inflow events (Figure 40). Methyl-mercury in the upstream segment decreases by about 3 percent on average, while the concentration in the bottom water increases by about 3 percent. The analysis is approximate without a high-resolution hydrodynamic model that can evaluate the effects of changing discharge location on lake stratification patterns.
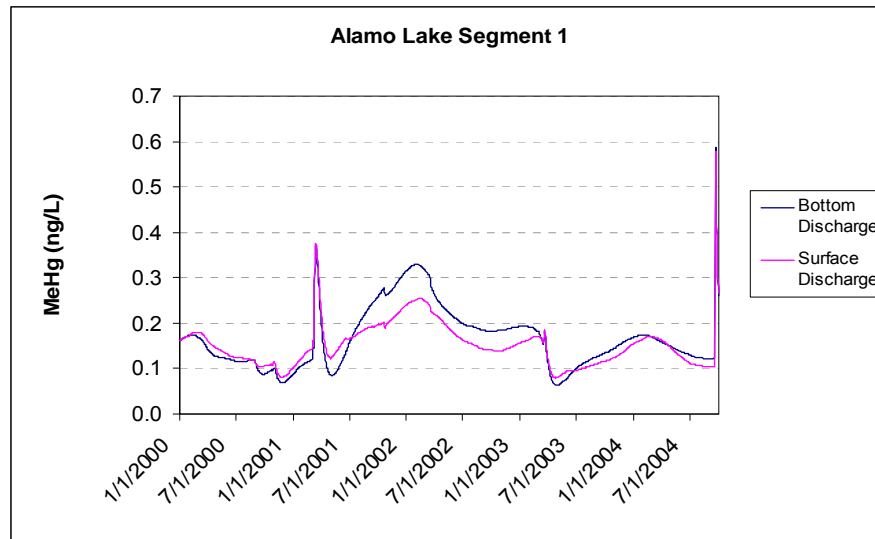
Figure 40. Modeled Changes to Inflow/Outflow

C.   Derivation of Bioaccumulation Factors

Sufficient data on population dynamics, feeding preferences, and mercury concentrations in lower trophic levels are not available 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 (TL-4), including largemouth bass, the highest TL-4 fish predator in Alamo Lake, the tissue concentration generally increases with age and length, though there was scatter in the relationship. Use of the "simple method" for deriving bioaccumulation factors (BAFs) does not account for length/age effects.

The simple BAF equation is: $BAF = C_T/C_W * 10^6$

> Where:
> > C_T = MeHg concentration in the fish tissue, mg/kg
> > C_W= MeHg concentration in the water, ng/L

Application of the simple BAF equation for Alamo Lake largemouth bass results in a BAF of 2.1 x 10^6 [0.74 mg/kg (C_T)/ 0.35 ng/L (C_W) * 10^6].

For comparison, Tetra Tech consulted a method put forth by Brumbaugh et al. (2001), which 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 methyl-mercury concentration in water:

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

For Alamo Lake, the model simulated average methyl-mercury concentration in water for 2002-2004 is 0.20 ng/L. Application of the Brumbaugh equation yields a value of 1.963 for Ln[Hg-fish/length] (mg/kg/m). The predicted fish tissue mercury concentration, at the mean length of 367.2 mm, is 0.721 mg/kg which agrees closely with the observed geometric mean concentration of 0.725 mg/kg.

There may be additional factors contributing to the scatter discussed earlier in Figure 11, such as fish population dynamics and localized habitat limitations, effects of wetting and drying of sediments, specificity in food choice and relative vulnerability by age class or sex to periodic inundation, drying, and mercury loading.

