

Mercury Total Maximum Daily Load  
for Parker Canyon Lake, Arizona  
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## **EXECUTIVE SUMMARY**

Parker Canyon Lake is a mesotrophic reservoir located in southern Arizona approximately 12 miles north of the United States-Mexico border. In 2001, it was discovered that resident fish of Parker Canyon Lake exceeded U.S. Environmental Protection Agency (USEPA) recommended limits of 0.3 mg/kg MeHg in fish tissue. The high mercury concentrations in the fish tissue required that Parker Canyon Lake be classified as an impaired waterbody and that a Total Maximum Daily Load (TMDL) for mercury be determined. A TMDL is the assimilative capacity or loading capacity of a waterbody.

Mercury loading into the lake Parker Canyon Lake Watershed was estimated using the USEPA's Geographical Information System (GIS) software program Watershed Characterization System (WCS). A water balance was developed to estimate losses and gains from the watershed. A new water quality goal for the lake was developed using a regional logarithmic bioaccumulation factor. Mercury transport within the lakes was modeled using the USEPA's software program Water Quality Analysis Simulation Program Version 7 (WASP7) and calibrated with water quality data from Arizona Department of Environmental Quality. Important results of the TMDL are:

<b>Existing Mercury Loading</b>	<b>Reduction Required</b>	<b>Total Maximum Daily Load (TMDL)</b>	<b>Waste Load Allocation (WLA)</b>	<b>Load Allocation (LA)</b>	<b>Margin of Safety (MOS)</b>
22.5 g/yr	83%	3.82 g/yr	0 g/yr	3.44 g/yr	0.38 g/yr

The Parker Canyon Lake TMDL study revealed that most of the mercury loading into Parker Canyon Lake results from atmospheric deposition with 28.9 percent being directly deposited onto the lake surface. Due to the high lake deposition fraction, the TMDL can not be achieved until atmospheric levels of mercury decrease. Recommendations for the Parker Canyon Lake include additional monitoring and continued fish consumption advisory warnings for the public.

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**LIST OF SYMBOLS AND ABBREVIATIONS**

<i>BAF</i>	Bioaccumulation factor	L/kg
<i>BW</i>	Adult human body weight	kg
<i>C<sub>fish</sub></i>	Concentration of MeHg in fish tissue	mg/kg
<i>C<sub>water</sub></i>	Concentration of MeHg in water column	ng/L
<i>FI</i>	Fish intake at trophic levels 2 to 4	gram /day
<i>LA</i>	Load Allocation	gram
<i>L<sub>fish</sub></i>	Length of fish in	mm
<i>MOS</i>	Margin of Safety	gram
<i>RfD</i>	Reference dose	MeHg/kg body weight-day
<i>RSC</i>	Relative source contribution	MeHg/kg body weight-day
<i>TMDL</i>	Total Maximum Daily Load	gram
<i>TRC</i>	Fish tissue residue criterion	mg/kg
<i>WLA</i>	Waste Load Allocation	gram

A&Wc	Aquatic and Wildlife Cold Water
ADEQ	Arizona Department of Environmental Quality
AgI	Agricultural Irrigation
AgL	Agricultural Livestock Watering
AMSL	Above Mean Sea Level
AZGFD	Arizona Game and Fish Department
BAF	Bioaccumulation Factor
BASINS	Better Assessment Science Integrating Point and Non-point Source
CRWQCB	California Regional Water Quality Control Board
CWA	Clean Water Act
DO	Dissolved Oxygen
DOC	Dissolved Organic Content
FBC	Full-body Contact
FC	Fish Consumption
GIS	Geographical Information System
Hg(II)	Divalent Mercury
Hg <sup>0</sup>	Elemental Mercury
LA	Load Allocations
MAS	Mineral Availability System
MDN	Mercury Deposition Network
MILS	Mineral Industry Location System
MOS	Margin of Safety
MRLC	Multi-Resolution Land Characteristics
NADP	National Atmospheric Deposition Program
NC DWQ	North Carolina Department of Water Quality
NRCS	National Resource Conservation Service
OMWR	Ontario Ministry of Water Resources
STATSGO	State Soil Geographic
TL	Trophic Level
TMDL	Total Maximum Daily Load
TRI	Toxic Release Inventory
USBOM	United States Bureau of Mines
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USFS	United States Forest Service
USGS	United States Geological Survey
USLE	Universal Soil Loss Equation
WCS	Watershed Characterization System
WASP7	Water Quality Analysis Simulation Program Version 7
WLA	Wasteload Allocations
WRCC	Western Regional Climate Center
WRPLOT	Wind Rose Plot

# 1 Introduction

A Total Maximum Daily Load (TMDL) is a federally mandated study of pollutant loads into a waterbody in order to determine the best methods to reduce the pollutant loading. The Federal Clean Water Act (CWA), 33 United States Code Section 1251, establishes water quality standards and the TMDL program which is administered by the United States Environmental Protection Agency (USEPA). The USEPA's definition of a TMDL is a calculation of the maximum amount of a pollutant that a waterbody can receive and still meet water quality standards, and an allocation of that amount to the pollutant's sources. A TMDL is normally expressed as the sum of the suspect pollutant that can enter a waterbody within a unit of time and is the assimilative capacity of a waterbody of that pollutant. (USEPA 2006b; USEPA 2006c)

Mercury is a potential neurotoxin that is present in the environment from natural and anthropogenic sources. The most common source of natural mercury is from a mineral called cinnabar, HgS. Common sources of anthropogenic mercury are medical wastes, metal smelting processes, residue from mining activities that used mercury amalgamation, and combustion of organics. Another major source of anthropogenic mercury, especially in the southwest, is thought to be coal-powered power plants. Mercury undergoes various transformations in the environment to produce methylmercury, a form of mercury that is the most toxic to humans and wildlife. (USEPA 2006b)

Over 8,500 individual waterbodies located in 42 states have been reported as being impaired due to mercury contamination in 2004. Several lakes in Arizona have methylmercury content in fish tissue above the USEPA recommended safe level for human consumption of 0.3 mg/kg MeHg in fish tissue. One of these impaired lakes is Parker Canyon Lake. Located in southern Arizona, Parker Canyon Lake is a 50 ha reservoir jointly operated by Arizona Game and Fish Department and the U.S. Forest Service. Fish sampling conducted by Arizona Department of Environmental Quality

(ADEQ) for Parker Canyon Lake has shown an average MeHg concentration of 0.92 mg/kg in fish tissue with levels as high as 1.6 mg/kg. (ADEQ 2005; USEPA 2006b)

The intent of this TMDL report is to describe the logical steps taken to establish allowable mercury loading for Parker Canyon Lake in order to promote safe levels of mercury in fish tissue. Industry accepted techniques and practices using the most current publically available computer models were used during the development of the mercury TMDL for Parker Canyon Lake. Parker Canyon Lake's watershed was characterized using the USEPA's Geographical Information System (GIS) program Better Assessment Science Integrating Point and Nonpoint Sources (BASINS), mercury loading into the lake was calculated by USEPA's program Watershed Characterization System (WCS) and mercury transport modeled with USEPA's program Water Quality Analysis Simulation Program Version 7 (WASP7). Parker Canyon Lake was visited during the study to assist with site characterization. The models were calibrated with available water quality data from ADEQ. Conservative values and assumptions were used during all phases of TMDL development. (TetraTech 1999a; TetraTech 2005)



## 2 TMDL Requirements

CWA section 303(d) and the TMDL regulations published in 1985 in 40 CFR 130.2 and 130.7 and amended in 1992 require states and authorized tribes track waters not meeting water quality standards or have impaired uses. Section 303(d)(1) of the CWA requires states and tribes identify and establish priority ranking for impaired or suspected waters within their jurisdiction in a biennial report to the USEPA which is commonly called the 303(d) list. Items listed are required to have a TMDL study conducted as a step to reach attainment of water quality goals. After the USEPA approves a TMDL report the water body is classified as Category 4a waterbody where it remains until compliance with water quality standards is achieved. (NC DWQ 2004; USEPA 2006c)

The objective of a TMDL is to estimate allowable pollutant loads so that limits may be imposed and action taken to restore water quality. In order to reach this objective, individual wasteload allocations (WLA) for point sources, load allocations (LA) for non-point sources, and a Margin of Safety (MOS) must be determined. The MOS accounts for the uncertainty in the relationship between pollutant loads and the quality of the receiving waterbody. The TMDL regulations state that a TMDL “can be expressed in terms of either mass per time, toxicity, or other appropriate measure.” Even though the terminology implies daily loading it is common that TMDLs be established on an annual basis. In addition to load allocations and safety margin a TMDL generally includes the following components: (NC DWQ 2004; USEPA 2006b)

- **Target Identification or selection of pollutant(s) and end-point(s) for consideration** - The pollutant and end-point are generally associated with measurable water quality standards.
- **Source Assessment** - Sources that contribute contamination should be identified and quantified.
- **Reduction Goal** - Estimation of reduction of pollutant loading needed to achieve water quality goal. Normally determined by water quality models.
- **Seasonal Variation** - The TMDL should consider seasonal variation in the pollutant loads and end-point.
- **Critical Conditions** - Conditions that occur infrequently that may result in the strictest loading requirements.

## 2.1 Mercury TMDL Development

Developing TMDLs for mercury impaired waterbodies raises unique technical and political issues. A major source of mercury contamination is from airborne mercury deposition that can originate from local, regional, and international sources. Identifying how each source contributes to the mercury load in the waterbody is often challenging and actually negotiating reduced emissions is unlikely due to economic pressures. Frequently, local environmental authorities do not have sufficient influence or power and must rely on the Federal Clean Air Act and international efforts to reduce mercury emissions. In addition to the political problems, two adjacent waterbodies may have different levels of mercury due to different water chemistry or geological structures. Detailed technical studies may be required to find the correct loading for individual waterbodies. (USEPA 2006b)

As of 2004, only 280 of the over 8,500 waterbodies with mercury impairment have had mercury TMDLs approved. The number of impaired waterbodies is expected to increase as more stringent USEPA recommended limits on mercury concentration in fish are implemented. Some states have begun to explore new techniques for quickly developing high quality mercury TMDLs. New approaches range from waterbody-specific TMDLs to regional-scale models. Tools that are currently in development to assist in future mercury TMDLs include screening level analyses of mercury loadings and sources using USEPA's Mercury Maps and more realistic water and air transport models. (USEPA 2006b)

Parker Canyon Lake has high levels of mercury in fish tissue even though water quality assessments for Parker Canyon Lake have shown acceptable levels of controlled pollutants. The first fish consumption advisory for Parker Canyon Lake was posted in 2002 as a result of the high mercury levels. When limited *fish consumption* or *no consumption* advisories are posted, the applicable waterbody are rated impaired. Parker Canyon Lake was listed in Arizona's *2004 Integrated 305(b) Assessment and 303(d) Listing Report*. This report meets the criteria listed in the CWA that requires that a mercury TMDL be developed for Parker Canyon Lake. (ADEQ 2005; NC DWQ 2004)

### 3 Mercury Properties and Environmental Transport

Mercury is a metallic element with the atomic number 80 and mass of 200.6 atomic mass units. The chemical and physical properties of mercury are highly dependent on the oxidation state of the element. Mercury can exist in three oxidation states: the elemental also known as metallic form, the mercurous form, and the divalent also known as the mercuric form. Mercurous mercury ( $\text{Hg}^{2+}$ ) is not stable and it is rarely found in the environment. Most of the mercury encountered in natural systems is in the form of inorganic mercuric salts and organomercurics, compounds that have a covalent C-Hg bond. The compounds most likely to be found under standard conditions are the mercuric salts ( $\text{HgCl}$ ,  $\text{Hg}(\text{OH})$ , and  $\text{HgS}$ ), the methylmercury compounds such as methylmercuric chloride ( $\text{CHHgCl}$ ) and methylmercuric hydroxide, ( $\text{CHHgOH}$ ) and other organomercurics such as dimethylmercury and phenylmercury. (USEPA 1997a)

Elemental mercury ( $\text{Hg}^0$ ) is a heavy, silvery-white liquid metal at standard temperature and pressure. The low vapor pressure of  $14 \text{ mg/m}^3$  causes  $\text{Hg}^0$  to volatilize at standard temperature meaning it is rarely found in nature as pure liquid. Approximately 90 to 95 percent of the mercury encountered in the atmosphere is elemental mercury vapor.  $\text{Hg}^0$  solubility in water is poor. (MDEQ 2000; USEPA 1997a; USEPA 1997b)

Divalent mercury ( $\text{Hg}(\text{II})$ ) can form numerous inorganic and organic chemical compounds. It is the primary form of mercury that is transported in the environment. It composes 97-99% of total mercury in soils.  $\text{Hg}(\text{II})$  is easily transformed to other forms of mercury. (MDEQ 2000; USEPA 1997a; USEPA 1997b)

Methylmercury ( $\text{CH}_3\text{Hg}^+$  or  $\text{MeHg}$ ) is the form of mercury that is the most concern to human health.  $\text{MeHg}$  compounds are highly soluble in water due to the strong hydrogen bonding capability with the hydroxide group.  $\text{MeHg}$  easily bioaccumulates in aquatic food webs.  $\text{MeHg}$  is also the most toxic form of mercury to birds, mammals, and aquatic organisms due to its strong affinity for sulfur-containing organic compounds such as proteins. (MDEQ 2000; USEPA 1997a; USEPA 1997b)

Mercury transformations in the environment involve biological, physical, and chemical processes. Figure 3.1 shows a flow diagram of the major transformation processes that occur in aquatic environments. Two competing biological processes called methylation and demethylation affect the concentrations of MeHg within an aquatic environment. Sulfate reducing bacteria convert sulfate to sulfides for energy and in the process methylate the mercury by converting Hg(II) into MeHg. Increased concentrations of sulfides and anaerobic conditions result in a significant increase in MeHg by increasing processes of the sulfate reducing bacteria. Dimethylmercury production occurs only in the marine environment via hydrolysis of MeHg. Demethylation occurs via biotic and abiotic mechanisms. Demethylation by microorganisms occurs in two-step process in which the methyl group is removed and then the Hg(II) is reduced to Hg<sup>0</sup>. Photo-demethylation is a process where MeHg is transformed into Hg<sup>0</sup> without the need for microorganisms to aid in the reaction. Finally, Hg<sup>0</sup> can transform into Hg(II) via oxidation processes. (MDEQ 2000; USEPA 1997a)

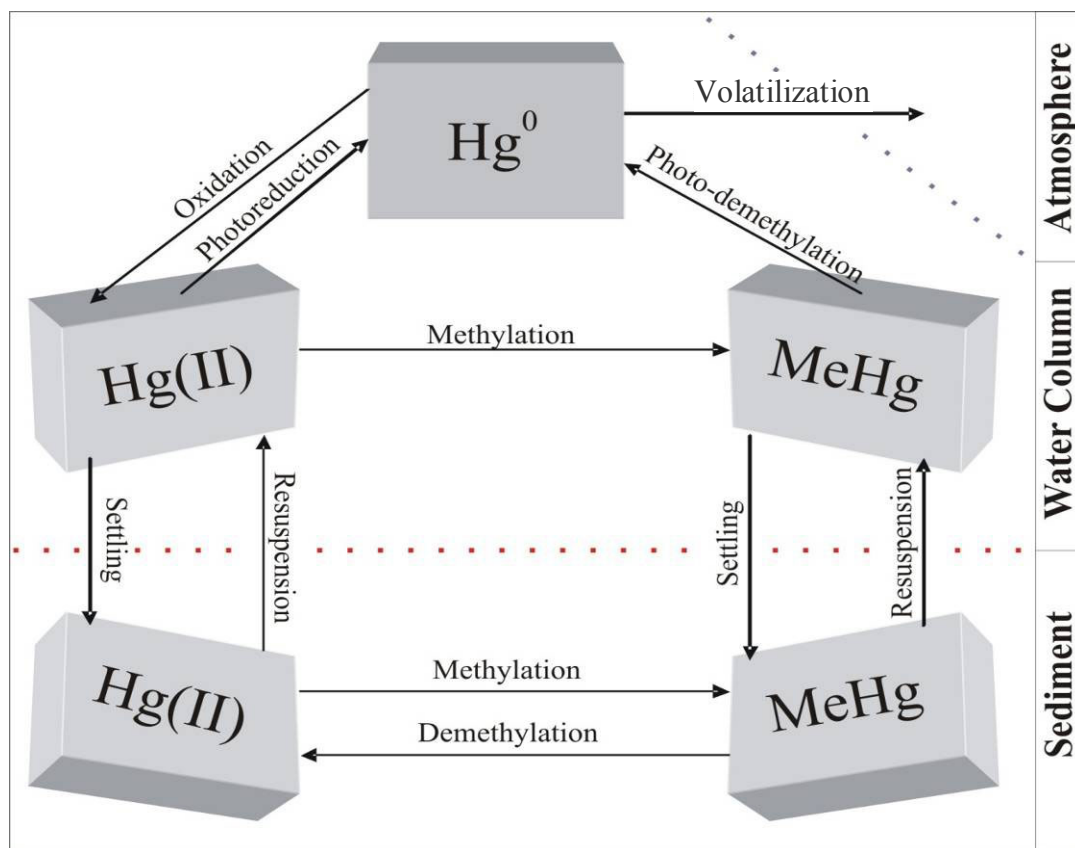


Figure 3.1 Aquatic transformation cycle of mercury.

MeHg production is often associated with sediments because most of a waterbody's Hg(II) and organic compounds are located in sediment. Additionally, sediment layers are the most likely to turn anaerobic which promotes sulfate reduction. Mercury contaminated sediments are a potentially dangerous mercury reservoir. There is a possibility that sediment bound mercury can recycle back into the aquatic ecosystem after decades following initial deposition. Benthic insects can also substantially increase transfer of MeHg since they may disturb contaminated sediment. (MDEQ 2000; USEPA 1997a; USEPA 1997b)

Approximately 5 to 10 percent of primary Hg(II) emissions are deposited within 100 km of the emission source. The remaining Hg(II) is transformed to Hg<sup>0</sup> which can remain vapor for years. Only a small fraction of mercury deposited on a watershed actually is transported into waterbodies. Once deposited, Hg(II) binds tightly to organic soil components. The deposited Hg(II) may volatilize to Hg<sup>0</sup> and be released back to the atmosphere as Hg<sup>0</sup>. Soil bound Hg(II) may also be methylated to form MeHg. The bound mercury may remain in the soil or be transported through the watershed via runoff and leaching. Mercury also enters the waterbody through direct deposition on the surface. (MDEQ 2000; USEPA 1997a)

The production of MeHg by microorganisms and the subsequent bioaccumulation in fish is the greatest human health concern associated with mercury transport. Bioaccumulation in fish results from the uptake of a mercury from the environment into biological tissue via direct contact with skin or gills and ingestion of contaminated food. MeHg can range from 10 - 90 percent of the total mercury in phytoplankton and zooplankton. In organisms higher in the food chain such as fish, MeHg generally comprises over 90 percent of the total mercury in fish. A contributor to MeHg bioaccumulation in fish is the long biological half-life of the compound in fish at 1-2 years versus a biological half-life of 1-3 months in humans and other warm-blooded creatures. (MDEQ 2000; USEPA 1997a)

Excessive mercury exposure has been well studied in both animals and humans. Biological membranes, including the blood-brain barrier and the placenta, allow MeHg to pass easily leading to death, neurological disorders, organ damage, impaired immune system, impaired growth and development and reduced reproductive ability. Developing fetuses are particularly sensitive to mercury exposure even though the mother may appear to be unaffected. (USEPA 1997a)

## 4 Description of Models

Two USEPA sponsored publicly available modeling software were used to develop the mercury TMDL for Parker Canyon Lake. The first model called the Watershed Characterization System (WCS) version 1.1 was used to determine mercury loading from the watershed. The second model called the Water Quality Analysis Simulation Program version 7 (WASP7) determined the fate of mercury in the lake.