The 2001 criterion document for methyl-mercury (EPA, 2001) presents BAFs for total methyl-mercury in biota as a function of dissolved methyl-mercury in water. However, the majority of the data are summarized from information on total mercury in tissue with the assumptions that dissolved methyl-mercury is 61.3 percent of total methyl-mercury, methyl-mercury 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 methyl-mercury are expected to be more accurate than predictions of dissolved methyl-mercury. Therefore, BAFs for TL-2 (zooplankton and benthos) and TL-3 (forage fish) were converted to a basis in which total mercury in biota is predicted from total methyl-mercury in water, using the median dissolved methyl-mercury BAF value as a starting point. EPA (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 higher 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 methyl-mercury is 3.2 percent of total mercury in the water column. It therefore makes sense to re-express the BAF (or bioconcentration factor, BCF) given in EPA (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 mercury and 0.20 ng/L methyl-mercury. The median BAF values and resulting predicted tissue concentrations resulting from a water column methyl-mercury concentration of 0.20 ng/L are shown in Table 11 for TL-1 through TL-3, in addition to the TL-4 BAF. The table also shows results obtained from limited sampling of plankton (TL-1) and benthos (TL-2) by ADEQ in September 2004. Crappie and catfish mercury levels were fairly high, so they may actually be filling a niche between TL-3 and TL-4.

Table 11. Methyl-mercury 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)
TL1: Phytoplankton	5.87×10^3 (total Hg)	0.00944 (dry weight)	0.0054 (dry weight)
TL-1: Zooplankton	1.67×10^5 (total MeHg)	0.0334 (wet weight)	NA
TL-2: Benthos	2.5×10^5 (total MeHg)	0.0515 (wet weight)	0.0525 (wet weight)
TL-3: Forage Fish	6.84×10^5 (total MeHg)	0.137 (wet weight)	NA
*TL-3.5 Crappie & Catfish	2.9×10^6 (total MeHg)	NA	0.58 (wet weight)
TL-4: Piscivores	2.74×10^7 (total MeHg)	0.721 (wet weight)	0.74 (wet weight)

* Crappie in particular, may be functioning in the TL-4 category

The Brumbaugh method yields a TL-4 BAF higher than that derived from the simple method, but the limited observed data are generally consistent with the estimates of tissue mercury concentrations obtained from BAFs in Table 11. Further, the ratio of the mean TL-4 concentration of 0.74 to the estimated TL-3 concentration of 0.137 is 5.3, reasonably consistent with the median predator-prey factor of 5 reported by EPA (1997b). However, the actual ratio of the mean TL-4 largemouth bass (0.74) to the actual mean TL-3 black crappie & catfish (0.58) is only 1.3. Crappie, in particular, may be functioning in the Alamo system in the TL-4 category, or, perhaps the water column levels of high methyl-mercury exposes both species similarly.

IX.   TMDL ELEMENTS

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 (NB) 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:

$$TMDL = \sum WLAs + \sum LAs + MOS + NB$$

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.

B.   Numeric Targets

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 (A.A.C., R-18-11, Appendix B). 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 (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 12.

Table 12. 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
Agricultural Livestock Watering (AgL)	10.0	total recoverable
Fish Consumption (Human Health)	0.3 (mg/kg)	methyl-mercury

The dissolved standards for protection of aquatic life and wildlife include both an acute standard, applicable to short-term exposures and a chronic standard, applicable to longer-term exposures. Therefore, the most stringent water column standard is 0.01 ug/L or 10 ng/L.

C.   Narrative Standards

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

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

A (1) Settle to form bottom deposits that inhibit or prohibit the habitation, growth, or propagation of aquatic life or that impair recreational uses; and,
A (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 and Listing of Impairment

The lake was assessed as inconclusive by ADEQ in the 2002 305(b) Water Quality Assessment. However, EPA listed Alamo as impaired for mercury in fish tissue based on the issuance of a consumption advisory.

Fish consumption advisories are issued based on assessment protocol that evaluates relative risk by category: 1) small children, 2) women of child-bearing age, 3) other adult women, and 4) adult men. Based on the EPA listing, an advisory was issued jointly by ADEQ and AGFD in 2002, and can be found on the AGFD web site. The advisory is summarized here:

Largemouth bass and Black crappie;
· Children under the age of six - no consumption
· Women of child-bearing age - one 8-ounce fish meal per month
· All other adult women - three 8 ounce meals per month
· Adult men - four 8-ounce meals per month

Channel catfish:
· Children under the age of six - no consumption
· Women of child-bearing age - one 8-ounce fish meal per month
· All other adult women - five 8 ounce meals per month
· Adult men - six 8-ounce meals per month

E.   Fish Tissue Criterion and Trophic Considerations

ADEQ formally adopted the 0.3 mg/kg fish tissue criterion for mercury in 2009. Modeling done by Tetra Tech, Inc. took the most conservative approach in using TL-4 fish species to derive target reductions necessary for achieving the 0.3 mg/kg. However, as previously mentioned, crappie in Alamo Lake also showed high mercury levels.

There are many factors affecting mercury bioaccumulation, including sulfate, sulfur-reducing bacteria, DOC, redox, and the specific structure and dynamics of a particular trophic system. Fish may fall into one trophic category part of the year, or for part of its lifespan, and another category as they age. A juvenile TL-3 or TL-4 can slide down a level as well as a very large predator in TL-3 can slide up a level, which may be the case with Alamo Lake crappie.

X.   TMDL TARGETS

A.   Trophic Level (TL) and Fish Consumption Risk

EPA cites the need to consider the trophic structure in setting TMDL reduction goals (*Guidance for Implementing the January 2001 Methyl-mercury Water Quality Criterion,* 2009).   Through application of TL-weighted analysis, TMDL goals can be tailored to reflect more realistic reduction goals that will ensure that the fishery as a whole will meet the tissue criterion. Using the same default trophic consumption factors as used in establishing the human Tissue Residue Criterion (TRC), ADEQ will derive a composite reduction goal for largemouth bass, black crappie, and catfish using the formula below:

$$C_{avg} = \frac{3.8 * C_2 + 8.0 * C_3 + 5.7 * C_4}{(3.8+8.0+5.7)}$$

Where:

C_2 = average weighted geometric mean mercury concentration for TL-2
C_3 = average weighted geometric mean mercury concentration for TL-3
C_4 = average weighted geometric mean mercury concentration for TL-4

The calculation apportions the 17.5 g fish/day national default consumption rate into: 5.7 g/day of TL-4 fish, 8.0 g/day of TL-3 fish, and 3.8 g/day of TL-2 fish.   There are no TL-2 fish data, so Table 13 summarizes TL-3 and TL-4 fish tissue data from Alamo Lake and shows trophic-weighted geomeans.

Table 13. Trophic-weighted Geomeans

Trophic Level	TL-4	TL-3	TL-3	TL-2
Fish Species	Largemouth Bass	Black Crappie	Catfish	none
Number of samples	38	5	4	NA
Species mercury geomeans	0.74	0.75	0.42	NA
Trophic level weighted geomeans	0.74	0.59		NA

B.   Mercury Reductions Needed

Based on 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 methyl-mercury concentrations.   Thus, the reduction target in fish can be interpreted as a reduction target in water column methyl-mercury concentration.   This assumption has been corroborated through modeling. The TMDL will be based on reductions necessary to achieve the combined TL-4 and TL-3 fish tissue criterion of 0.3 mg/kg methyl-mercury.

Based on the formula cited in Section A. above, the trophic-derived assessed fish tissue concentration is:

$$\frac{8.0 * 0.59 + 5.7 * 0.74}{13.7} = 0.66 \text{ mg/kg}$$

The trophic-derived target ratio is: 0.30/0.66 = 0.46, therefore, the needed reduction in methyl-mercury is 54 percent (100 percent current minus 54 percent = 46 percent).   From the relationship in Figure 39, the associated reduction needed in total mercury is 61 percent (100 percent current minus 61 percent = 49 percent).