### 4.1 Watershed Characterization System

The WCS is based on the USEPA's Better Assessment Science Integrating point and Non-point Sources (BASIN) Geographical Information System (GIS). WCS uses similar inputs as BASIN model and data files can be interchanged between the two programs with little modification. WCS requires ESRI's ArcView program with Spatial Analyst extension to operate. WCS was developed by Tetra Tech, Inc. for USEPA's Region 4. Additional modules are available for WCS that increase the capabilities to calculate sediment and mercury loading. The mercury loading module has been used extensively for mercury TMDLs in USEPA's Region 4 and for Arizona's Alamo Lake. (NC DWQ 2004; NC TetraTech 2005)

The WCS model is GIS based system that gives the user advantages not available to previous watershed characterization models. One advantage of calculating loads with a GIS based systems is that analysis results can be visualized thus reducing data review time. Another advantage of using a GIS based system is that the model can easily be transferred to a different region by changing the databases and spatial data files. The sources of the various databases and spatial data used for the mercury TMDL of Parker Canyon Lake are listed in Appendix A. (NC DWQ 2004; NC TetraTech 2005)

The WCS Mercury Tool is a GIS implementation of the IEM-2M watershed module. IEM-2M is the most common model used to determine mercury fate in the environment and the only transport model presented in the *1997 Mercury Study Report to Congress*. IEM-2M uses a two-dimensional grid and simplified mass balance and partition

equations to determine the fate of  $\text{Hg}^0$ ,  $\text{HG(II)}$ , and  $\text{MeHg}$  in a watershed. The model calculates deposition and subsequent mercury levels in soils or water based on first order equations. A difficulty in using the IEM-2M model is correctly selecting partition coefficients and other constants. Many of the USEPA listed values have a large range, up to five orders of magnitude, that can cause large variances in model results. (USEPA 1997a)

In addition to mercury levels calculated by IEM-2M methodology, the WCS Mercury Tool calculates erosion and sediment delivery rates using the National Engineering Handbook Area-based sediment loss and the United States Department of Agriculture (USDA) Universal Soil Loss Equation (USLE). The National Resource Conservation Service (NRCS) curve number method was also used by the program to determine runoff volumes. Finally, the WCS Mercury Tool automatically calculates direct deposition of airborne mercury on open water surfaces. Actual mercury delivery is calculated from the sum of runoff volumes, soil mercury concentration, and atmospheric deposition rates. (NC DWQ 2004; NC TetraTech 2005)

## **4.2 Water Quality Analysis Simulation Program**

The WASP line of water quality models provided by the USEPA has been used to develop numerous TMDLs throughout the United States. The most current version of the program is 7.2 which was released July 31, 2006. The model is an uncoupled, unsteady, continuous simulation that is used to simulate the fate of chosen compounds in aquatic systems. WASP7 uses finite differences to solve mass balance equations, contaminant kinetics equations, and transport equations at set simulation times in each modeled cell to determine the fate of the modeled compound in the flow system. The model has the ability to calculate water quality in one-dimension in which exchanges occur along a single flow stream, two-dimensions where exchanges can occur within a single plane, or three-dimensions in which exchanges can occur in all directions. The flow system can range from a simple single cell lake to a complex million cell lake-river-estuary system. Increasing the complexity of the flow system normally results in a model that is closer to reality. The primary sub-models of WASP7 include EUTRO for modeling eutrophication



and water quality constituents, TOXI for modeling the fate of toxins, and HEAT for modeling heat transport. (Hammond 2004; USEPA 2002)

The MERCURY module of WASP7 is an adaptation of the TOXI sub-model. The module tracks the movement and exchanges of  $\text{Hg}^0$ ,  $\text{Hg(II)}$ , and  $\text{MeHg}$  within the user specified flow system. The model uses partition coefficients to obtain equilibrium between  $\text{Hg(II)}$  and  $\text{MeHg}$  and govern exchanges with solids and dissolved organic carbon. The three mercury species are subject to additional transformation reactions controlled by first order reactions and governed by specified rate constants. The transformation include oxidation of  $\text{Hg}^0$  in the water column, reduction and methylation of  $\text{Hg(II)}$  in the water column and sediment layer, and demethylation of  $\text{MeHg}$  in the water column and sediment layer. Additional reactions tracked with WASP7 are reduction and demethylation that is driven by sunlight. Other user specified variables that control the transport and exchanges of mercury in the WASP7 model are temperature, volume of water, and exchanges between model cells. The partition coefficients, rate constants, and other variables used in the WASP7 model of Parker Canyon Lake are summarized in Appendix B. (Hammond 2004; USEPA 2002 )

## 5 Watershed Characterization

In order to develop the mercury TMDL for Parker Canyon Lake, the watershed that could contribute mercury to the lake was characterized. Sources of information were environmental studies, GIS data, climate data, and chemical results provided by ADEQ.

### 5.1 General Information

Parker Canyon Lake is a mesotrophic reservoir located in southern Arizona approximately 12 miles north of the United States-Mexico border. The lake surface area ranges between 50 and 53 ha depending on water volume stored. The lake center is at latitude N31.4282° and longitude W110.4552° which is located in Section 18 Township 23S Range 19E. The lake is part of the Upper Santa Cruz Watershed, Cataloging Unit 15050301, with the unique USEPA classification of AZL15050301-1040. Figure 5.1 provides a map of region. Figures 5.2 and 5.3 provide more detailed images of the Parker Canyon Lake Watershed. (AZ A.A.C. 2003; AZGFD 2006d)

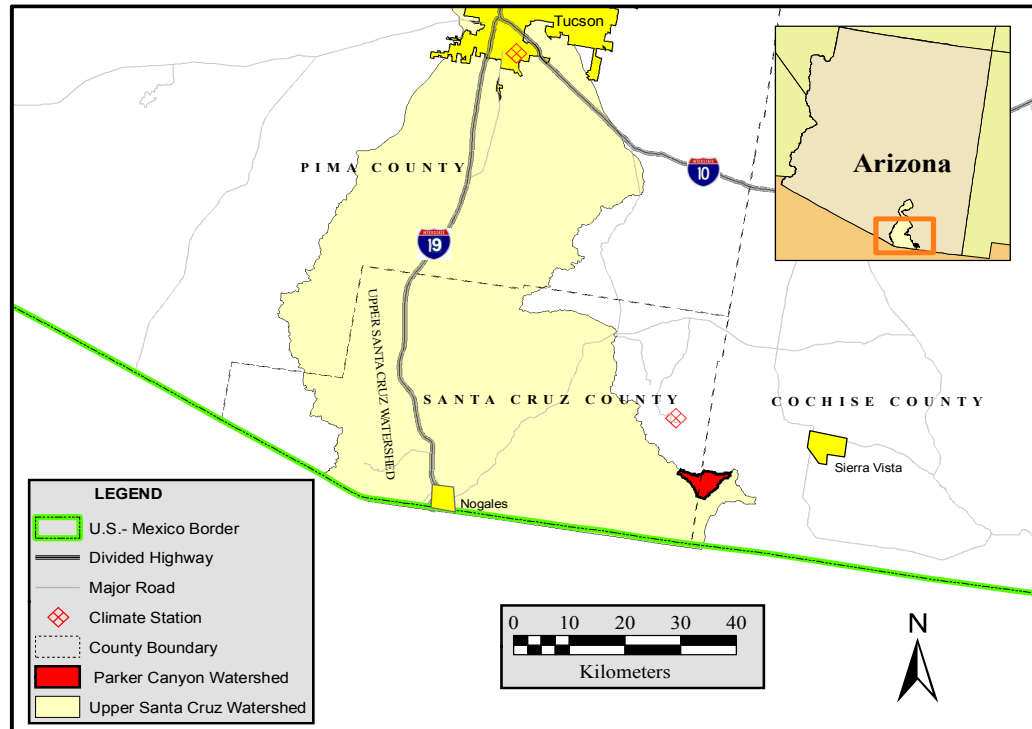


Figure 5.1 Location of Parker Canyon Lake Watershed. Parker Canyon Lake is located in the southwest corner of the Parker Canyon Watershed.

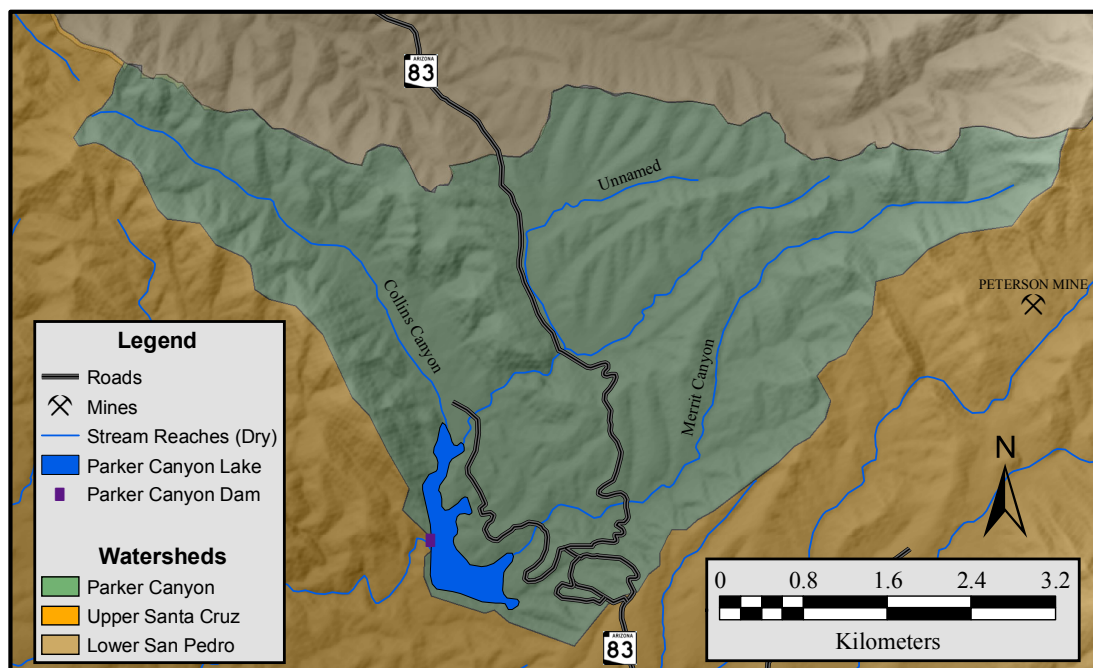


Figure 5.2 Map of Parker Canyon Lake Watershed.

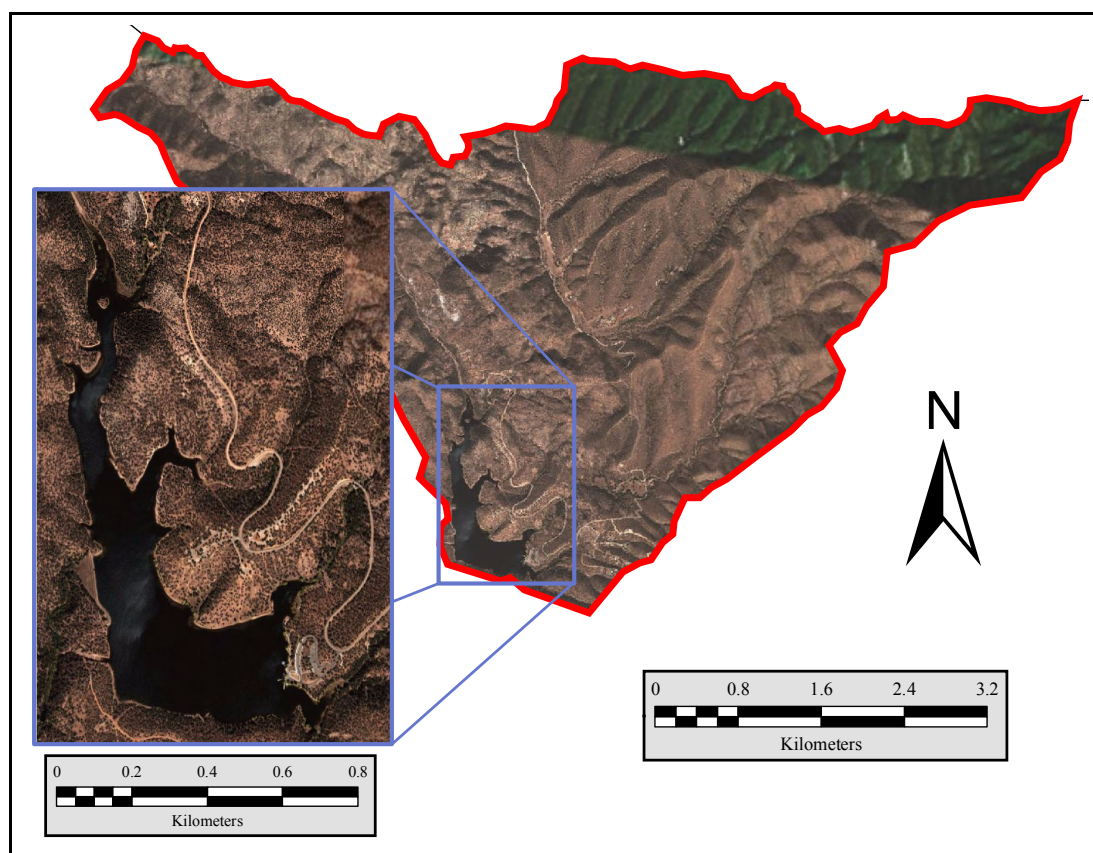


Figure 5.3 Satellite imagery of Parker Canyon Lake Watershed with insert of Parker Canyon Lake. (Google Earth! 2006)

The lake is located in the Huachuca Mountains at an elevation of 1640 m above mean sea level (AMSL). The Parker Canyon Lake Watershed extends approximately 10 km along the longest reach to a peak elevation of 2320 m AMSL as shown in Figure 5.4. The watershed area that contributes to the lake is approximately 2300 ha.

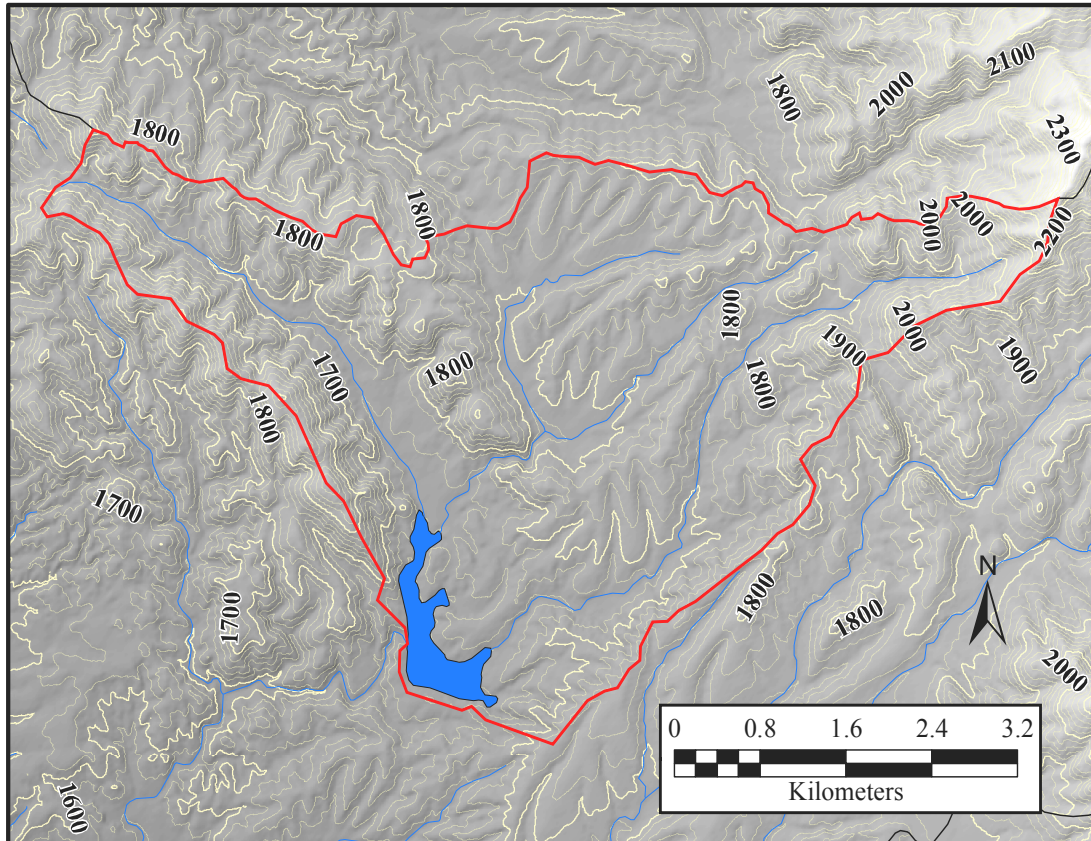


Figure 5.4 Topographic map of Parker Canyon Lake Watershed. Elevations given are in meters AMSL.

The Parker Canyon Lake Watershed hillsides are relatively steep with an average slope of 0.26 m/m while the large Santa Cruz Watershed, the regional watershed that contains the Parker Canyon Lake Watershed, has an average slope of 0.08 m/m. The steep slopes cause precipitation to concentrate faster leading to higher peak runoff rates. The steep slopes also increase the amount of erosion in equivalent soils. Figure 5.5 and Figure 5.6 show the distribution and frequency of hillside slopes in the Parker Canyon Lake Watershed, respectively. Figure 5.7 and Figure 5.8 are provided to show the distribution and frequency of slopes in the Santa Cruz Watershed, respectively.

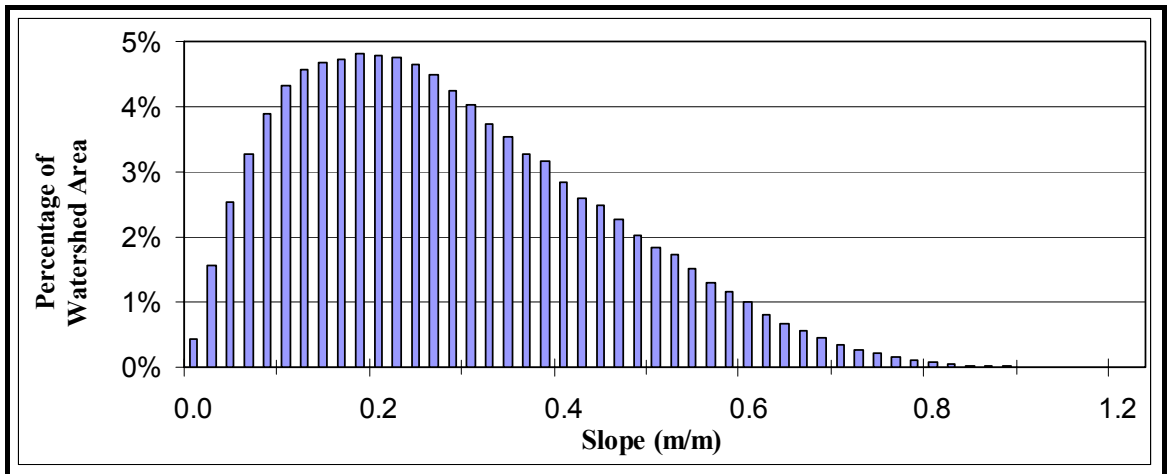


Figure 5.5 Histogram of hillside slopes for the Parker Canyon Lake Watershed. The high frequency of larger slopes indicate a watershed that is relatively steep.

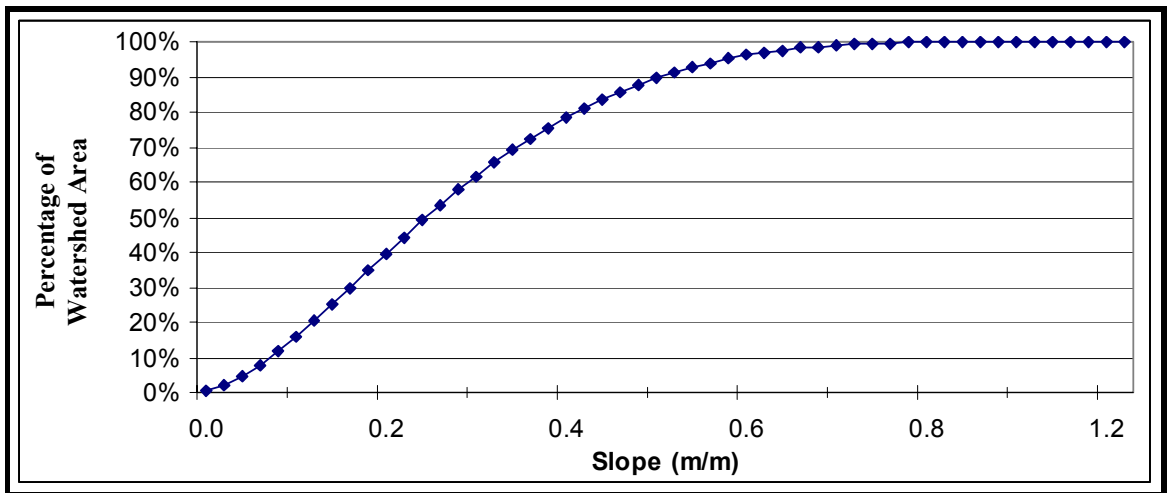


Figure 5.6 Cumulative frequency distribution graph of hillside slopes for the Parker Canyon Lake Watershed.