C.   Critical Conditions

As discussed above, a 61 percent watershed load reduction in total mercury is required to meet the 54 percent water column reduction target for methyl-mercury in Alamo Lake. The watershed load 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. There are very few locations within the Alamo watershed where flow is perennial. Most streams are ephemeral, and those that do flow, flow seasonally or are interrupted. The most critical flow condition for transport of mercury to Alamo Lake is the fall-winter storm period, as seen in 2004-2005, in which there were three storms greater than the 10 year-24 hour event of 3.10 inches precipitation. "Wet year" allocations will be derived using data from this high flow season. (Figure 41), in which the average flow was 925 cfs.
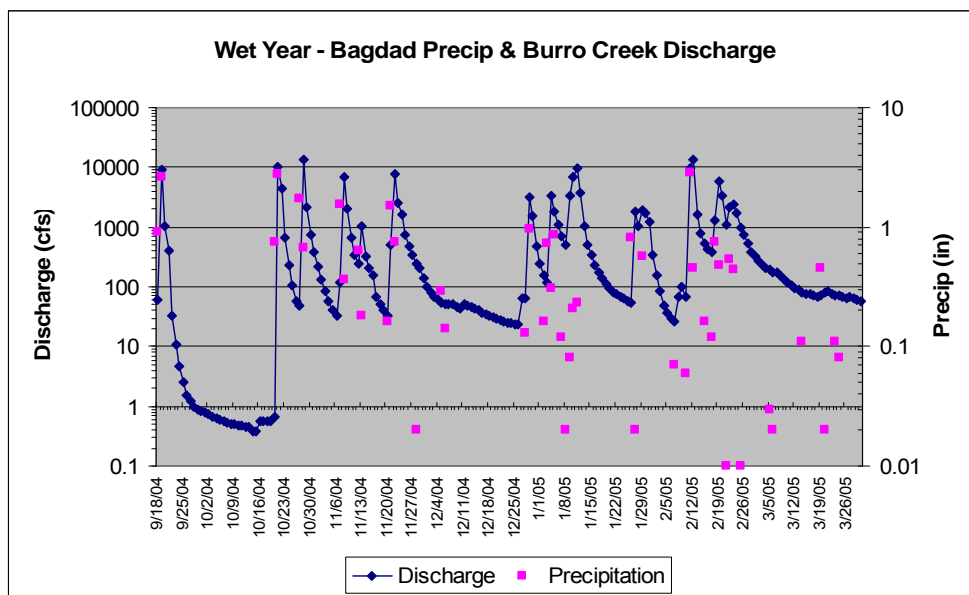
Figure 41.   2004/2005 Seasonal Flow for Wet Yr

Allocations for the annual average flow condition will be based on the Tetra Tech, (2006) analysis of flow data between 1990 and 2004. The 12-year cross-section of flow data corresponds well with the 40-year annual averages (Figure 42). Relative flow distribution will be helpful in setting priorities for TMDL implementation, in combination with empirical data on mercury in water, mercury in relationship to suspended sediment, and suspended sediment loading in general.
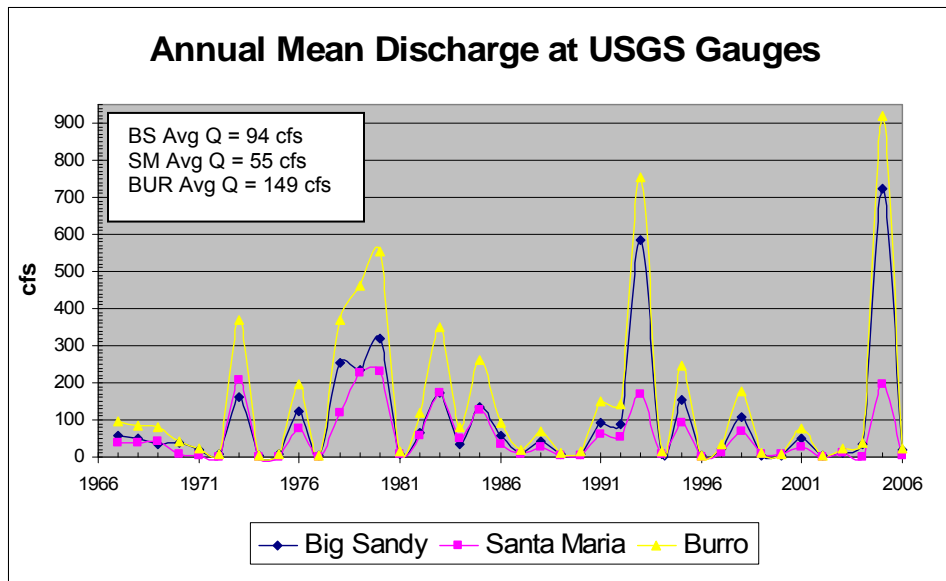
Figure 42. Average Annual Flows at the three USGS Gauges (1967-2006)

D.   Wasteloads and Wasteload Allocations (WLAs)

1.   Permitted Aerial Sources

According to ICF International (August 5, 2008), AZ North Star Steel (NNSA) in Kingman, Arizona, was a major source of mercury emissions from 1996 to 2003, when the plant ceased operation due to economic problems. The plant included a melting facility with a production capacity of 650,000 tons annually and a rebar and wire rod rolling facility capable of processing more than 500,000 tons per year.

Modeling of emissions data by ICF International suggested North Star contributed 99.8 percent of total mercury emissions within Arizona in 2001. The airshed that includes Kingman would also include a portion of the upper Big Sandy River watershed and Knight Creek, where relatively higher total mercury was found at an average of 1,449.0 ng/L.

The plant was subsequently purchased by NUCOR in 2003. By 2004, NUCOR decided to reopen only the rebar and wire rod rolling portion of the operation.   An air permit was issued to NUCOR in the spring of 2010. The plant is no longer classified as a Clean Air Act Title V major polluter and will not receive a wasteload allocation in this TMDL.

2. Arizona Pollution Discharge Elimination System (AZPDES)

There are currently four individual AZPDES point source discharge permits in the Alamo watershed. Three permits include mercury monitoring within the Big Sandy watershed: 1) Blue Beacon #AZ0023035, 2) Blake Ranch #AZ0023507, and Petro Stopping Center (Petro) #AZ0022756. Two of these facilities are truck wash facilities. Petro receives wastewater from the other two facilities, treats the wastewater and discharges to a tributary of Knight Creek, east of Kingman. These permits require only assessment monitoring for mercury and do not carry

actual permit limits for mercury. Both the tributary and Knight Creek are ephemeral washes and are unlikely to reach Alamo Lake itself. However, during extreme flow events, such as occurred in 2004 and 2005, Knight Creek contributed substantial flow to the Big Sandy River. Because these three facilities currently do not have discharge limits for mercury, they will not receive separate allocations at this time.

The fourth permitted facility is the Freeport McMoRan Bagdad Copper Mine (formerly Phelps Dodge Bagdad Copper Mine). The Freeport AZPDES individual discharge permit (#AZ0022268) applies to three outfalls that potentially discharge to Burro Creek and/or Boulder Creek, tributary to Burro Creek:

- Outfall #001: Copper Basin: mine process water, mine drainage, and stormwater resulting from storm events greater than the 100-year 24-hour storm event (capacity 39 MG)
- Outfall #003: Mulhulland Wash: tailings reclaim water, mine process water, or mine drainage and stormwater resulting from a 10- year 24- hour storm event
- Outfall #006: Mammoth Wash: tailings reclaim water, mine process water, or mine drainage and stormwater resulting from a 10- year 24- hour storm event

The Bagdad mine discharged from Outfall 003 and Outfall 006 in the spring of 2005, following the extremely wet fall and winter. Outfall 003 discharged to Mulhulland Wash (tributary to Boulder Creek) at an average reported rate of 0.57 MGD (0.88 cfs) for sixty days. Mercury data were collected twice, showing <0.2 ug/L (detection limit) both times. Outfall 006 discharged to Mammoth Wash (tributary to Burro Creek) at an average reported rate of 2.92 MGD (4.53 cfs) for ninety days. Three monitoring events showed average mercury at the detection limit of <0.2 ug/L (<200 ng/L) total mercury. The permit has been written to specify ongoing monitoring in the event of discharge and incorporate low-level lab mercury analysis.   Discharges from Outfall 003 and Outfall 006 are only permitted during wet periods, or during rain events >10yr/24hr event.