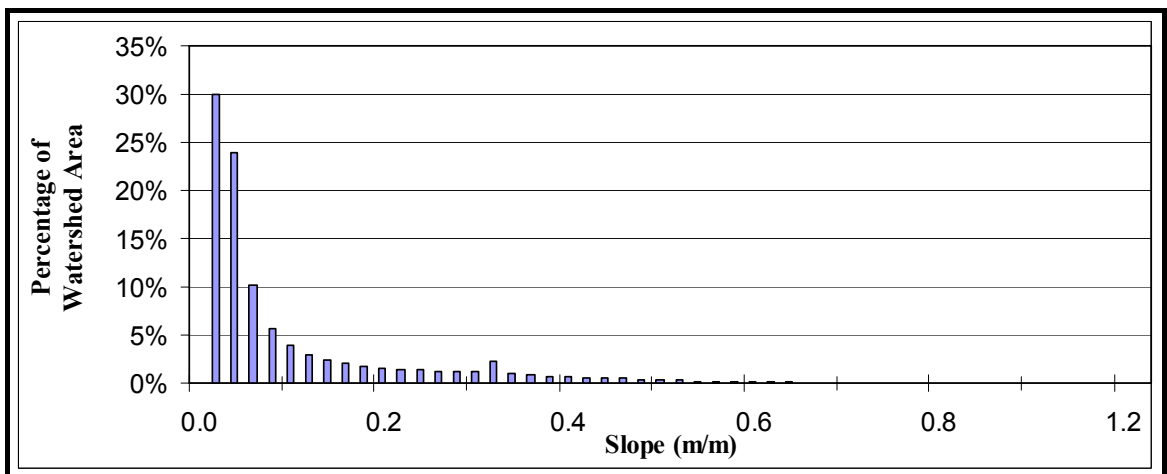


Figure 5.7 Histogram of hillside slopes for the Santa Cruz Watershed. The high frequency of gradual slopes indicate a watershed that is generally flat.



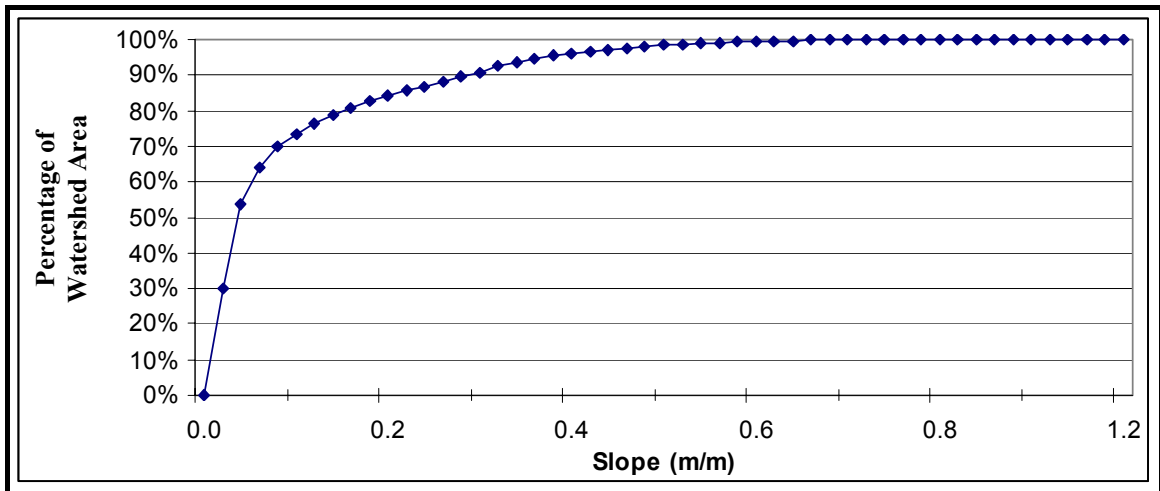


Figure 5.8 Cumulative frequency distribution graph of hillside slopes for the Santa Cruz Watershed.

The reservoir was impounded by the Parker Canyon Dam in 1966 in a project sponsored by AZGFD to provide an area for recreation. The lake is located in the Coronado National Forest and is maintained with joint efforts of the AZGFD and the United States Forest Service (USFS). The USFS maintains three small campgrounds and a boat ramp for the lake. Parker Canyon Lake is popular area for anglers with up to 30,000 visitors a year and several long standing state records for the largest fish. Water supply for the lake is from rainfall events and at least one groundwater spring, which is fed from a confined aquifer in the San Rafael Basin. Lake level is primarily controlled by a single spillway. (Fishinaz.com 2006; Towne 2003)

## 5.2 Climate

Temperature and precipitation data for the Parker Canyon Lake Watershed were obtained from data collected at the Canelo 1 NW COOP weather station. The weather station is located 21 km from the lake on the same side of the Huachuca Mountains as the lake at latitude 31.5589°N and longitude 110.529°W. The station has an elevation of 1527 m AMSL which is similar to Parker Canyon Lake at a mean elevation of 1640 m AMSL. It was assumed that the station and Parker Canyon Lake Watershed have similar weather patterns due to their proximity.

The Canelo 1 NW station has been in operation since 1910 when it started recording daily temperature readings and total rainfall. Snow fall has been measured at the Canelo 1 NW station, but never reported as more than trace amounts. The volume of snow that accumulates at the higher elevations of the Parker Canyon Lake Watershed which has a peak elevation of 2320 m AMSL has not been recorded. Average monthly precipitation data from the Canelo 1 NW Station for the thirty year period of 1972 to 2002 are shown in Table 5.1 with graphical representation of rainfall for the 12 year modeling period used in WASP7 shown in Figure 5.9. The monthly average temperature for the Canelo 1 NW station is shown in Table 5.2. For an unknown reason the Canelo 1 NW station, which had recorded daily precipitation levels since 1910, had a gap in precipitation data from September 2003 to August 2005. After August 2005, data recording at the station continued normally. (NCDC 2006a; WRCC 2005a)

Table 5.1 Average monthly precipitation (cm) at Canelo 1 NW weather station for the thirty year period of 1972-2002.

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
3.63	2.90	2.76	1.32	0.60	1.56	9.41	9.08	4.44	3.62	2.35	3.49	45.16

Table 5.2 Average monthly temperature (°C) at Canelo 1 NW weather station for the thirty year period from 1972-2002.

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Average
2.6	3.0	5.2	9.7	14.7	20.7	23.4	20.9	16.5	13.9	8.3	5.0	12.0

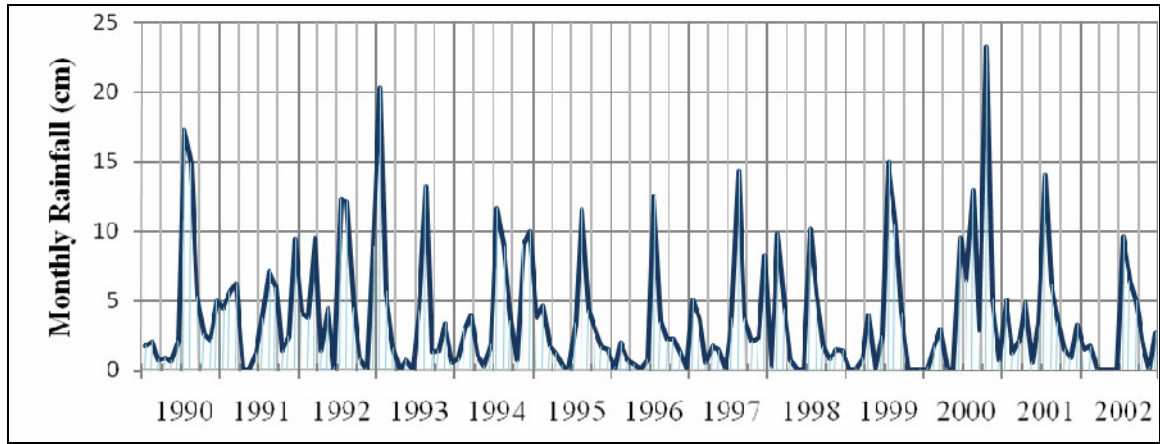


Figure 5.9 Monthly precipitation (cm) at Canelo 1 NW weather station for the WASP7 modeling period from 1990-2002.

Wind speed and direction was not available from the Canelo 1 NW station, but data from Tucson International Airport located approximately 80 kilometers to the northwest was available. As shown in Figure 5.10, predominate wind direction is from the southeast. The actual wind patterns at Parker Canyon Lake may be different, but the general trend is assumed to be the same throughout the region. The wind rose in Figure 5.10 was developed using Lakes Environmental Wind Rose Plot (WRPLOT) Version 5.3. (WebMet.com 2002)



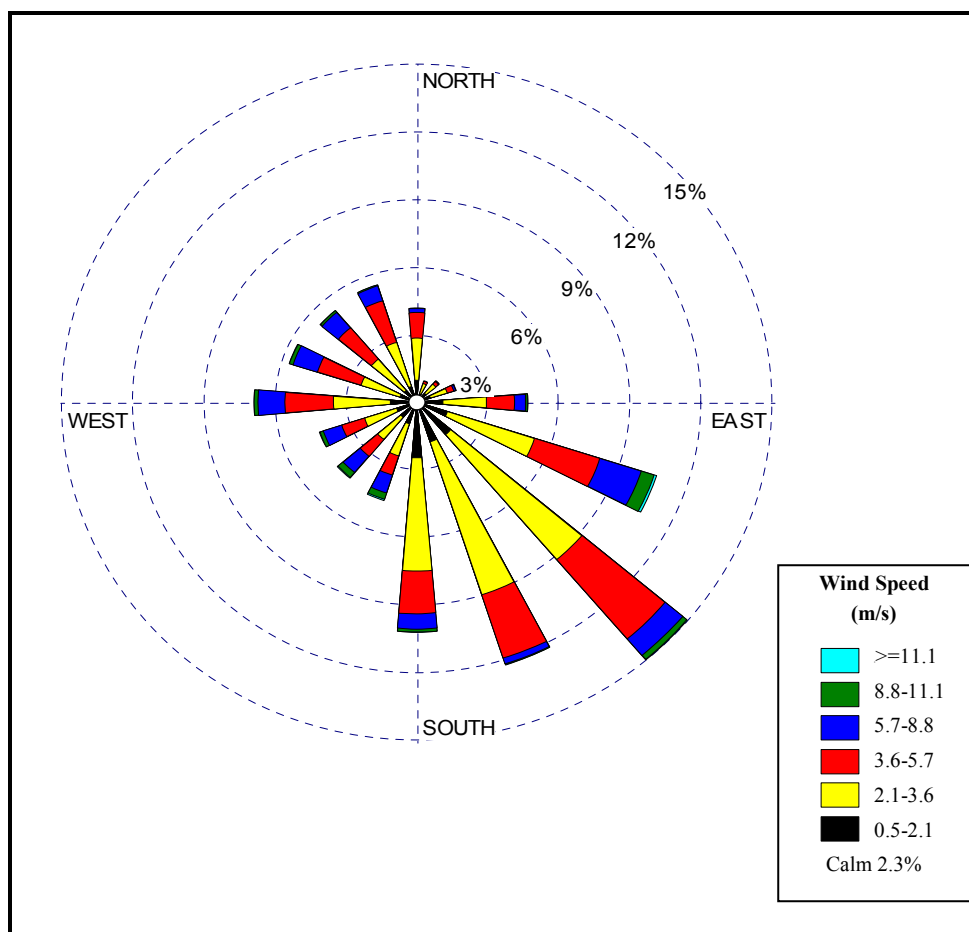


Figure 5.10 Wind rose indicating direction that wind is blowing from near ground surface for Tucson International Airport Weather Station #23160 during 1980-1990.

### 5.3 Land Use Classification

The Parker Canyon Lake Watershed is primarily wild shrubland with small evergreen trees growing at higher elevations. There is a mixed cottonwood riparian habitats around the lake, evergreen woodland, and shrubland for a majority of the watershed, and ponderosa pine and mixed-conifer forests at elevations greater than 2100 m AMSL. Parker Canyon Lake is part of the San Rafael Basin that is part of the Madrean Sky Island bioregion, which has the largest diversity of mammal species in North America. A poorly maintained paved road crosses the watershed from the north to the south and a paved access road runs along the northeast side of the lake. There is not a significant amount of farming, grazing, or other human disturbance in the watershed. There are approximately 20 single story seasonally occupied houses located east of the lake and

three additional ranch houses distributed throughout the watershed. It is unknown where the residence dispose of their refuse, but it is probable that a landfill would not be a significant point source for mercury. Finally, there are no known mines in the area according the US Bureau of Mines Mineral Availability System/ Mineral Industry Location System (MAS/MILS). (ADEQ 2003; TetraTech 1999a; USGS 2006)

The Multi-Resolution Land Characteristics (MRLC) database was used to further characterize the watershed. The database developed by a consortium of the USEPA, USFS, USGS, and other federal agencies. The 1990s MRLC is a spatial computerized classification of land use based on an analysis of satellite imagery and standards developed in the 1990s. Table 5.3 summarizes the 1990s MRLC data and Figure 5.11 shows the 1990s MRLC land use map of the Parker Canyon Lake Watershed. (USEPA 2006d)

Table 5.3 Summary of 1990s MRLC land use data for Parker Canyon Lake Watershed

	Shrubland	Evergreen Forest	Water	Mixed Forest	Grassland	Deciduous Forest	Other	Total
Area (ha)	1920.9	332.3	50.2	48.9	11.8	2.8	0.3	2367
Fraction (%)	81.1	14.0	2.1	2.1	0.5	0.12	0.01	100

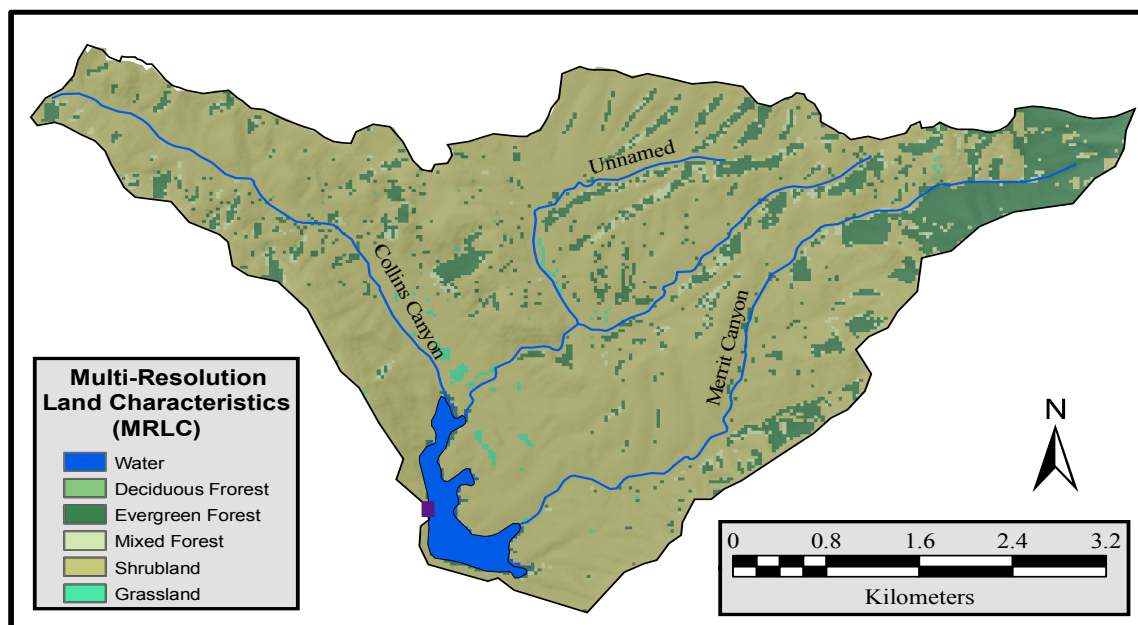


Figure 5.11 Map of 1990s MRLC land use for Parker Canyon Lake Watershed.

## 5.4 Soil Characteristics

Parker Canyon Lake is located in the Huachuca Mountains which consist of shallow loams and rock outcrops of the Tortugas-Rock outcrop association. There are three different classifications for surface soils (> 25 cm) located in the Parker Canyon Lake Watershed according to the State Soil Geographic (STATSGO) database. The STATSGO database is a digital general soil association map developed by the National Cooperative Soil Survey. It consists of a broad based inventory of soils that occur in repeatable pattern and was compiled from individual soil tests aided by satellite images. Table 5.4 contains the soil characteristics for the three soil classifications in the Parker Canyon Watershed. Those soils are displayed spatially in Figure 5.12. (ADEQ 2003; USEPA 2006a)

Table 5.4 STATSGO top layer soil characteristics for Parker Canyon Lake Watershed.

Characteristic	Units	Soil Classification		
		AZ146	AZ272	AZ273
Hydrologic Group	---	C	D	C
Available Water Capacity	cm/cm	0.1	0.1	0.07
Permeability	cm/hr	6.1	2.3	2.3
Bulk Density	g/cc	1.42	1.01	0.97
Soil pH	---	6.95	5.41	4.67
Percent Clay	%	14.6	18.43	17.14
Percent Silt and Clay	%	31	60.21	43.21
Estimate Soil Texture		Sandy Loam	Loam	Sandy Loam
Percent Organic Matter	%	1.18	0.51	1.03
Soil Erodibility ( $K_m$ )	---	0.19	0.18	0.1
Soil Erodibility Range ( $K_m$ )	---	0.05 - 0.28	0 - 0.37	0 - 0.2

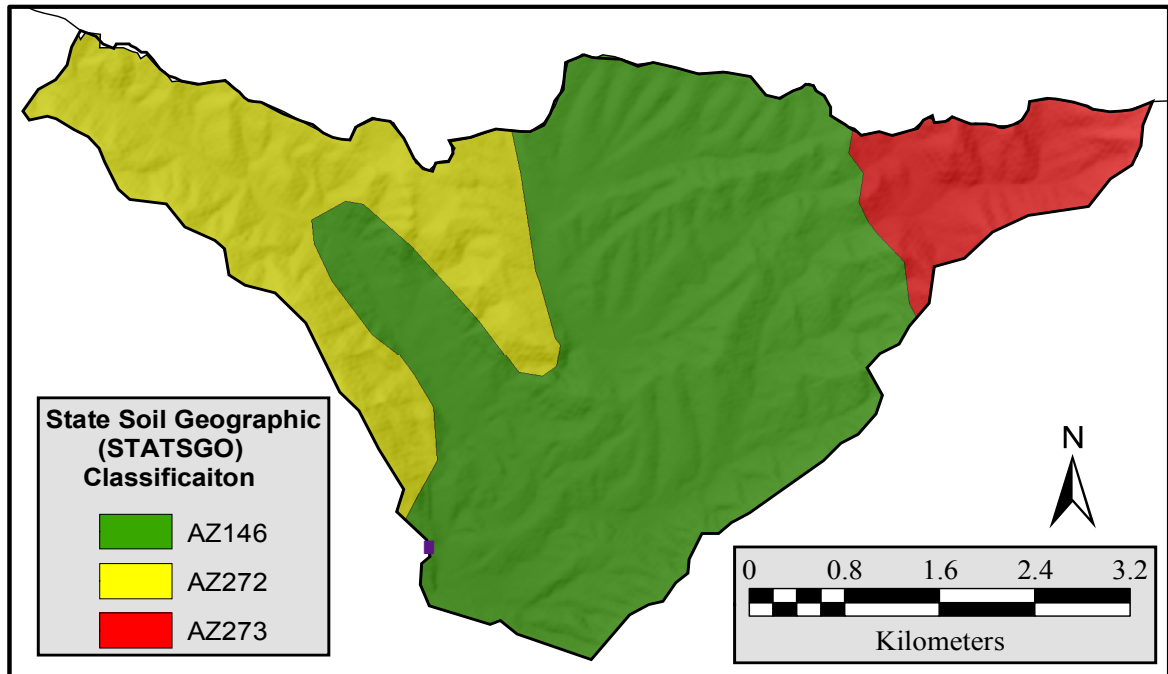


Figure 5.12 Map of STATSGO soils in the Parker Canyon Lake Watershed.

## 5.5 Parker Canyon Lake

Parker Canyon Lake is a relatively warm lake that has historically had large volume fluctuations. There is evidence of stratification of the lake starting from April and continues until Late October. The lake has a thick concentration of aquatic plants and a large amount of sun exposure that allows for a thriving aquatic ecosystem. The lake contains resident northern pike, black bullhead, bluegill, largemouth bass, sunfish, and channel catfish. Rainbow trout of desirable size (20 – 26 cm) have historically been added to the lake between October and March; however, the lake has not been stocked in recent years. The northern pike is considered an invasive species that is adversely impacting the ecosystem. (AZGFD 2006e; Fishinaz.com 2006; Kerr and Lasenby 2000)

The aquatic ecosystem of Parker Canyon Lake contains a food chain that has been categorized by the USEPA by using standardized trophic levels: (CRWQCB 2006)

- Trophic Level 1 (TL1) - Aquatic Plants (e.g., periphyton, phytoplankton)
- Trophic Level 2 (TL2) - Herbivores and Detritivores (e.g., copepods, water fleas)
- Trophic Level 3 (TL3) - Predators of TL2 organisms (e.g., minnows, sunfish)
- Trophic Level 4 (TL4) - Predators near the top of the aquatic food chain that feed on TL3 organisms (e.g. northern pike, largemouth bass)

A species representative of the TL3 fish present in the Parker Canyon Lake is the Bluegill, while the Largemouth Bass and Northern Pike are examples of TL4 species. (AZGFD 2006a; AZGFD 2006b; AZGFD 2006c)

### 5.5.1 Parker Canyon Lake Chemistry

ADEQ collected water samples from two different locations that measured general lake chemistry. The samples were collected between 1992 and 2006 for sediment and water column for Parker Canyon Lake. Water chemistry for Parker Canyon Lake is summarized in Table 5.5. Organic and nutrients constituents are summarized in Table 5.6, non-mercury sediment data is summarized in Table 5.7, and metals in the water column are summarized in Table 5.8. The standard total mercury testing conducted prior to 2003 showed no detectable mercury in the water, but lower detection limit for the test was relatively high at 0.5 µg/L. In October 2003 and February 2006, low-level mercury tests were performed on water and sediment samples at Parker Canyon Lake in response to reports of high mercury levels in fish tissue. The results of those two sampling periods are summarized in Table 5.9.