For the TMDL, the conservative point source mercury load for these discharges is calculated using the daily maximum permit limit of 0.02 ug/L, or 20 ng/L total mercury. The AZPDES permit specifies the mercury limit is to be met end-of-pipe, or at the point of discharge in the respective wash. Freeport McMoRan has stated that, for all intents and purposes, Outfall 001 is managed to be non-discharging. Based on their statement, the TMDL will not include a WLA for Outfall 001, however, any discharge from Outfall 001 must also meet permit discharge limits (0.02 ug/L).

Outfall #003   Mulhulland Wash (0.57MGD)
WLA (g/day)   = [Hg (ug/L)] * flow (cfs * conversion)
                   = 0.02 ug/L * 0.88 cfs * 24.47 = 0.430 g/day

Outfall #006   Mammoth Wash (2.92MGD)
WLA (g/day)   = [Hg (ug/L] * flow (cfs * conversion)
                   = 0.02 ug/L * 4.53 cfs * 24.47 = 2.22 g/day

3. General Permits, Current and Future Permittees

The purpose of Arizona's multi-sector general permit (MSGP) and construction general permit (CGP) is to protect the quality and beneficial uses of Arizona's surface water resources from

pollution in stormwater runoff resulting from mining, non-mining, and construction operations and activities. Under the Clean Water Act and Arizona Revised Statutes, it is illegal to have a point source discharge of pollutants that is not authorized by a permit, including stormwater runoff from industrial or construction sites to a water of the United States. To protect water quality, general permits require operators to plan and implement appropriate pollution prevention and control practices for stormwater runoff.

A concentration-based WLA equivalent to the applicable aquatic and wildlife water quality standard for mercury is established for existing and future permittees covered under the Non-Mining MSGP, Mining MSGP and Construction General Permits. Discharges to ephemeral streams will be assigned a WLA equal to 2.4 ug/L, the default A&We standard while those to intermittent or perennial waters will be assigned the A&W cold or warmwater standard of 0.01 ug/L.

The permitting agency may impose additional monitoring requirements to determine compliance in context with the general permit. Specific monitoring requirements and BMP requirements will be addressed in SWPPPs to be reviewed by the ADEQ Stormwater and General Permits Unit.

Industrial and construction activities covered by the MSGP or CGP where mercury is not considered a constituent of concern by ADEQ are not subject to the TMDL WLA provisions.

XI.   PROPOSED TMDLs

A.   Standards Attainment

This TMDL is calculated to meet the fish tissue standard of 0.3 mg/kg using the weighted trophic fish geomean approach.   The reduction targets have been established based on the relationship of linearity between increasing methyl-mercury in water and impairment to the food chain. Because the model demonstrated that virtually all mercury lost to sediment is not available, there is no sediment target proposed.   To ascertain downstream impacts, ADEQ and EPA Region 9 tested fish tissue from the lower Bill Williams River and Lake Havasu in 2007. Results showed very low levels of mercury, even in tissue from top predator species, such as striped bass, largemouth bass, and flathead catfish.   It appears that conditions in Lower Lake Havasu are not conducive to methylation and the fish tissue standard is being met.

B.   Review of TMDL Targets for Average and Wet Years

In the original 2006 Tetra Tech model, loads were partitioned between "dry", "normal", and "wet" conditions based on the flow history between 1992 and 2004. Due to the intermittent nature of stream hydrology (observed low flow percentiles from 20 percent for Big Sandy; 37 percent for Burro; 72 percent for Santa Maria), ADEQ dropped the "dry" designation completely, and reinterpreted "normal" or "average" to be the weighed average of the remaining flows.   Thus, "average" condition numbers in Table 13 do not match "normal" condition numbers in Tetra Tech, 2006. "Wet" year condition, as interpreted by Tetra Tech, corresponds closely with the 2004 and 2005 winter flows (from 95 percent to 99 percent), so ADEQ will apply the wet year loads as derived by Tetra Tech (Table 14).

Table 14. Existing Loads and Load Reductions

Sub-Watershed	Average Year Existing Load (g/year)	Reduction Needed	TMDL Average Year (g/year)	**TMDL Average Year (g/day)**	Wet Year Existing Load (g/yr)	Reduction Needed	TMDL Wet Year (g/year)	**TMDL Wet Year (g/day)**
Big Sandy River	5490*	61 %	2141	**5.87**	50,879	61 %	19,843	**54.36**
Burro Creek	5118*	61 %	1996	**5.47**	45,900	61 %	17,901	**49.04**
Santa Maria River	2935*	61 %	1145	**3.14**	14,224	61 %	5,547	**15.20**
Total to Alamo Lake	13543*	61 %	5182	**14.20**	111,003	61 %	43,291	**118.60**

* Note: weighted average of flow percentiles between 20 percent to 95 percent

C. Discussion of Margin of Safety (MOS) and Natural Background (NB)

This study has demonstrated that most watershed loading will occur during wet years. The decision to use both the weighted average condition and the 2004/2005 wet year condition to set the target reductions are conservative assumptions. Therefore, ADEQ proposes an additional 10 percent of the TMDL for the explicit MOS rather than a higher percentage (Table 15).

Table 15. Margin of Safety

Sub-watershed	TMDL Average Year g/day	MOS Average Year g/day	TMDL Wet Year (g/day)	MOS for Wet Year (g/day
Big Sandy River	5.87	0.587	54.36	5.44
Burro Creek	5.47	0.547	49.04	4.90
Santa Maria River	3.14	0.314	15.20	1.52
Total to Alamo Lake	14.2	1.42	118.60	11.86

In calculation of NB, ADEQ derived both aerial and soil background loads from relationships established by Tetra Tech modeling. Aerial background loads for each sub-watershed were calculated as a ratio of average sub-surface soil mercury to IEM analysis-projected load attributed to aerial deposition within each sub-watershed by the. ADEQ included a factor of 15 percent of average sub-surface soil mercury to account for leaching of mercury from the soil surface to the sub-surface, yielding an average pre-anthropogenic background soil value of 17 ng/g. The ratio of 17 ng/g to 276 ng/g, the IEM-projected surface soil concentration after 50 years, is 0.062, or 6.2 percent of long-term aerial loading as natural background.

Soil background load for each sub-watershed was calculated to be approximately 13 percent of the total in average flow conditions and 10 percent in wet conditions. For both average and wet period loading, the soil background load was combined with the aerial background load (Table 16) and subtracted from each sub-watershed reduction goal. All values were converted to g/day.

Table 16. Natural Background

Sub-watershed	Existing Load* Average Year g/day	Average Year Soil Background 13 % of existing (g/day)	Average Year Aerial Background 6.2 % of existing (g/day)	Total Background for Average Year	Existing Load* Wet Year g/day	Soil Background 13 % of existing (g/day)	Aerial Background 6.2 % of existing (g/day)	Total Background for Wet Year
Big Sandy River	5.87	0.763	0.364	1.13	54.36	7.067	3.370	10.437
Burro Creek	5.47	0.711	0.339	1.050	49.04	6.375	3.041	9.416
Santa Maria River	3.14	0.408	0.195	0.603	15.20	1.976	0.942	2.918
Total to Alamo Lake	14.2	1.846	0.8804	2.726	118.60	15.418	7.353	22.771

*   Note: taken from existing load values given in g/day in Table 15

D.   TMDL Tables for Sub-watersheds and Alamo Lake

WLA loads reflect a combination of permitted concentrations converted to loads under Individual AZPDES# AZ0022268, and concentration-based WLAs for storm water discharges covered by Multi Sector and Construction General Permits.   Tables 17 and 18 show the final TMDL equations for each sub-watershed plus the composite TMDL for loading to Alamo Lake.   The Alamo Lake TMDL is the sum of the three watershed loads for average or wet years.