Table 5.5 Water chemistry for Parker Canyon Lake (1992 – 2006).

Characteristic	Units	Number of Data Points	Minimum	Maximum	Standard Deviation	Average
Temperature	°C	147	7.09	25.01	4.66	13.1
Turbidity	NTU	13	1.16	21.2	6.18	6.28
Secchi Disc Transparency	meters	11	1	4	1.03	2.91
Total Dissolved Solids	mg/L	53	108	243	48.9	165.6
Specific Conductance	µmhos/cm	147	169	373	49.1	234
pH	---	136	6.8	9.0	0.57	7.96

Table 5.6 Organic compounds and nutrients in water column of Parker Canyon Lake (1992 – 2006).

Constituent	Units	Number of Data Points	Minimum	Maximum	Standard Deviation	Average
Alkalinity, Total as CaCO <sub>3</sub>	mg/L	18	80	114	8.22	93.3
Dissolved Organic Carbon (DOC)	mg/L	5	7.3	13.4	2.47	9.2
Total Organic Carbon (TOC)	mg/L	5	7.3	13.4	2.38	9.6
Hardness as CaCO <sub>3</sub>	mg/L	17	83	114	6.98	97.9
Nitrate and Nitrite	mg/L	11	0.01	0.05	0.01	0.02
Total Kjeldahal Nitrogen	mg/L	18	0.46	98.0	22.88	6.3
Dissolved Oxygen	mg/L	136	0.09	11.8	3.25	6.2
Phosphorus, Total	mg/L	17	0.008	0.2	0.04	0.03
Sulfate, Total	mg/L	18	4.0	19.0	5.08	11.2

Table 5.7 Non-mercury sediment characteristics of Parker Canyon Lake (1992 – 2006).

Characteristic	Units	Number of Data Points	Minimum	Maximum	Standard Deviation	Average
Solids in Sediment Sample (Dry)	%	1	27.76	27.76	---	27.8
Sulfates in Sediment Sample	mg/kg	2	318	375	40.3	347
Total Organic Carbon in Sediment (Dry)	mg/kg	2	5.3	6	0.49	5.65

Table 5.8 Non-mercury metal constituents in the water column of Parker Canyon Lake (1992 – 2006).

Constituent	Units	Number of Data Points	Minimum	Maximum	Standard Deviation	Average
Antimony, Total	µg/L	1	2	2	---	2.0
Arsenic, Total	µg/L	4	3	4	0.58	3.5
Barium, Total	mg/L	9	0.007	0.70	0.205	0.154
Calcium, Total	mg/L	14	29.3	37.6	2.28	32.7
Iron, Total	mg/L	7	.002	0.210	0.616	0.08
Magnesium, Total	mg/L	12	3.4	5.0	0.71	4.2
Manganese, Total	mg/L	9	0.03	1.52	0.51	0.43
Potassium, Total	mg/L	12	3.1	4.4	0.44	3.9
Sodium, Total	mg/L	11	6.7	11	2.00	8.8

Table 5.9 Mercury constituents in water column and sediment of Parker Canyon Lake (2003 – 2006).

Constituent	Units	Number of Data Points	Minimum	Maximum	Standard Deviation	Average
Unfiltered Total Mercury	ng/L	4	0.76	0.95	0.08	0.85
Filtered Total Mercury	ng/L	4	0.38	0.82	0.21	0.51
Dissolved Methylmercury	ng/L	8	0.126	11.4	3.83	2.05
Fraction of Dissolved Methylmercury to Total Mercury <sup>1</sup>	---	4	0.132	0.282	0.062	0.199
Total Mercury in Sediment	ng/g	3	65.1	77.233	6.68	72.8
Methylmercury in Sediment	ng/g	3	0.223	1.264	0.53	0.69
Fraction of Methylmercury to Total Mercury in Sediment <sup>1</sup>	---	3	0.0034	0.0166	0.0068	0.0092

1. Fraction only determined when both total Hg and MeHg data available.

Depth profiles were taken by ADEQ for pH, Dissolved Oxygen (DO), and temperature at Parker Canyon Lake to determine how seasonal changes affected lake chemistry. As shown in Figure 5.13, the lake has a distinct line of stratification or thermal layering that occurs sometime in April and continues until late October. This stratification causes two virtually independent chemical layers of water in the lake. The upper water body, called the epilimnion, is warmer and has higher DO content and the preferred layer for fish species to live. The lower water body is called the hypolimnion and is colder with low amounts of DO and may undergo anaerobic processes. The anoxic conditions in the sediment set up conditions that enhance methylation of mercury. (CRWQCB 2006)

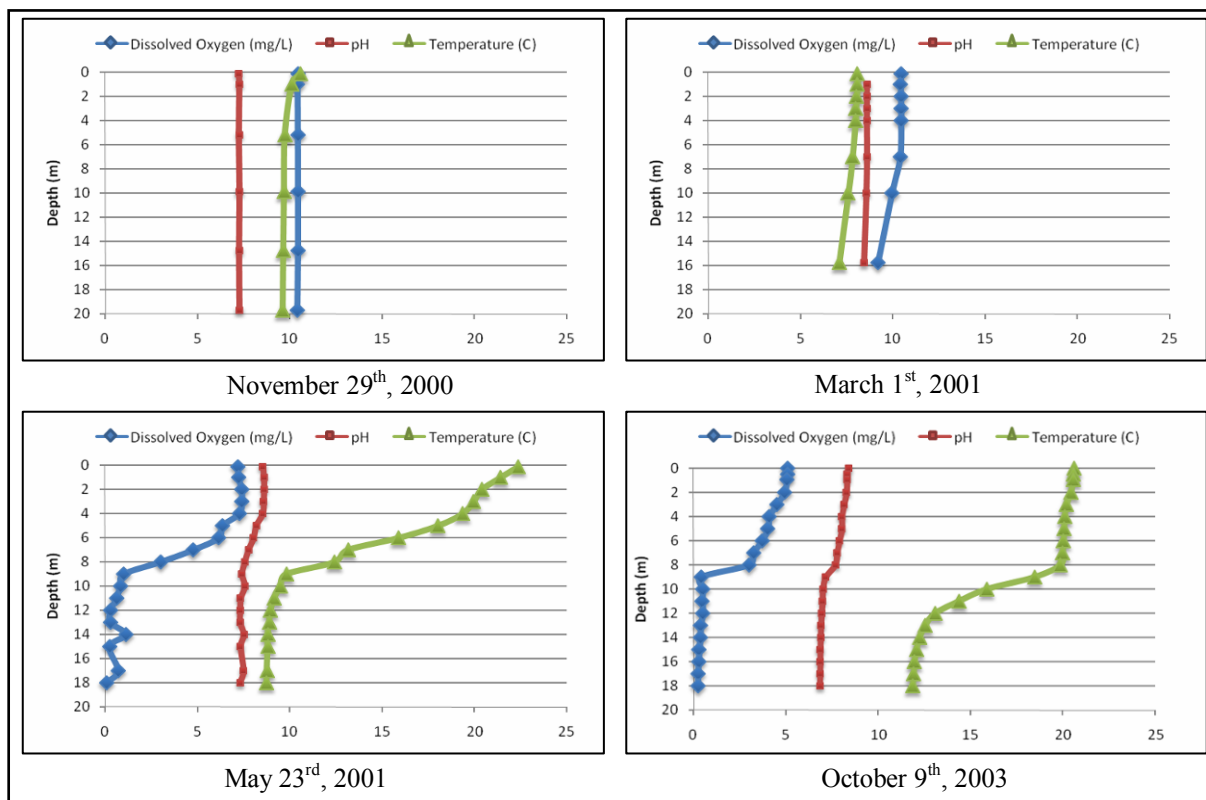


Figure 5.13 Depth Profile of dissolved oxygen, pH, and temperature for Parker Canyon Lake at representative time periods.



## 6 Mercury Source Assessment

There are a variety of sources of mercury that can enter a waterbody. Some examples of anthropogenic sources are industrial discharge, wastewater treatment plants, acid mine drainage, and solid waste containing mercury. In the past, mercury was used in the mining industry to extract other metals such as silver and gold. Mercury is still used in modern medical application including dental amalgam. Anthropogenic sources also include airborne mercury emissions from combustion processes such as burning coal for electric power production, medical and waste incinerators, and chlor-alkali plants. (USEPA 2006b)

Mercury can also occur naturally in geologic materials or volatilize from large waterbodies such as the ocean. The primary mercuric ore shown in Figure 6.1 is called Cinnabar and has the chemical structure of  $\text{HgS}$ . Other natural sources of mercury are volcanic eruptions, which have been shown to release large amount of elemental mercury into the atmosphere. Additionally, sediment that contains natural elemental mercury can contribute mercury to overlying waterbody if disturbed. (USEPA 2006b)

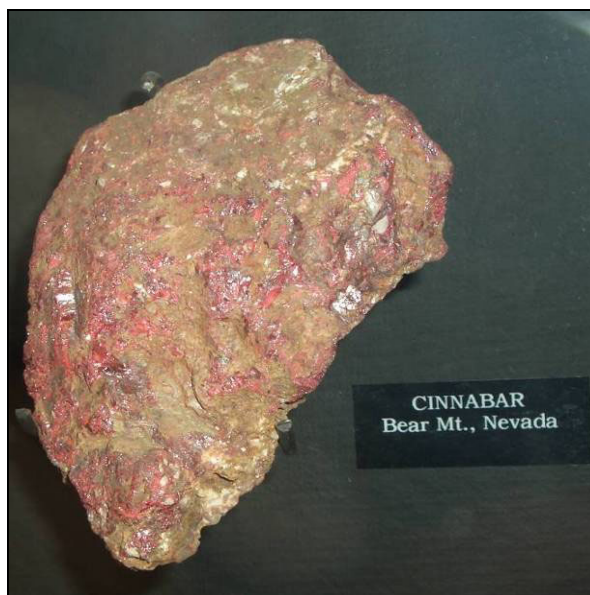


Figure 6.1 Photograph of the primary mercuric mineral called cinnabar from Bear Mountain, NV on display in the Death Valley Visitor Center, Furnace Creek, CA.

Point and non-point sources of mercury can be transported into receiving waterbodies where it can accumulate in aquatic life. Point sources are often limited to industrial discharges where a pipe or exhaust stack is the source. Point sources can also be landfills or other hotspots that have a relatively small area when compared to rest of the watershed. Non-point sources of mercury cannot easily be traced to a single source and often contribute from a large area. Examples of non-point sources are divalent mercury released from wildfires, natural mercury in soils that is released through the movement of organic carbon within the watershed, and atmospheric deposition. Atmospheric deposition of mercury is the most common non-point source of mercury in the United States. In some cases, atmospheric deposition accounts for 99 percent of all mercury loading into a waterbody either directly through contact or indirectly via runoff, erosion of soils, or delivered bound to organic carbon. (USEPA 2006b)

Discharges of mercury from point sources are easier to monitor than non-point sources. The Permit Compliance System (PCS) as well as a study of domestic mercury sources by the National Association of Clean Water Agencies (NACWA), formerly known as the Association of Metropolitan Sewerage Agencies, have recorded toxic discharges within the United States. While large dischargers of toxins, including mercury, have public records of discharge, many smaller dischargers are not required to report or even monitor for mercury in their waste streams. Non-point sources of mercury into a waterbody are often determined by taking representative samples in the watershed and assigning a value based on the total area of the contributing watershed. (USEPA 2006b)

## **6.1 Mercury Sources inside the Parker Canyon Lake Watershed**

The relatively small and remote Parker Canyon Lake Watershed has no obvious point sources of mercury. There is a small community of approximately 20 houses near the lake and a few ranches spread throughout the watershed, but there is no industry or other permitted discharge facilities within the watershed. Site investigation showed no visual signs of mercury containing soils such as cinnabar. It is likely that the source of mercury is from outside in the form of airborne emissions or from dumping of mercury contaminated wastes within the watershed.

There are no known measurements of mercury in the soils within the Parker Canyon Lake Watershed. To determine a concentration of mercury present in the soils, the soil mercury map shown in Figure 6.2 was produced using ERSI's ArcView and known mercury sample data from the Environmental Mercury Mapping, Modeling, and Analysis (EMMMA) database. Strict quality assurance practices were not enforced when the database was first developed during the 1980s, and there may be slight errors in reported results due to atmospheric contamination. Using Figure 6.2 shows that there is an estimated 40 ng/g of mercury in the soil in the Parker Canyon Lake Watershed. (EMMMA 2006)

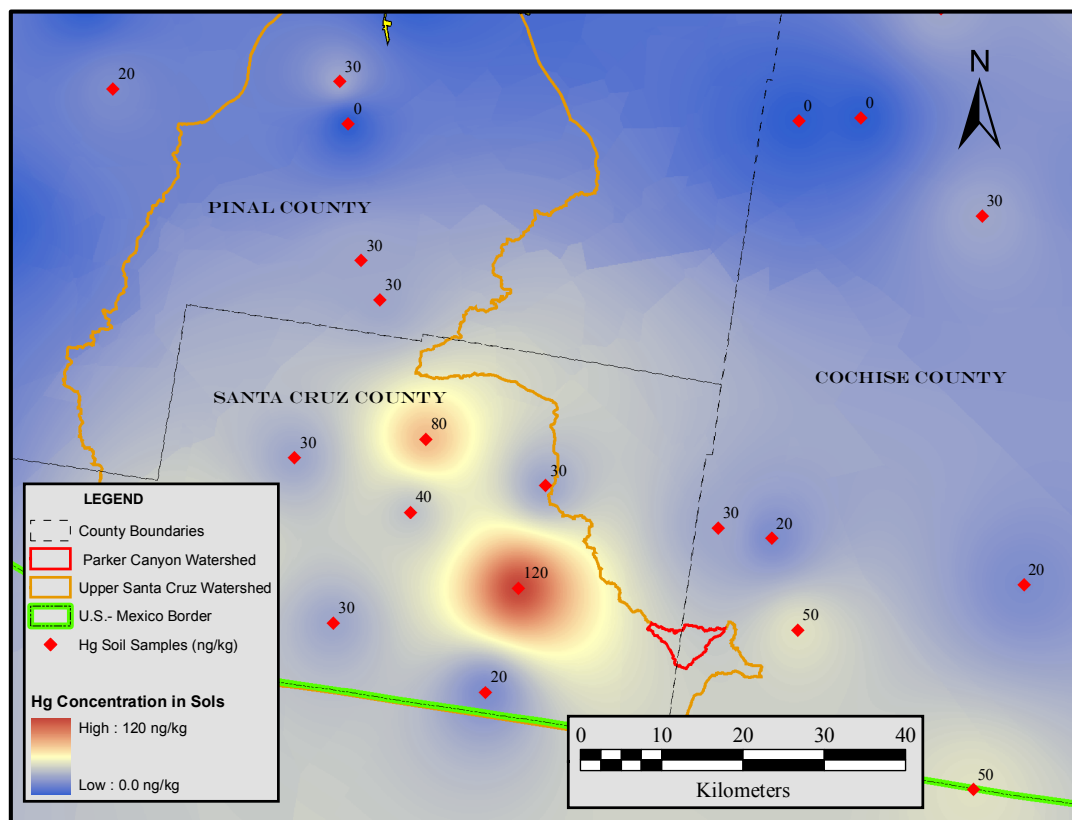


Figure 6.2 Total mercury in soils from data collected between 1980-2003. Samples nearest Parker Canyon Lake watershed were taken in the first calendar quarter of 1980. (EMMMA 2006)

## 6.2 Mercury Sources outside of the Parker Canyon Watershed

Atmospheric deposition is a major source of mercury contamination in many parts of the country. A trace metal analysis of reservoirs in New Mexico found that 80 percent of

mercury was from atmospheric deposition. In another study, it was found that atmospheric deposition was the primary and possibly the only source of mercury in remote areas of Wisconsin, Sweden, and Canada. The mercury is deposited both as fallout of dry particulates and wet deposition which is scrubbed out of the air during precipitation events. Figure 6.3 shows a historical record of mercury deposition in a glacier located in Wyoming. Mercury sampling of a core from the glacier shows that total atmospheric anthropogenic mercury deposition has increased in the past century. The sampling also shows that there have been occurrences when distant natural volcanic events increase worldwide airborne mercury levels. (TetraTech 1999a; USGS 2002)

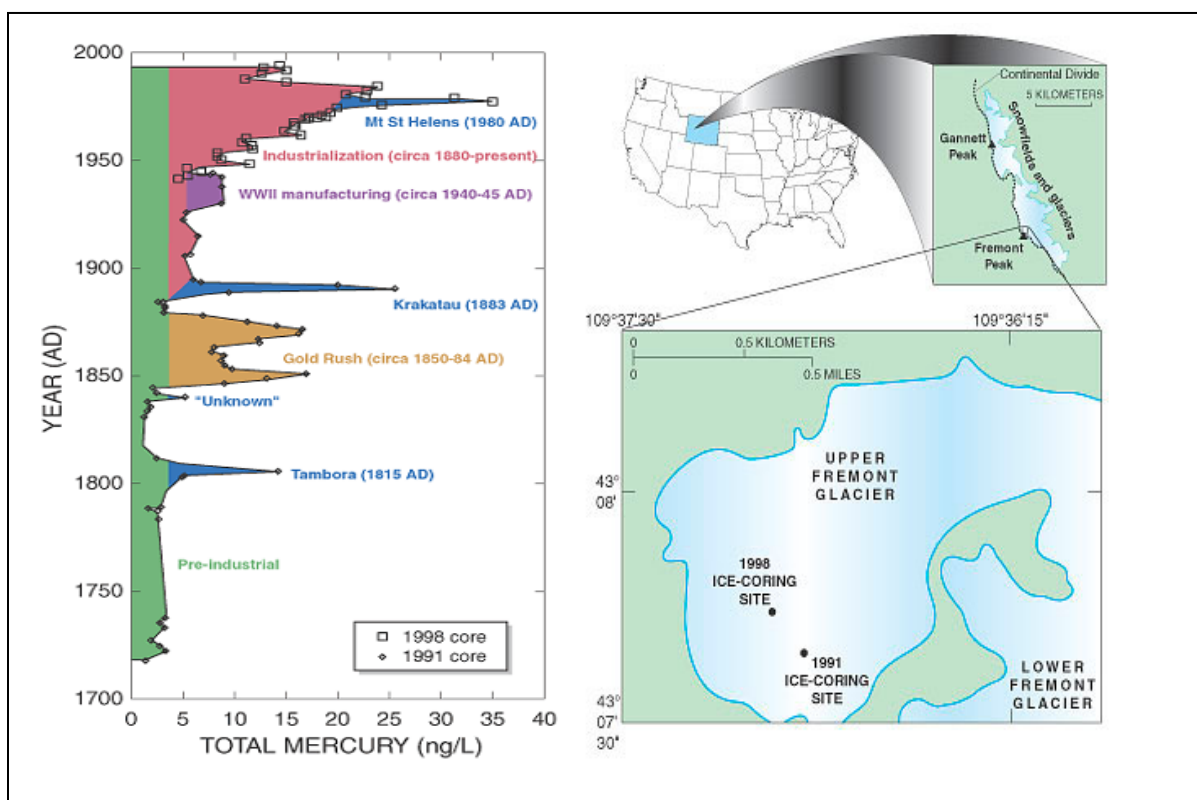


Figure 6.3 Historical record of mercury deposition in the United States obtained from a coring of the Upper Fremont Glacier in Wyoming. (USGS 2002)

The sources of airborne mercury deposition for Parker Canyon Lake can occur from local or long-range sources. Local sources were determined from the USEPA's Toxic Release Inventory (TRI). The TRI tracks emissions and discharges of toxic substances, including mercury, from government and industrial sources. The latest data from USEPA, released to the public on April 12, 2006, tracks the emissions from 23,675 facilities. A reported