Table 17. TMDL Equations by Sub-watershed Drainage and Flow Condition

Burro Creek Average Year	TMDL (g/day) = 3.87 (LA) + 0 (WLA)* + 1.05 (NB) + 0.55 (MOS) = 5.47 g/day
Burro Creek Wet Year	TMDL (g/day) = 32.07 (LA) + 2.65 g/day (WLA)* + 9.42 g/day (NB) + 4.90 g/day (MOS) = 49.04 g/day
Big Sandy River Average Year	TMDL (g/day) = 4.15 g/day (LA) + 0 g/day (WLA) + 1.13 g/day (NB) + 0.59 g/day (MOS) = 5.87 g/day
Big Sandy River Wet Year	TMDL (g/day) = 38.48 g/day (LA) + 0 g/day (WLA) + 10.44 g/day (NB) + 5.44 g/day (MOS) = 54.36 g/day
Santa Maria River Average Year	TMDL (g/day) =2.23 g/day (LA) + 0 g/day (WLA)* + 0.60 g/day (NB) + 0.31 g/day (MOS) = 3.14 g/day
Santa Maria River Wet Year	TMDL (g/day) = 10.76 g/day (LA) + 0 g/day (WLA)* + 2.92 g/day (NB) +1.52 g/day (MOS) = 15.20 g/day

* Includes concentration based WLA for General Permit discharges

Table 18. TMDL Equations for Alamo Lake by Flow Condition

Alamo Lake Average Year	TMDL= 10.05 (LA) + 0 (WLA)* + 2.73 (NB) + 1.42 (MOS) = 14.2 g/day
Alamo Lake Wet Year	TMDL = 81.32 (LA) + 2.65 (WLA)* + 22.77 (NB) + 11.86 (MOS) = 118.6 g/day

* Includes concentration based WLA for General Permit discharges

E. Wildlife Targets and Threatened and Endangered (T&E) Species

The Bald Eagle, on the federal Threatened and Endangered Species list until 2007, is the highest level avian predator at Alamo Lake. The U.S. Fish and Wildlife Service (USFWS) evaluated the fish tissue mercury criterion of 0.3 mg/kg in light of protectiveness for threatened and endangered species in 2003 and concluded that taking the highest trophic level approach would be protective of Bald Eagles (USFWS, 2003). The Bill Williams National Heritage River web site states that the area also provides important habitat for endangered birds such as the southwestern willow flycatcher, brown pelican, Yuma clapper rail, and secretive yellow-billed cuckoo, a candidate

species. In the 2003 USFWS evaluation, the Yuma clapper rail was also cited as protected at the 0.3 mg/kg mercury target; the other species are not piscivores. An ADOT planning document prepared in 2008 cites the following additional piscivores as Wildlife (Species) of Special Concern, a designation made by the AGFD: Clark's Grebe, Great Egret, and Snowy Egret. These species would likely consume only smaller TL-3 fish and would also be protected.

F. Monitoring Plan

Fish tissue will continue to be collected every few years to assess progress made in reducing the weighted trophic level fish tissue mercury for TL-4 and TL-3.   ADEQ will work with AGFD to collect a broad spectrum of fish species and sizes. The ADEQ ambient lake monitoring program and/or the TMDL targeted monitoring program will continue to sample Alamo Lake every few years.   In addition to monitoring mercury, ADEQ has scheduled a TMDL for low DO, high pH, and ammonia at Alamo Lake to begin in 2012.

G. Implementation Plan

ADEQ will develop an implementation plan for the mercury TMDL within six months of TMDL approval.

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