1.9 million metric tons of on-site and off-site disposal or other releases of toxic chemicals occurred in 2004. Mercury and mercury compound releases accounted for 2200 metric tons in 2004. Figure 6.4 shows the 2004 releases of mercury around Parker Canyon Lake. Local mercury emissions near the Parker Canyon Lake Watershed are relatively small indicating that most of the airborne mercury deposition must have come from distant sources or sources in Northern Mexico. Mercury emission data is not available from industrial sources south of the border since there is no systematic inventory of mercury emissions in Mexico. A large potential source of mercury in Mexico is the Nacozari Smelter which is located approximately 200 km southwest of the Parker Canyon Watershed. The Nacozari Smelter utilizes basic emission controls including double-contact sulfuric acid units. (CEC 2006; Green *et al.* 2003; USEPA 2006e)

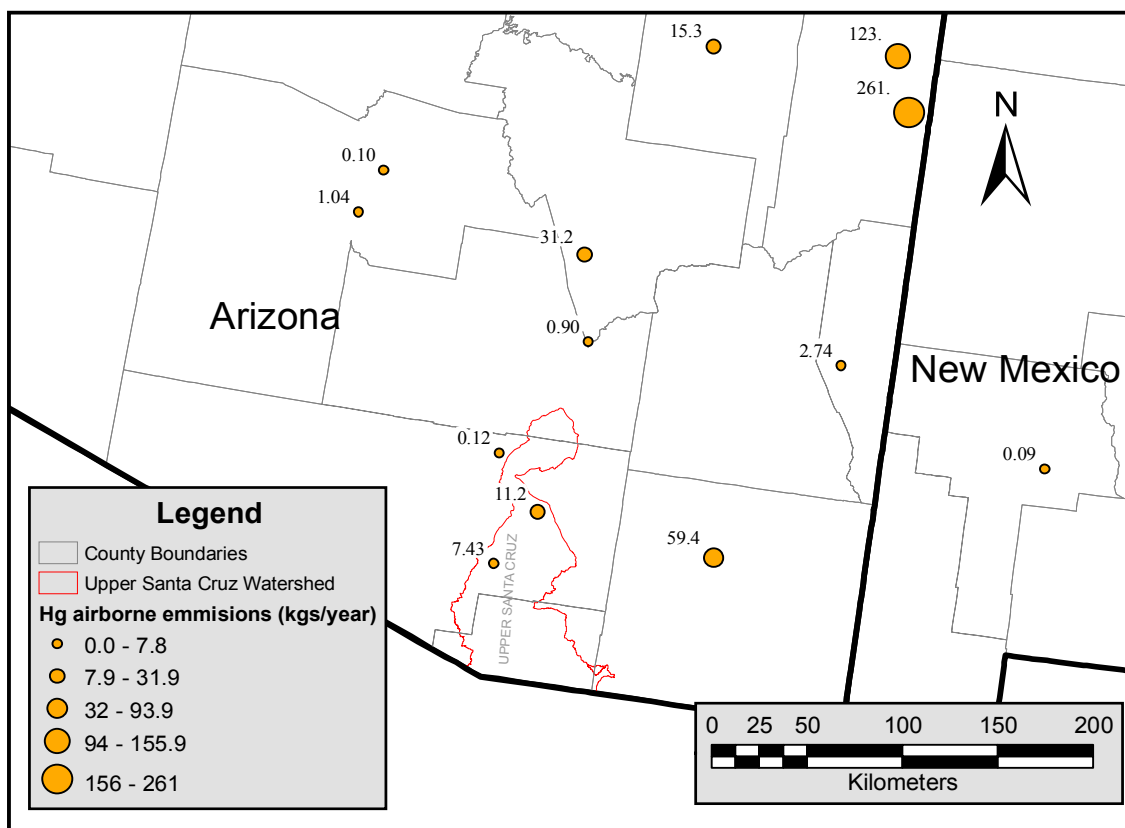


Figure 6.4 Airborne emissions of mercury around the Parker Canyon Lake Watershed based on information from the USEPA Toxic Release Inventory.

To account for distant sources of atmospheric mercury, including sources in Mexico, mercury deposition data from the Mercury Deposition Network (MDN) was utilized.

The MDN is operated by the U.S. Department of Agriculture's National Atmospheric Deposition Program (NADP) which is a collection of 250 atmospheric monitoring sites throughout North America. Precipitation from each of the 250 station is collected weekly and sent to a central laboratory where it is analyzed for pH, sulfate, nitrate, ammonium, chloride, and various ions. The MDN utilizes select NADP stations that send collected precipitation to a single laboratory for mercury analysis. The MDN shown in Figure 6.5 is composed of 90 stations. The MDN officially started operation in 1995. The closest monitoring point to the Parker Canyon Lake Watershed is the NM10 station at Caballo, NM located at a Latitude 33.0625°, Longitude -107.2917°, and elevation of 1280 m AMSL. This site is approximately 350 km west of the study area and is the best source of mercury deposition for the region. The next closest MDN station, AZ02, is located in northern Arizona and has been in operation since the end of February 2006; however, data from MDN station AZ02 is not yet available to the public. The atmospheric mercury deposition data reported by the Caballo, NM MDN station is summarized in Table 6.1 and graphically represented in Figure 6.6. (NADP 2006)



Figure 6.5 Locations of stations in the Mercury Deposition Network provided on the NADP website with the location of AZ02 and Parker Canyon Lake study area marked. (NADP 2006)

Table 6.1 Annual summary of atmospheric deposition of mercury at the Caballo, NM MDN station. (NADP 2006)

	1998	1999	2000	2001	2002	2003	2004	2005	Average
Hg Concentration in Precipitation (ng/L)	23.0	21.3	19.4	28.4	26.4	27.0	17.5	17.5	22.6
Hg Wet Deposition ( $\mu\text{g}/\text{m}^2/\text{yr}$ )	4.0	6.0	5.6	5.0	3.6	4.0	5.9	2.5	4.6
Hg Dry Deposition ( $\mu\text{g}/\text{m}^2/\text{yr}$ )	8.0	12.0	11.2	10.0	7.2	8.0	11.8	5.0	9.2
Total Deposition ( $\mu\text{g}/\text{m}^2/\text{yr}$ )	12.0	18.0	16.8	15.0	10.8	12.0	17.7	7.5	13.7

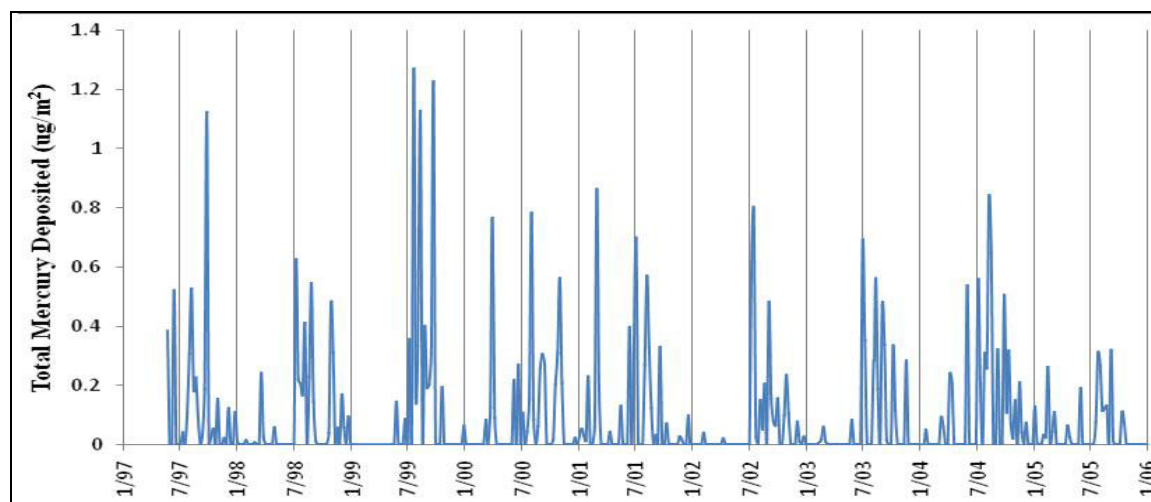


Figure 6.6 Graph of atmospheric deposition at the Caballo, NM MDN station since mercury deposition measurements began in 1997. (NADP 2006)

### 6.2.1 Historic Mercury Sources near Parker Canyon Lake

The TRI and MDN are recent mercury tracking methods in the United States, but they cannot account for long-term atmospheric mercury deposition into the Parker Canyon Lake Watershed. This lack of historic data prevents accurate estimation of deposited mercury that still is contributing to Parker Canyon Lake due to erosion and runoff. There is also the possibility that high levels of mercury are sequestered in the sediment and may cause problems in the future. (TetraTech 1999a)



Parker Canyon Lake is located in close proximity to three long operating smelters as shown in Figure 6.7. These smelters may have historically increased localized airborne mercury levels. The most likely source of historic airborne mercury for the Parker Canyon Lake Watershed was the copper and gold Cananea Smelter located approximately 80 km southeast of the Parker Canyon Lake. The smelter was a significant source of sulfur pollution in southern Arizona due to the prevailing northeastern winds. There were no emission controls at the Cananea Smelter and operations are likely a significant source of mercury for region; however, no data was found to confirm airborne mercury levels. The Cananea Smelter stopped operation in 1998 and was closed in February 1999. Figure 6.8 shows a photograph of the emissions from the smelter prior to it being shutdown permanently. Another large potential emission source was the lead and zinc Douglas Smelter located 175 km east of the Parker Canyon Lake Watershed. The Douglas Smelter was shutdown in 1987. (Cananea Co. 2003; Bravo 2003; CEC 2001)

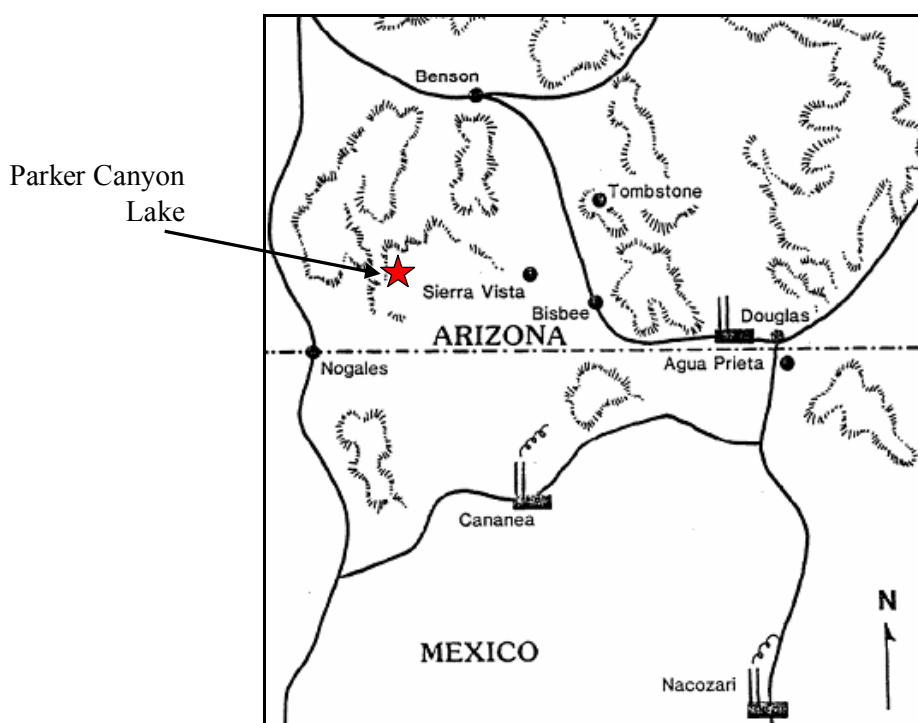


Figure 6.7 Map of historical potential mercury emission sources near Parker Canyon Lake. The Cananea Smelter and Douglas Smelter are no longer in operation. (USFWS 1988)





Figure 6.8 Photograph of Cananea Smelter emissions prior to shutdown in February 1999. (Alamy 2006b)

### 6.3 Estimated Mercury Load into Parker Canyon Lake

The WCS spatial model was used to calculate mercury loading into Parker Canyon Lake. Climate data, deposition rates, soil characteristics, reaction rates, partition coefficients, land use, roads, digital elevation models, drainage paths, and watershed boundaries were entered into the WCS model. Additional inputs and numerical values used for the WCS model are summarized in Appendix A. The WCS model automatically divided the watershed into 237,000 individual 10 m x 10 m modeling cells. The WCS model was simulated for 100 years in order to obtain steady state conditions with both erosion rates and mercury soil levels. Additionally, the past century has seen an increase in atmospheric mercury that was assumed to be deposited in the Parker Canyon Lake Watershed. (NCDWQ 2004; TetraTech 2005)

The sediment and hydrological results calculated by the WCS model are summarized in Table 6.2. The mercury loading calculated by the WCS model are summarized in Table 6.3. Detailed results from the model are presented in Appendix A. As shown in Figure 6.9 the sediment loading occurs from areas of steeper slopes and less compacted soils in the western side of the watershed. Figure 6.10 shows the actual sources of mercury loading in the watershed. It should be noted that the lake itself has the largest

load in the watershed due to direct deposition of airborne mercury onto the lake.(TetraTech 1999a; TetraTech 2005)

Table 6.2 Summary of modeled WASP7 sediment and hydrological characteristics for Parker Canyon Lake.

Data Layer	Units	Mean Value
Annual Source Sediment	kg/km <sup>2</sup> -yr	9780
Average Annual Infiltration	cm	8.89
Average Annual Evapotranspiration	cm	28.4
Average Annual Runoff	cm	7.93
Average Annual Precipitation	cm	45.2
Weighted R_factor	---	81.6
K_factor	---	0.178
Ls_factor	---	4.18
C_factor	---	0.004
P_factor	---	1

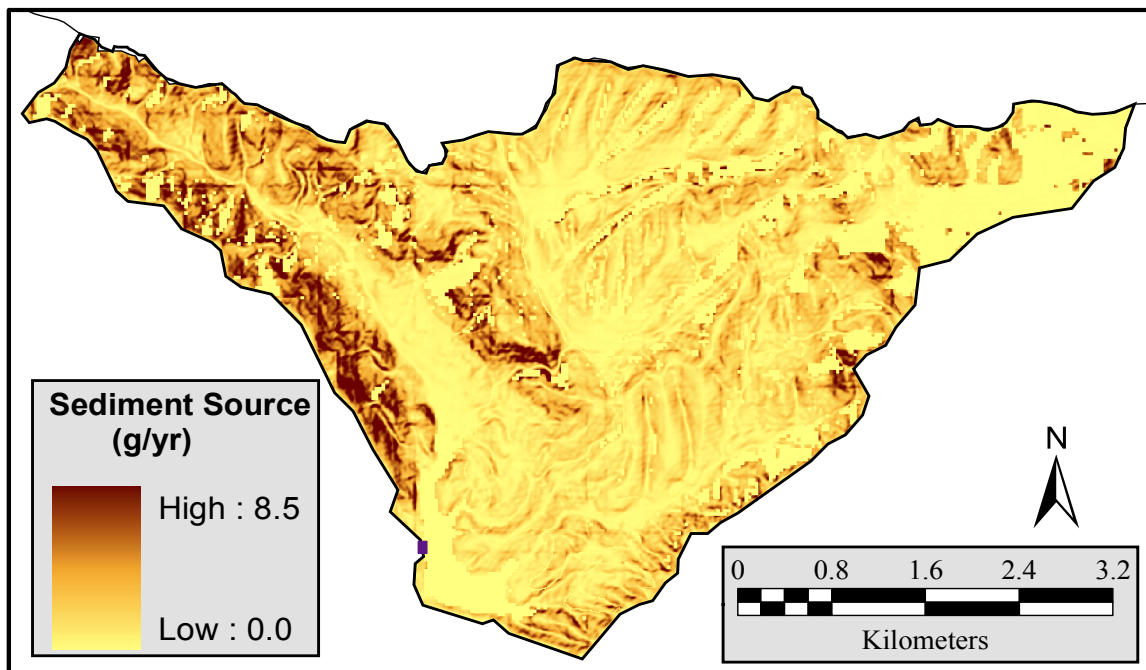


Figure 6.9 Annual sediment loading into Parker Canyon Lake Watershed determined by the WCS model.

Table 6.3 The mercury loading calculated by the WCS model for Parker Canyon Lake.

Characteristic	Units	Mean Value	Fraction of Lake Loading
Annual Mercury Deposition on Watershed	gram	326.3	---
Annual Mercury Deposition Directly on Lake	gram	6.5	28.9%
Annual Mercury Deposition from Runoff	gram	1.2	5.3%
Annual Mercury Deposition from Point Sources	gram	0.0	0.0%
Annual Mercury Load from Sediment	gram	14.8	65.8%
Total Annual Mercury Load	gram	22.5	100.0%

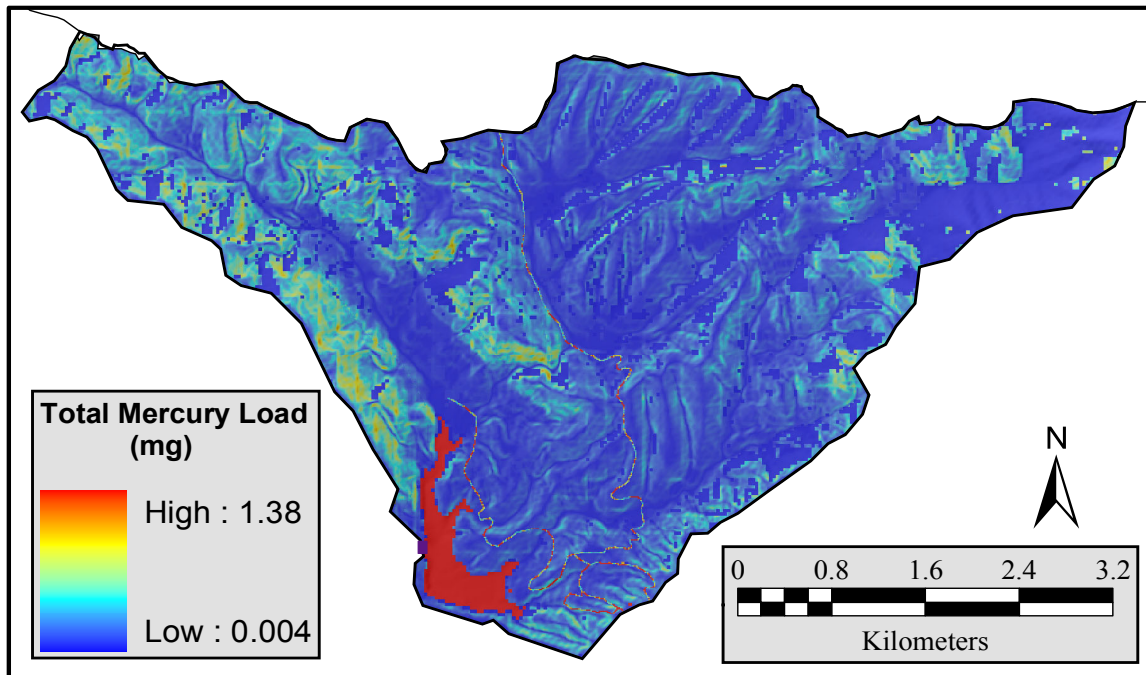


Figure 6.10 Total annual mercury loading into Parker Canyon Lake Watershed determined by the WCS model.

## 7 Water Balance

A water balance was performed for Parker Canyon Lake to determine lake volumes over time for the WASP7 model. Figure 7.1 graphically displays the basic hydrological processes that occur at Parker Canyon Lake. The water balance for Parker Canyon Lake was limited to recharge of water from precipitation events and groundwater and losses due to evaporation and seepage.

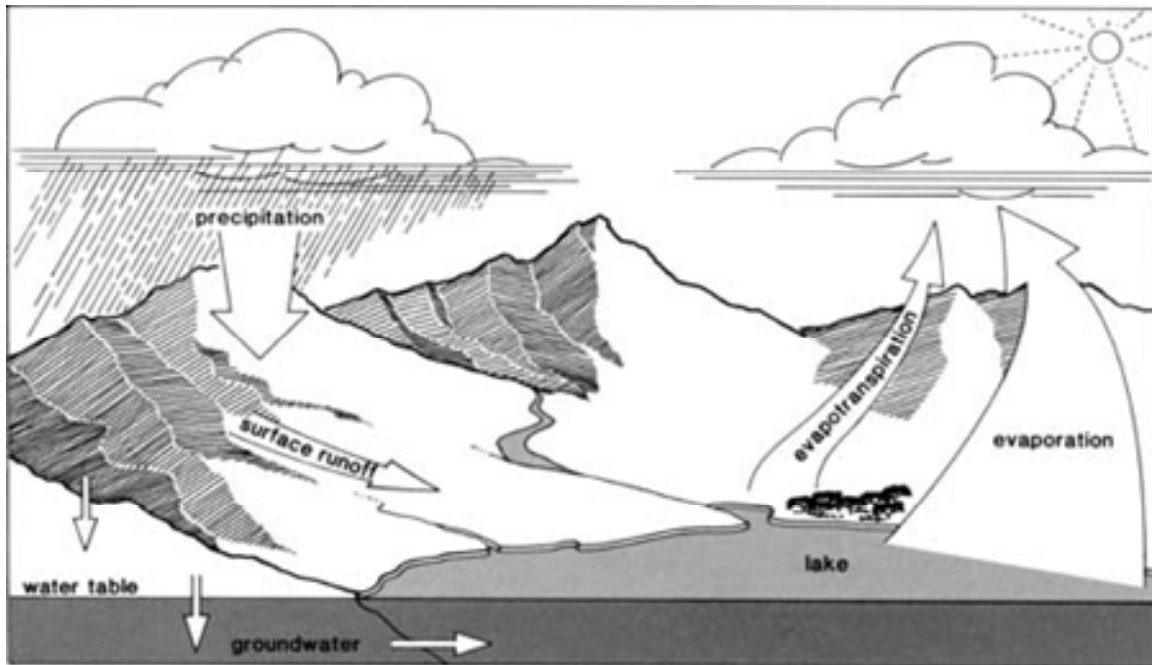


Figure 7.1 Hydrological processes that occur at Parker Canyon Lake. (Hendricks 1995)

### 7.1 Water Sources

The volume of runoff from the watershed was found by establishing a weighted average of the potential runoff calculated by the WCS. Running the model for 100 years to ensure steady state conditions resulted in an estimated 17 percent of rainfall enters the lake as runoff. The remaining 83 percent of the water infiltrates into the ground or is lost via evapotranspiration processes. Figure 7.2 shows the spatial distribution of runoff in the watershed. Using an average annual runoff of 7.9 cm, annual runoff volume from the 2300 ha watershed was calculated to be  $1.82 \times 10^6 \text{ m}^3$ . Direct rainfall onto the 50 ha lake

was calculated  $1.8 \times 10^5 \text{ m}^3$ ; therefore, the annual recharge of water from precipitation was calculated to be  $2.0 \times 10^6 \text{ m}^3$ .

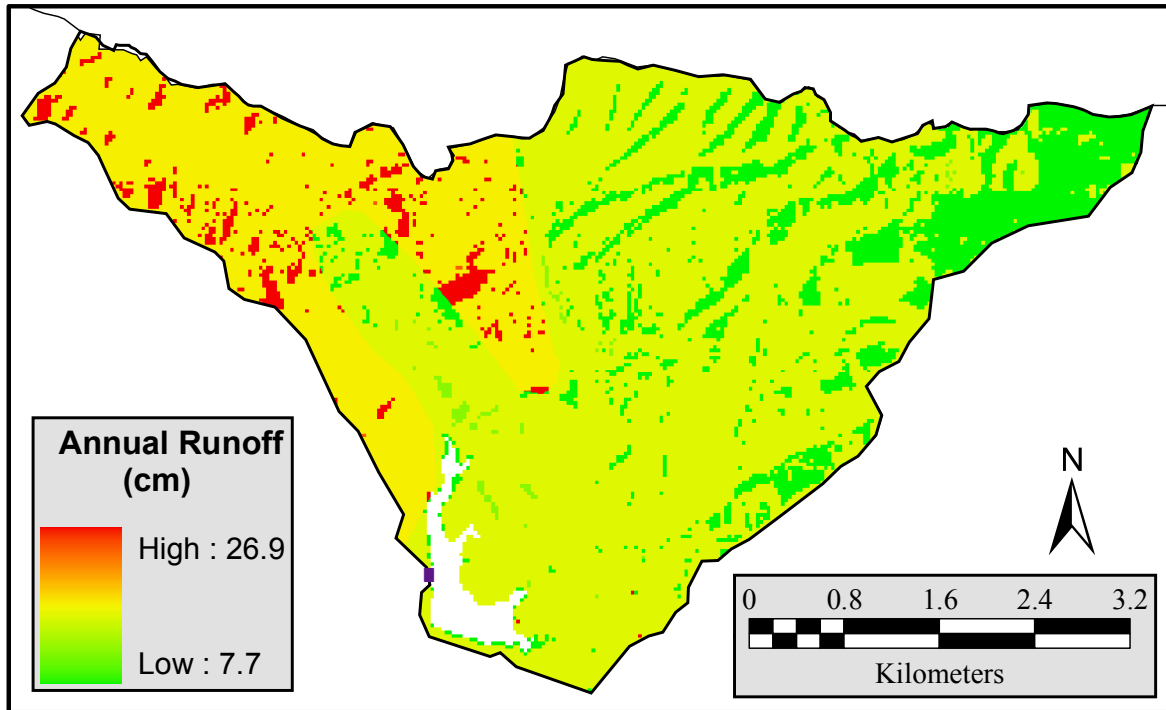


Figure 7.2 Map of annual runoff from the Parker Canyon Lake Watershed.

In addition to surface water runoff, there is at least one groundwater source in the northern portion of the Parker Canyon Lake named Collins Springs that feeds the lake. After an analysis of oxygen-18 isotopes, an ADEQ 2003 baseline report of the San Raphael Basin concluded that Collins Springs originates from a deep groundwater source. Deep groundwater sources are not impacted by recent precipitation events and it was assumed there was no change in groundwater feed rates in the lake during the period of study. The volume of recharge from Collins Springs or additional sources of groundwater into the lake is unknown. (Towne 2003)

## 7.2 Water Losses

Temperature is the primary driving force for evaporation, but multiple other factors such as wind speed, vapor pressure, and humidity prevent an accurate calculation of an evaporation rate for the lake. Rather than calculate an evaporation rate, data was

obtained from the closest evaporation pan at the Nogales 6 N COOP weather station. The station is located approximately 50 km southwest and 555 m lower in elevation than Parker Canyon Lake at a latitude 31.45°N and longitude 110.97°W with an elevation of 1085 m AMSL. The temperatures average about 2.5 °C warmer at the Nogales 6 N station than Parker Canyon Lake and it was assumed that evaporation rates were close to that of Parker Canyon Lake. The average evaporation data from the Nogales 6 N station for the period between 1952 and 2005 is shown in Table 7.1. (Lenters *et al.* 2005; NCDC 2006b; WRCC 2005b)

Table 7.1 Average monthly pan evaporation (cm) for Nogales 6 N weather station for the period from 1952-2005.

Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
9.1	11.3	17.8	23.7	30.3	33.8	25.4	21.0	20.5	18.2	11.4	9.1	231.6

A pan coefficient of 0.7 was used to convert the class A pan potential evaporation rates to actual evaporation rates. Pan evaporation coefficient values fall between 0.58 and 0.78, but the value of 0.7 is normally used for lakes and reservoirs. The annual evaporation volume from the surface of the 50 ha Parker Canyon Lake was calculated to be  $8.1 \times 10^5 \text{ m}^3$ . (Schwarz 2003; WRCC 2005b)

The annual recharge from rainfall is approximately twice the estimated losses to evaporation. This greater inflow should cause a condition where the lake surface continues to rise and eventually overflow the spillway shown in Figures 7.3 and 7.4. There is no evidence of deposited lake sediments or water caused erosion in the spillway and it is possible that overflow via the spillway has never occurred. In order to avoid overflowing the spillway, the lake would lose water at a rate faster than could be attributed to evaporation.





Figure 7.3 Photograph of lakeside of Parker Canyon Lake spillway.



Figure 7.4 Photograph of the back of spillway. The lack of erosion and sedimentation indicates infrequent use of spillway.

There is evidence of significant water loss from Parker Canyon Lake that cannot be attributed to evaporation loss and is likely caused by seepage through the earthen dam and/or infiltration into a shallow aquifer. A review of satellite photography taken in 2006 indicates that vegetation in the reach downstream of the dam is more lush and green than surrounding areas as shown in Figure 7.5. The satellite photography also reveals small ponds that have formed downstream of the dam indicating the water availability is higher than plant consumptive use and evaporation loss. The USFS is planning to repair the structure of the dam in early 2007. The scheduled repair supports the possibility that structural flaws may promote seepage through the aging dam. Additionally, it is possible that the lake level is periodically lowered by the use of an installed drainage valve; however, the preliminary site inspection of the dam revealed no obvious level control device. (Google Earth! 2006; USFS 2006)

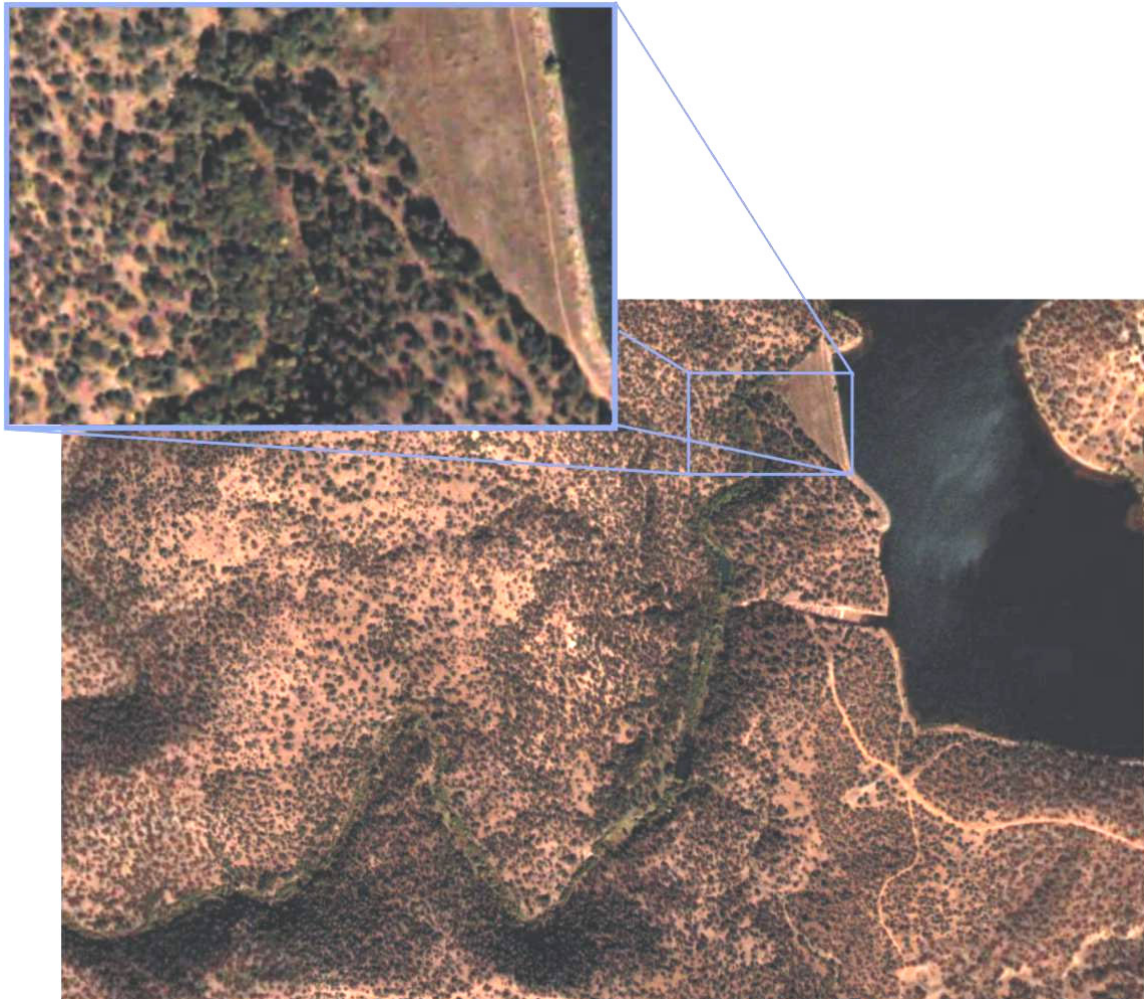


Figure 7.5 Satellite photograph of channel reach downstream of Parker Canyon Dam with close-up of vegetation adjacent to dam. (Google Earth! 2006)

During the water balance calculation, it was assumed that the lake would maintain a relatively constant level over a long period of time. It was also assumed that losses via infiltration and/or seepage did not change with fluctuating lake levels. Using these assumptions, the annual losses from seepage and infiltration was calculated to be  $1.51 \times 10^6 \text{ m}^3$  greater than inflow from groundwater.

### 7.3 Lake Volume

Inquiries of responsible government agencies did not uncover reliable information about past lake levels; therefore, that variable was not available for development of the water balance. During the preliminary site investigation in July 2006, it was observed that the



bottom of the staff gage shown in Figure 7.6 was located above the surface of the water. This improperly installed level gage may be the reason why no serious attempt has been made to record the lake's levels.



Figure 7.6 Photograph taken June 2006 of ineffective Parker Canyon Lake level gage.

ESRI's ArcView 3D-Analyst extension and available USGS digital elevation models (DEM) were used to determine the lake storage capacity at various depths shown in Figure 7.7. The bottom profile of the lake and estimated elevation of spillway were determined using the same DEM data. The lake bottom profile is shown in Figure 7.8.

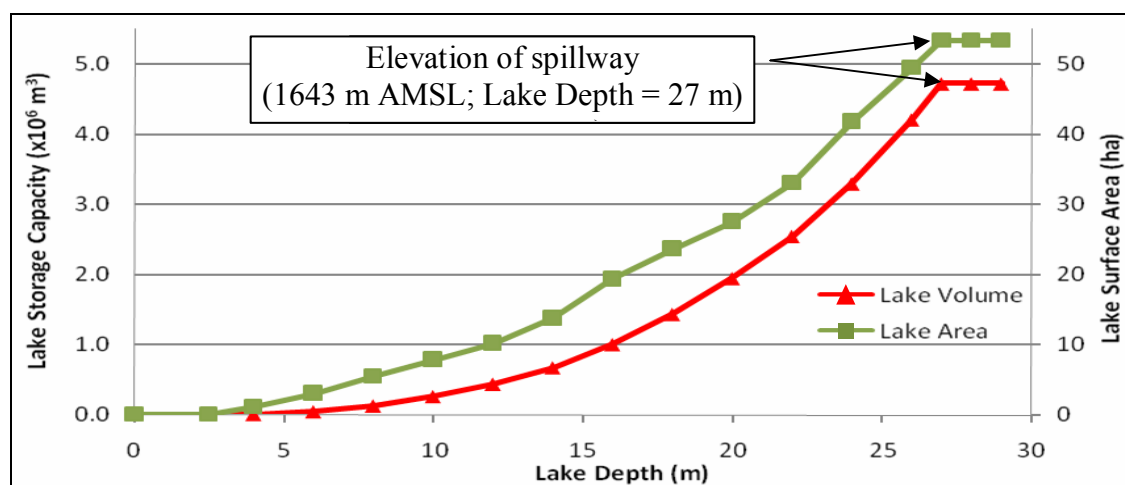


Figure 7.7 Graph of Parker Canyon Lake storage capacity and lake surface area for a given lake depth.

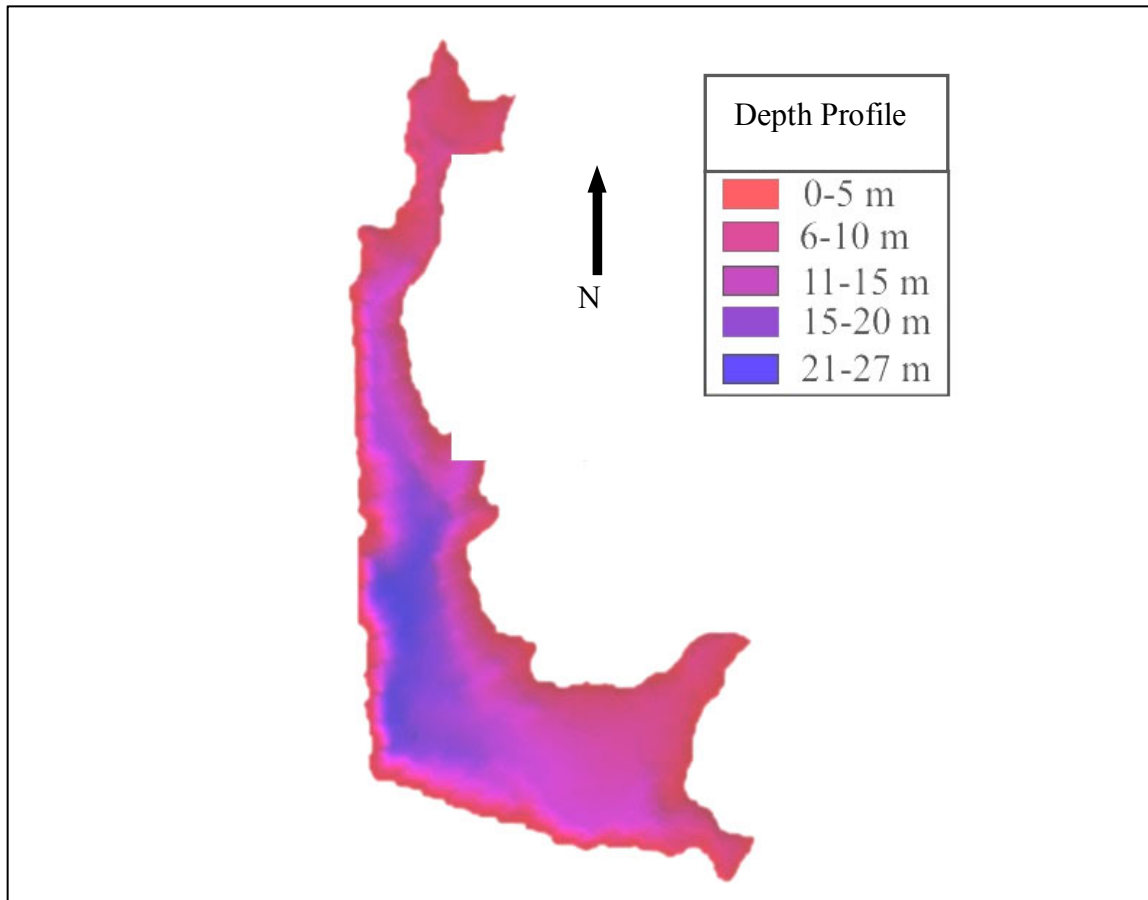


Figure 7.8 Bathymetric map of Parker Canyon Lake using USGS 1/3-arc second digital elevation data and extrapolation with ESRI's ArcView 3D-Analyst extension. The depth is based on a maximum lake height at the spillway with an elevation of 1643 m.

A clear line of sediment and organic deposition was visible on the shoreline during the preliminary site investigation of the lake as shown in Figure 7.9. It was assumed that this line corresponded to the maximum long-term storage volume in the lake. The sedimentation line is approximately one meter below the highest point in the spillway corresponding to a lake storage capacity of  $4.2 \times 10^6 \text{ m}^3$ .



Figure 7.9 Photograph of southern shoreline of Parker Canyon Lake taken June 7th, 2006 showing line of sedimentation.

## 7.4 Water Balance Results

The water balance accounts for all the known sources and sinks of water in the Parker Canyon Lake. Those sources and sinks are summarized in Table 7.2.

Table 7.2 Summary of annual water balance used for Parker Canyon Lake.

Characteristic	Volume (m <sup>3</sup> )
Annual inflow from precipitation	2.0 x10 <sup>6</sup>
Annual outflow due to evaporation	8.1 x10 <sup>5</sup>
Annual outflow due to seepage/infiltration	1.21x10 <sup>6</sup> greater than inflow from groundwater
Maximum water storage capacity evidenced by sedimentation on the shoreline	4.2 x10 <sup>6</sup>

The lake surface elevations were estimated for the time period from 1990 to 2002. Table 7.3 summarizes notable data points for the water balance. Figure 7.10 graphically shows the lake levels estimated from the water balance and depth-volume profile.

Table 7.3 Summary of notable data points from the water balance for 1990 to 2002.

Characteristic	Date of Occurrence	Volume (m <sup>3</sup> )	Lake Depth (m)
Initial Volume	January 1990	2.15 x 10 <sup>6</sup>	20.5
Minimum Volume	July 1990	1.3 x 10 <sup>6</sup>	17.3
Maximum Volume	February 1993	4.20 x 10 <sup>6</sup>	26.0
Average Volume	N/A	2.76 x 10 <sup>6</sup>	22.6

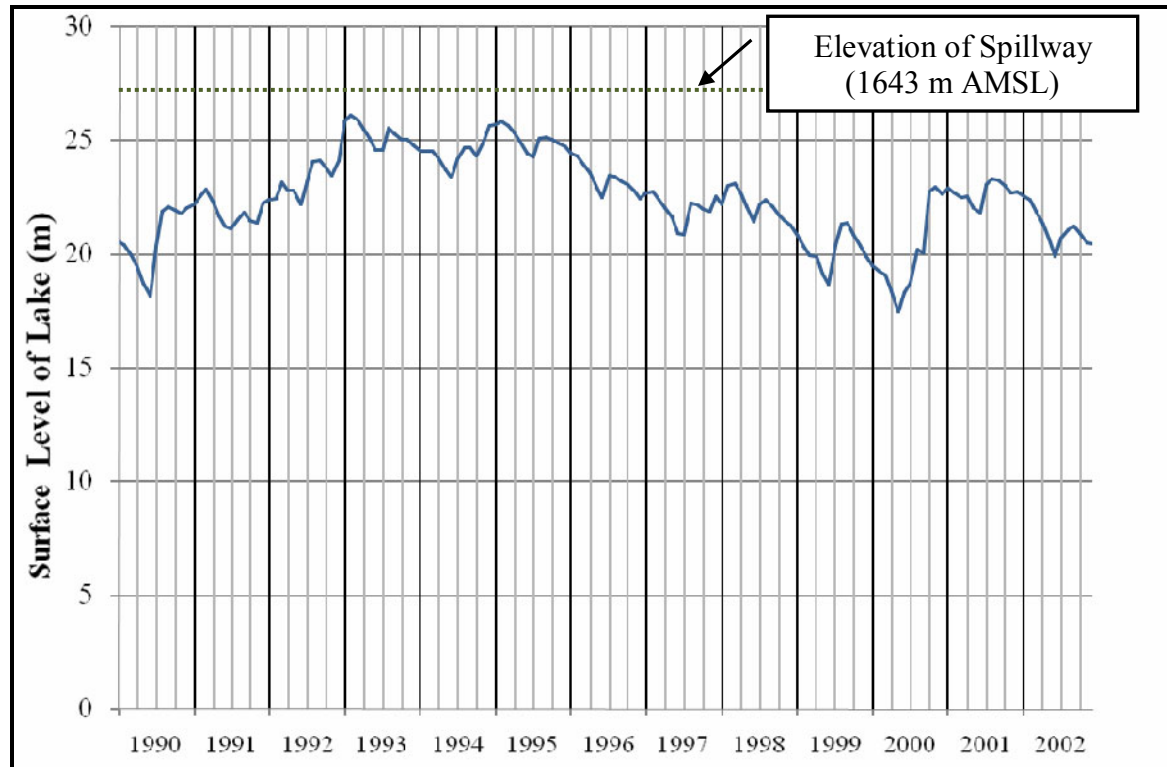


Figure 7.10 Surface level of Parker Canyon Lake above lowest point based on developed water balance for period 1990 to 2002.

In an October 1999, *Arizona Daily Star* reported that “Parker Canyon is anywhere between 10 and 15 feet below pool level ... the lake is so low that the docks and the boat ramp don't even touch the water.” The estimated water level from the water balance for October 1999 was 20.8 m. This level is 1.8 m below the estimated average lake capacity and 3.2 m below the observed maximum sedimentation level. The lake surface level from the developed water balance corresponds well with the newspaper article. (Wagner 1999)

## 8 Water Quality Goal Development

The Arizona Administrative Code Title 18, Chapter 11, Appendix B lists Parker Canyon Lake designated uses as Aquatic and Wildlife cold water (A&Wc), Full-body Contact (FBC), Fish Consumption (FC), Agricultural Irrigation (AgI), and Agricultural Livestock Watering (AgL). The applicable Arizona mercury standards for each of these levels are shown in Table 8.1. (A.A.C. 2003).

Table 8.1 Arizona mercury standards for Parker Canyon Lake designated water uses.

Designated Use	Mercury Standard (µg/L)
Aquatic and Wildlife Cold Water	acute: 2.4 dissolved
	chronic: 0.01 dissolved
Full Body Contact	42.0 total recoverable
Fish Consumption	0.6 total recoverable
Agricultural Irrigation	No Standard
Agricultural Livestock Watering	10.0 total recoverable

The lowest mercury levels allowed for the designated uses of Parker Canyon Lake is 0.6 µg/L for total recoverable mercury and chronic exposure of 0.01 µg/L for dissolved mercury. Chronic levels are determined from the geometric mean of the last four samples taken at least 24 hours apart. Available mercury sampling data conducted by ADEQ has never had dissolved or total recoverable mercury above the analytical detection limit of 0.5 µg /L; therefore, a new mercury water quality limit was developed for Parker Canyon Lake to achieve levels of MeHg in fish tissue safe for human consumption.

### 8.1 Fish Mercury Limits

The first step in developing a water quality goal for mercury in Parker Canyon Lake required establishing a limit for mercury allowed in fish. The limit was based on the amount of MeHg present in fish tissue since it comprises of 90-100% of total mercury found in fish tissues. Mercury limits to protect wildlife were not found due to the low

risk of exposure to predatory species. The only wildlife species that would consume enough fish to pose a health concern are large predatory birds. The only large birds present in Arizona that are believed to be capable of catching the larger fish at Parker Canyon Lake are bald eagles and Osprey. Bald eagles are not regularly found in the region and there are no known nesting sites within 150 kilometers. Osprey have been observed migrating through the region but there are no known nesting sites within 200 kilometers. (Corman 2005; SBEMC 2006; TetraTech 1999a; USEPA 1997a; USEPA 2006b)

The US Food and Drug Administration (FDA) set the consumption limit of mercury in fish and shellfish to 0.5 mg/kg in 1969. The limit was raised to the current limit of 1.0 mg/kg in 1979 because people were eating less fish than originally believed. The increase was also allowed as “a significant economic benefit to those industries most seriously affected by regulatory actions under the 0.5 [mg/kg] guideline.” (Bender 2003; SeafoodNIC 2005)

In 2001, the USEPA recommended a national criterion of 0.3 mg/kg total MeHg in wet fish tissue. The 0.3 mg/kg level is based on the toxicology analysis of mercury for an average adult and Equation 8.1. The non-cancer reference dose (RfD) of  $1 \times 10^{-4}$  mg MeHg/kg body weight-day was based on the Faroe Islands study where developmental effects were observed after the population was exposed to low levels of mercury for an extended period. A factor of 10 was incorporated in the RfD to account for uncertainty in biology. The relative source contribution of  $2.7 \times 10^{-5}$  mg MeHg/kg body weight-day accounts for other sources of MeHg in the environment. The amount of fish consumed are based on 90<sup>th</sup> percentile population estimated intake of uncooked aquatic TL2 = 3.8 g fish/day; TL3 = 8.0 g fish/day; and TL4 = 5.7 g fish/day. (NC DWQ 2004; USEPA 2001)

$$TRC = \frac{BW \times (RfD - RSC)}{FI} \quad (8.1)$$

Where	<i>TRC</i>	Fish tissue residue criterion for freshwater and estuarine fish
	<i>BW</i>	Human body weight, adult default value of 70 kg
	<i>RfD</i>	Reference dose of $1 \times 10^{-4}$ mg MeHg/kg body weight-day
	<i>RSC</i>	Relative source contribution of $2.7 \times 10^{-5}$ mg MeHg/kg body weight-day
	<i>FI</i>	Fish intake at trophic levels 2 to 4, total default intake for fish is 17.5 g /day for the general adult population.

The goal to obtain a wet tissue concentration of 0.3 mg/kg MeHg was used for the Parker Canyon Lake TMDL calculation because it is the most conservative of the various consumption limits. The level of 0.3 mg/kg is very conservative when compared to other mercury TMDLs completed in the United States. For example, a concentration limit of 1.0 mg/kg MeHg was used in the TMDL development of Arivaca Lake and Peña Blanca Lake both of which are located in southern Arizona. A problem with using the conservative limit of 0.3 mg/kg MeHg is that high natural background mercury may prevent the goal from being reached economically. (TetraTech 1999a; TetraTech 1999b)

## 8.2 Mercury Levels in Parker Canyon Fish

ADEQ conducted biological sampling during May 2001 and June 2002 to determine the extent of mercury contamination in Parker Canyon Lake's fish population. During the two different sampling periods a total of fourteen largemouth bass, four northern pike, and one black bullhead were caught. Table 8.2 contains the results from fish caught by ADEQ during two separate sampling periods at Parker Canyon Lake.

Table 8.2 Data reported by ADEQ for fish located in Parker Canyon Lake.

Date	Length (mm)	Weight (g)	MeHg in tissue (mg/kg)
<b>Largemouth bass (<i>Micropterus salmoides</i>)</b>			
5/22/01	265	300	0.95
5/22/01	304	456	0.99
5/22/01	330	602	0.9
5/22/01	345	645	0.85
5/22/01	346	695	1.2
5/22/01	360	783	1.1
5/22/01	370	915	0.66
5/22/01	383	991	0.43
5/22/01	388	1178	0.58
5/22/01	518	2453	0.62
6/28/02	379	967	1.4
6/28/02	414	1160	0.92
6/28/02	415	1257	1.6
6/28/02	436	1588	0.95
6/28/02	465	1720	0.61
<b>Northern Pike (<i>Esox lucius</i>)</b>			
6/28/02	531	1092	0.44
6/28/02	565	1629	0.4
6/28/02	628	2159	0.37
6/28/02	715	3400	0.69
<b>Black Bullhead (<i>Ictalurus melas</i>)</b>			
6/28/02	420	1252	0.73

A comparison of largemouth bass length versus weight was conducted using Microsoft Excel's least square linear regression to determine if any individual fish was abnormal when compared to the rest of the sample. Figure 8.1 shows that the growth of the largemouth bass follows a linear regression relationship as expected, i.e. the longer fish weighs more than the shorter fish. Table 8.3 contains the arithmetic and geometric mean for length, weight, and mercury content per mass of wet tissue for largemouth bass.



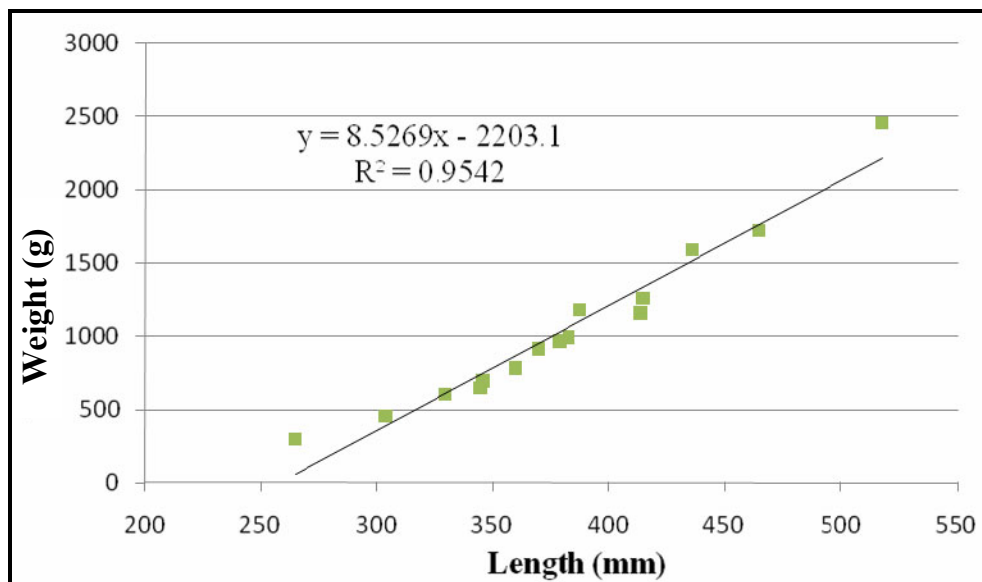


Figure 8.1 Fish length and weight of large mouth bass sampled.

Table 8.3 Arithmetic mean for largemouth bass in Parker Canyon Lake.

	Length (mm)	Weight (g)	Hg in Tissue (mg/kg)
Arithmetic Mean	381	1047	0.92

Aged fish are exposed to mercury content in the water over a longer period than young fish. Since fish length is a good indication of age, larger fish should have more mercury accumulated in their tissue than smaller fish. This was confirmed for both largemouth bass and northern pike by determining the least squares regression equation with Microsoft Excel shown in Figure 8.2 and Figure 8.3 respectively. The regression equations also show that largemouth bass concentrate more mercury per unit length than northern pike. (CRWQCB 2006)

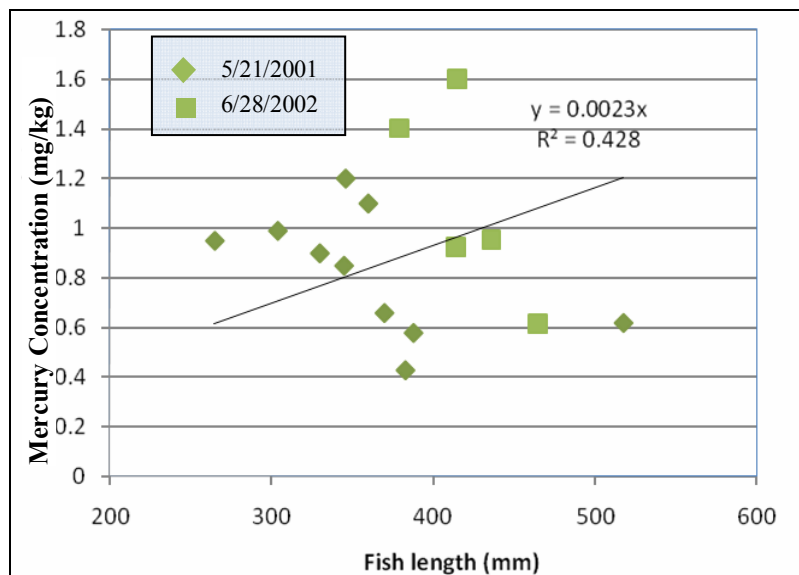


Figure 8.2 Largemouth bass sampled 5/22/2001 and 6/28/2002 for MeHg in wet tissue.

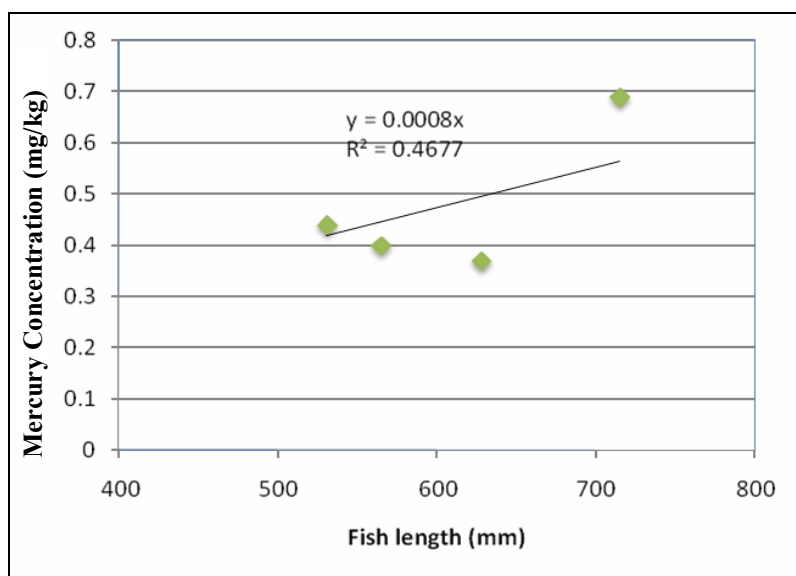


Figure 8.3 Northern pike sampled 6/28/2002 for MeHg in wet tissue.

Largemouth bass was selected as the reference aquatic species since it is a predatory TL4 fish that is frequently caught in Parker Canyon Lake. To be consistent with standardized practices a reference size fish of 40 cm was selected. Equation 8.2, obtained by the least squares method of Microsoft Excel's trendline function shown in Figure 8.2, was used to relate fish size with MeHg content in Parker Canyon Lake. (NC DWQ 2004)

$$C_{fish} = 0.0023 \cdot L_{length} \quad (8.2)$$

Where  $C_{fish}$  Concentration of MeHg in wet tissue in mg/kg  
 $L_{fish}$  Length of fish in mm

Using Equation 8.2, it was determined that a largemouth bass of 40 cm living in Parker Canyon Lake would be expected to have a wet tissue concentration of  $0.92 \pm 0.18$  mg/kg MeHg with 95% confidence. Since the calculated level of MeHg in fish tissue is higher than the USEPA recommended limit of 0.3 mg/kg, more stringent mercury water quality limits are required to have achieved acceptable levels in the fish.

### 8.3 Bioaccumulation Factor

In order to relate the levels in the water to the fish tissue a bioaccumulation factor (BAF) was found. The levels of MeHg in fish tissue can be used to determine the levels of MeHg in the water column where the fish lives by using Equation 8.3. (NC DWQ 2004)

$$C_{fish} = \frac{BAF \cdot C_{water}}{10^6} \quad (8.3)$$

Where  $C_{fish}$  Concentration of MeHg in fish tissue in mg/kg  
 $BAF$  Bioaccumulation factor in L/kg  
 $C_{water}$  Concentration of MeHg in water column in ng/L

BAFs are very difficult to determine since they are affected by numerous factors such as the age or size of the organism; food web structure; water quality parameters such as pH, Dissolved Organic contents, sulfates, alkalinity, dissolved oxygen, mercury loadings history; proximity to wetlands, watershed land use characteristics; and water body productivity, morphology, and hydrology. Since bioaccumulation is different for various water bodies due to changes in environmental conditions and ecosystems, several methods have been approved by the USEPA:

- Use of national methylmercury BAFs derived from empirical data
- Use of scientifically defensible bioaccumulation model
- Use of site-specific methylmercury BAFs derived from field studies.

The USEPA recommends the development of site specific BAF whenever possible to reduce possible errors by using generalized equations or models. There was not enough data to develop a scientifically defensible bioaccumulation model for Parker Canyon Lake. Generalized equations and site-specific methylmercury methods were used to find BAF for Parker Canyon Lake. (NC DWQ 2004; USEPA 2001; USEPA 2006b)

### 8.3.1 BAF from USEPA national empirical data

The USEPA has developed aquatic BAFs for various trophic levels obtained from nationally published reports. These BAFs are shown in Table 8.4. (USEPA 2006b)

Table 8.4 BAFs for different trophic levels based on USEPA national data.

Percentile	TL2 (L/kg)	TL3 (L/kg)	TL4 (L/kg)
5 <sup>th</sup>	$1.8 \times 10^4$	$7.43 \times 10^4$	$2.50 \times 10^5$
50 <sup>th</sup> (Geometric Mean)	$1.17 \times 10^5$	$6.80 \times 10^5$	$2.67 \times 10^6$
95 <sup>th</sup>	$7.70 \times 10^5$	$6.23 \times 10^6$	$2.84 \times 10^7$

The average MeHg content for the 40 cm reference largemouth bass was determined to be 0.92 mg/kg MeHg. Using this value and the national USEPA empirical geometric mean value BAF of  $2.67 \times 10^6$  L/kg for a TL4 fish in Equation 8.3 results in a calculated mercury concentration in the water column of 0.345 ng/L. Additionally, in order to obtain the mercury concentration goal in fish tissue of 0.3 mg/kg MeHg the mercury in the water column needs to be less than 0.112 ng/L.

### 8.3.2 BAF from USGS generalized equation

The USGS conducted a study of 20 different watersheds throughout the United States to develop a generalized BAF for mercury in fish. The results of study resulted in equation 8.4 for mercury concentrations in Large Mouth Bass. The equation sometimes referred to as the Brumbaugh equation has a correlation coefficient ( $R^2$ ) of 0.5075 which is relatively good for biological systems. The USGS report also stated that other factors such as watershed land use, percentage of wetlands, and pH of water drastically impact the accumulation equation. (USGS 2001)

$$\ln \left[ \frac{1000C_{fish}}{L_{fish}} \right] = 0.3999 \cdot \ln [C_{water}] + 1.3184 \quad (8.4)$$

Using Equation 8.4 and a fish concentration of 0.92 mg/kg MeHg results in a calculated mercury concentration in the water column of 0.297 ng/L. Additionally, in order to obtain the mercury concentration goal in fish tissue of 0.30 mg/kg MeHg the mercury in the water column needs to be less than 0.018 ng/L.

### 8.3.3 Direct extrapolation of BAF for single water body

Another method used to determine BAF for mercury in fish at Parker Canyon Lake was direct extrapolation of available sample data. The average MeHg concentration in the water column from seven samples taken by ADEQ in October 2003 and February 2006 was 2.17 ng/L  $\pm$  2.45 ng/L with 95% confidence. Since there cannot be less than zero mercury in the water, the true concentration of MeHg in the water lies between 0 and 4.62 ng/L with 95% confidence. This concentration in the water column and a fish concentration of 0.92 mg/kg MeHg results in a calculated BAF of  $4.24 \times 10^5$  L/kg. Additionally, in order to obtain the mercury concentration goal in fish tissue of 0.3 mg/kg MeHg the mercury in the water column needs to be less than 0.707 ng/L.

### 8.3.4 Regional analysis derivation of BAF

In addition to national empirical equations and sampling data from Parker Canyon Lake, data obtained from similar lakes in southern Arizona were used to develop a regional BAF. The three lakes were the 20 ha Peña Blanca Lake located 50 km away, the 36 ha Arivaca Lake located 70 km away, and the 81 ha Patagonia Lake located 30 km away. All regional lakes are manmade reservoirs with similar aquatic ecosystems as Parker Canyon Lake. The observed concentrations of MeHg and BAFs for all four regional lakes are shown in Table 8.5. (TetraTech 1999a)

Table 8.5 Observed mercury concentrations in fish tissue and water column for southern Arizona lakes.

Water Body	Observed MeHg in the water column (ng/L)	Observed average MeHg in fish tissue (mg/kg)	BAF (L/kg)
Parker Canyon Lake	2.05	0.92	$4.24 \times 10^5$
Peña Blanca Lake	3.92	1.42	$3.62 \times 10^5$
Arivaca Lake	14.3	1.18	$8.25 \times 10^4$
Patagonia Lake	0.78	0.14	$1.79 \times 10^5$
Arithmetic Mean	5.29	0.92	$2.62 \times 10^5$

The arithmetic mean BAFs of regional lakes is  $2.62 \times 10^5$  L/kg with an estimated MeHg concentration of 0.92 mg/kg for the reference 40 cm fish. This BAF was used in Equation 8.3 resulting in MeHg concentration in the water column of 4.21 ng/L. In order to obtain the level of 0.3 mg/kg MeHg in the fish tissue the concentration of MeHg in the water column was calculated to be less than 1.374 ng/L.

### 8.3.5 Regional analysis derivation of logarithmic BAF

A plot of the regional lakes mercury levels are shown in Figure 8.4. The values listed in Table 8.5 were analyzed using Microsoft Excel's trendline function to find a least square equation that related MeHg in the water column to MeHg in fish tissue for the regional lakes. The best fit for the trendline was the logarithmic function shown in Equation 8.5 with an  $R^2$  value of 0.618.

$$C_{fish} = 0.3597 \ln(C_{water}) + 0.5056 \quad (8.5)$$

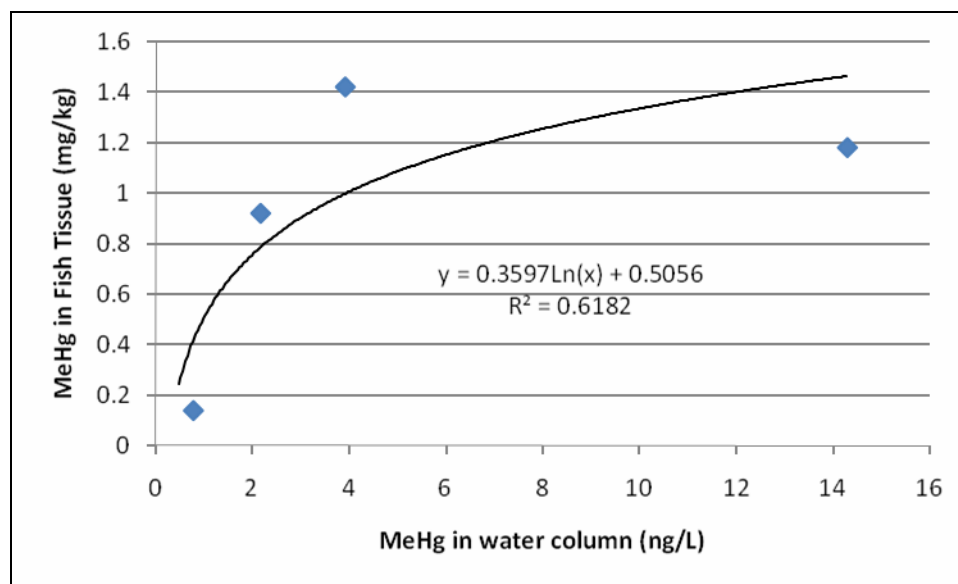


Figure 8.4 Southern Arizona lakes MeHg levels in water column and fish tissue plotted with logarithmic least square regression line.

Using Equation 8.5 and a fish concentration of 0.92 mg/kg MeHg results in a calculated mercury concentration in the water column of 3.16 ng/L. In order to obtain the mercury concentration goal in fish tissue of 0.3 mg/kg MeHg the mercury in the water column needs to be less than 0.56 ng/L.

### 8.3.6 Comparison of the different BAF development methods

The summary of the different methods used to determine BAF and the required reduction to obtain the limit of 0.3 mg/kg MeHg in the fish tissue is shown in Table 8.6. It should be noted that the estimated levels of MeHg in the water column shown in Table 8.6 are based on obtaining 0.92 mg/kg MeHg found in the reference 40 cm largemouth bass fish tissue and the derived BAF.

Table 8.6 Summary of the different methods used to derive BAF and required reduction in MeHg in the water column to obtain the goal of less than 0.3 mg/kg MeHg in the fish tissue.

Method	BAF for a 40 cm TL4 fish (L/kg)	Estimated MeHg in the water column (ng/L)	MeHg in water column to meet fish tissue goal (ng/L)	Reduction of MeHg required
EPA draft value for TL4 species	$2.67 \times 10^6$	0.345	0.112	68%
USGS logarithmic equation for Largemouth Bass	$3.10 \times 10^6$	0.297	0.018	94%
Arithmetic mean for only Parker Canyon Lake	$4.24 \times 10^5$	2.17	0.707	68%
Regional arithmetic mean	$2.62 \times 10^5$	4.21	1.374	68%
Regional logarithmic regression equation	$2.91 \times 10^5$	3.16	0.56	83%

While all methods are valid and have been used for mercury TMDL development in the past, there are several advantages for using the water quality limits found by the regional logarithmic regression equation method. The regional approach allows more data points to the sample set; therefore, the margin of error is reduced. Additionally, the approach is less dependent on natural variability during an individual sampling period. The logarithmic equation also mimics the levels of MeHg in fish tissue observed in the natural environment in that it increases rapidly at lower concentrations of MeHg in the water column and plateaus at higher concentrations. Finally, the reduction of 83% is conservative when compared to all the other methods with the exception of the USGS equation method that has documented inaccuracies at low mercury levels. (NC DWQ 2004; USGS 2001)



## **8.4 Mercury Water Quality Standard for Parker Canyon Lake**

As discussed previously, none of the state of Arizona water quality standards for mercury have been exceeded at Parker Canyon Lake; however, the fish contain approximately three times the recommend limit of mercury within their tissue. In order to obtain the proposed limit of 0.3 mg/kg MeHg, the regional logarithmic approach to development of a BAF was used to develop a unique mercury water quality standard of 0.56 ng/L MeHg for Parker Canyon Lake. The developed water quality standard of 0.56 ng/L total MeHg requires 83% reduction in MeHg in the water column and should result in acceptable levels of mercury in fish for human consumption.

## 9 Linkage Analysis

Mercury levels can be different in lakes that have a close proximity, the same atmospheric deposition, same recreation uses, and similar geological characteristics. This variation can be seen in southern Arizona's regional lakes. Patagonia Lake has had safe levels of mercury in fish, but two other lakes near Parker Canyon Lake, Arivaca Lake and Peña Blanca Lake, have had levels that exceed regulatory reporting requirements indicating that mercury reactions occur at different rates under similar conditions. (TetraTech 1999b)

In order to determine the fate of mercury species in Parker Canyon Lake, internal lake cycling, and the assimilative capacity, a linkage analysis using the WASP7 model was developed and calibrated. The water quality model was then used to determine the maximum mercury loading into the lake that would meet the water column MeHg goal of 0.56 ng/L.

### 9.1 WASP7 Model Inputs

The WASP7 model for mercury in Parker Canyon Lake was run for period between January 1990 and January 2003. The lack of precipitation data from the nearest weather station, Canelo 1 NW, from 2003 to 2005 required that the model run be limited. The thirteen year period that was modeled is sufficient to obtain mercury equilibrium in the lake without errors caused by changes in atmospheric mercury deposition rates or land use. (NC DWQ 2004; USEPA 2002 )

The WASP7 model has the ability to change to complexity of flows and exchanges based on the need of the modeler. The Parker Canyon Lake WASP7 model evolved from a simple one-dimensional single-layer to three-dimensional multi-layer system. Each step in the evolution made the model a better representation of mercury fate and transport within Parker Canyon Lake. The final three-dimensional multi-layer system used by WASP7 to model Parker Canyon is shown in Figure 9.1. (USEPA 2002)

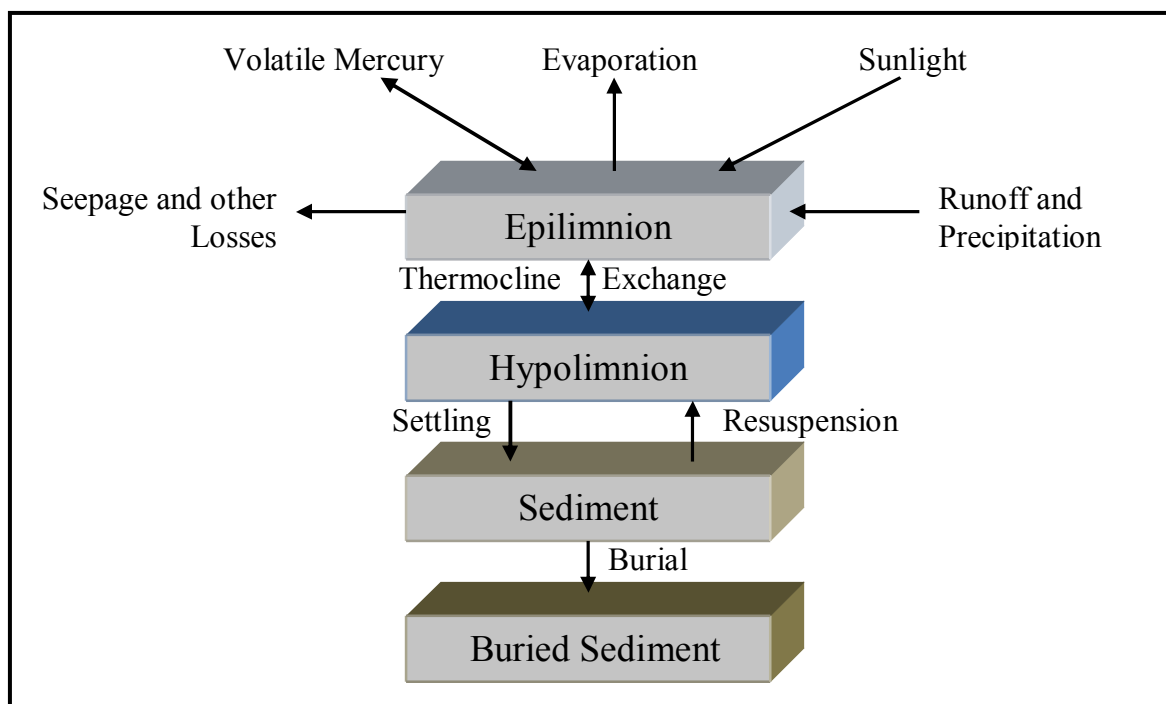


Figure 9.1 The layers, sources, losses, and exchanges modeled with WASP7 linkage analysis for Parker Canyon Lake.

The upper layer, labeled the epilimnion, was simulated as a surface water layer that had contact with the atmosphere. The epilimnion layer also was modeled as the receiving layer for runoff, precipitation, and external mercury loads. It is also the layer where water loss via evaporation and seepage occurred. Annual changes in lake level due to evaporation, seepage, runoff, and precipitation caused the epilimnion layer to have changes in volume and depth. (USEPA 2002)

The second layer, labeled the hypolimnion, was modeled as a constant eight meter thick subsurface layer that interacted with the epilimnion and lake sediment. The exchanges of chemicals and particulates between the hypolimnion and epilimnion were simulated as unobstructed from November through April to represent complete mixing of the lake during non-stratified period. Between May and October exchanges of chemicals and particulates were reduced to one tenth of unobstructed mixing rates. This reduction of one tenth simulated stratification of the lake during warmer months. (USEPA 2002)

The third layer, labeled the sediment layer, was modeled as a 10 cm thick benthic layer with exchanges between the sediment and water layers. Silt, clay, and sand were simulated to settle and resuspend between the water column and the sediment layer. The cycling of the solid particles in the water ensured that sediment sorbed mercury would reenter the waterbody. (USEPA 2002)

The fourth and deepest layer, labeled the buried sediment layer, was modeled as a subsurface benthic layer that was a sink for mercury in the lake. The layer was simulated as a constant one meter thick particulate layer that interacted only with the sediment layer. The chemical species were also allowed to be absorbed or buried into the bottom layer where they would be isolated and not undergo any further reactions. Mercury burial rates of 12.2 cm/yr were used based on sediment deposition from Northern Arizona lakes. The burial rates are likely higher for Parker Canyon Lake due to larger amount of eroded soils that enter the lake. (Gremillion and Toney 2005; USEPA 2002)

The WASP7 model simulates the reactions of three components: elemental mercury, inorganic divalent mercury, and monomethylmercury. These reactions are complicated and rely on bacterial growth, pH, temperature, light intensity, organic material, dissolved content, and many other variables. The complexity of the reactions makes it difficult to assign viable reaction rates for the equations that are used by WASP7. In fact, many of the reaction rates have acceptable ranges over three or four orders of magnitude. Since no reaction rates have yet been determined for Parker Canyon Lake, previously used reaction rates from USEPA approved documents were used to develop the Parker Canyon Lake WASP7 model. The reaction rates and other parameters that were used in the WASP7 model development are summarized in Appendix B. A sensitivity analysis was not performed for the model. (DWQ 2004; USEPA 1997a)

The average concentration of mercury in the incoming water was determined from mercury load from WCS and inflows from the water balance. Table 9.1 lists the annual mercury load determined by the WCS model. In wetland areas methylmercury in runoff can be up to 20% of total mercury loading; however, the values used in the WASP7

model were based on experiments conducted in arid regions where mercury is primarily the divalent form at 96.9%, followed by methylmercury at 3%, and elemental mercury a much smaller contributor at 0.1%. (Foster *et al.* 2006)

Table 9.1 Inputs into WASP7 water quality model from WCS spatial model.

Characteristic	Units	Mean Value
Hg Deposition Directly on Lake	gram	6.5
Hg Deposition from Runoff	gram	1.2
Hg load from Sediment	gram	14.8
Total Annual Mercury Load	gram	22.5

The earliest available ADEQ low level mercury sampling for Parker Canyon Lake occurred in 2003. The lack of concurrent sampling data with modeling period prevented accurate calibration of the model. The model was instead calibrated using the percentage of methylmercury to total mercury, peak mercury concentration detected during ADEQ testing, and estimated average MeHg level of 3.17 ng/L found by the regional logarithmic bioaccumulation factor.

## 9.2 WASP7 Model Results

Figure 9.2 shows the mercury species modeled with WASP7 after calibration. Figure 9.3 shows a more detailed view of methylmercury and elemental mercury species in the epilimnion. The epilimnion is shown because it is the layer that fish normally inhabit due to the higher levels of dissolved oxygen. The modeled results are close to as expected with total mercury levels increasing after periods of rainfall and decreasing during periods of drought. The methylmercury levels peak shortly after divalent mercury levels peak indicating that the model is simulating transformations and exchanges in the water and sediment. The model results show that methylmercury species periodically increase after precipitation events. With no additional loading, levels decrease due to volatilization and sediment burial within a period of months. When the lake was not stratified, the WASP7 model simulated the lake as a single waterbody with no difference in mercury concentrations. When the lake was stratified during warmer months, there

was still little difference in the methylmercury levels in the hypolimnion and epilimnion due to modeled exchanges between the layers. These results match the ADEQ sample data that show concentrations of methylmercury as high as 11.4 ng/L during October 2003 shortly after the monsoon season and concentrations as low as 0.154 ng/L during February 2006 following a relatively dry period. Figure 9.3 also shows that elemental mercury levels remain lowest with gradual increases that match the other species as expected. (TetraTech 2005; USEPA 2006b)

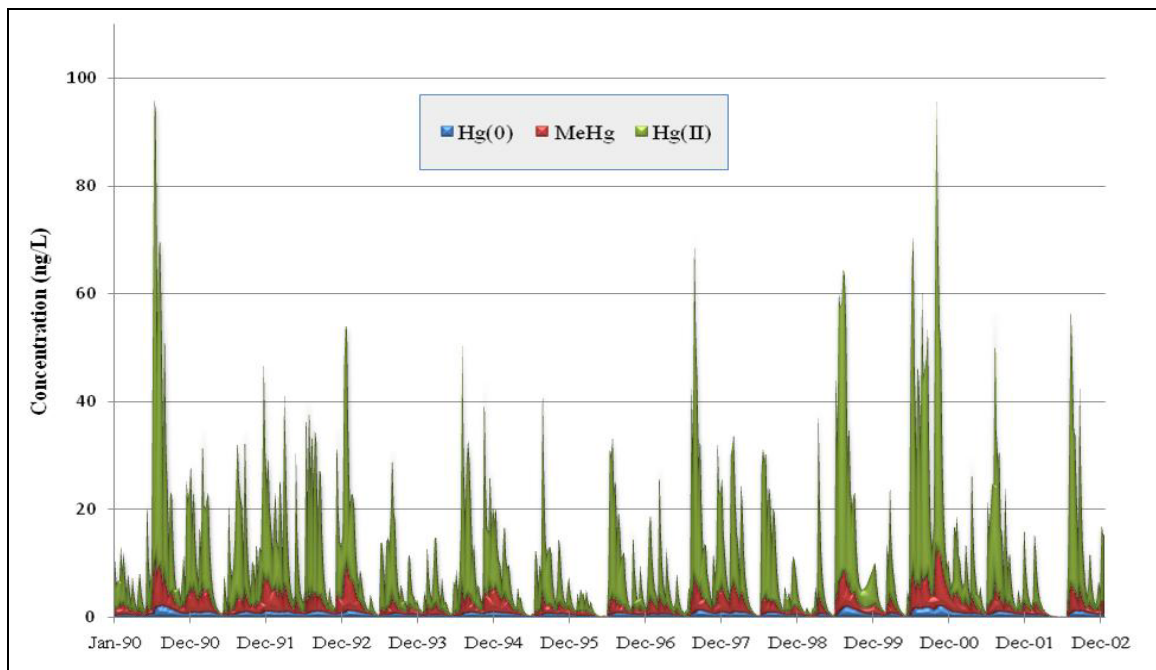


Figure 9.2 Results of WASP7 model for Parker Canyon Lake showing concentrations of elemental mercury, methyl mercury, and divalent mercury in the epilimnion layer.

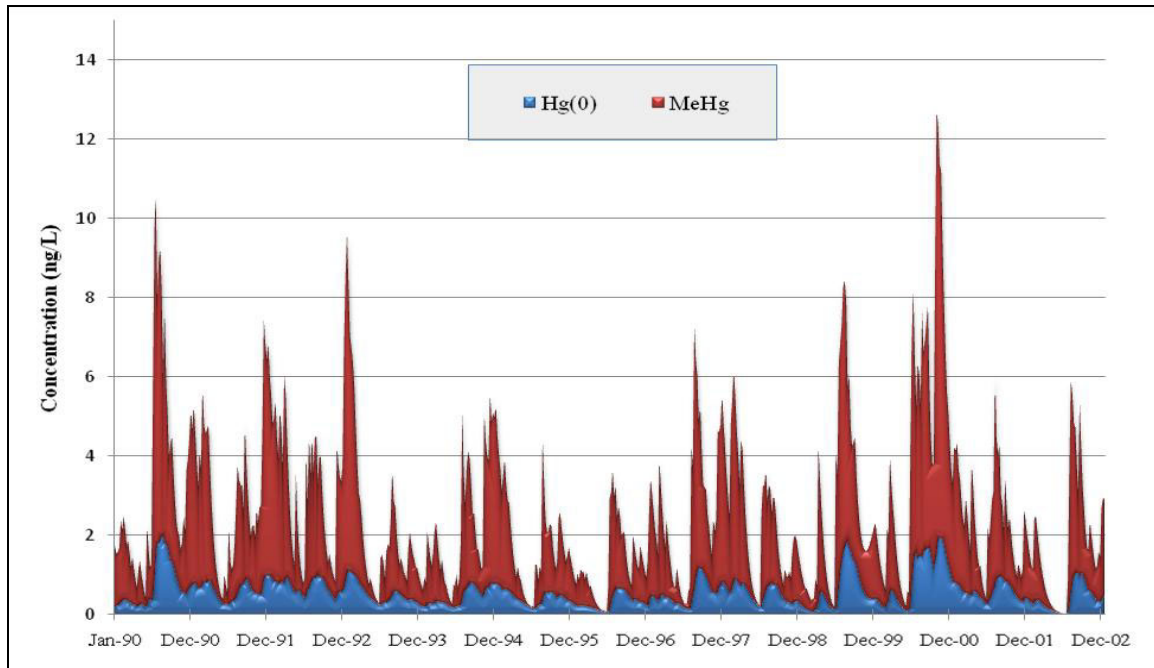


Figure 9.3 Results of WASP7 model for Parker Canyon Lake showing more detail on the concentrations of elemental mercury and methylmercury in the epilimnion layer.

The model was also used to determine the impact of different mercury loads on the lake. Several scenarios with varying concentrations of mercury in the runoff and precipitation were simulated using the calibrated WASP7 model. The constants and parameters were not changed for each scenario. The resulting mercury levels in the water column for each scenario were plotted as shown in Figure 9.4.

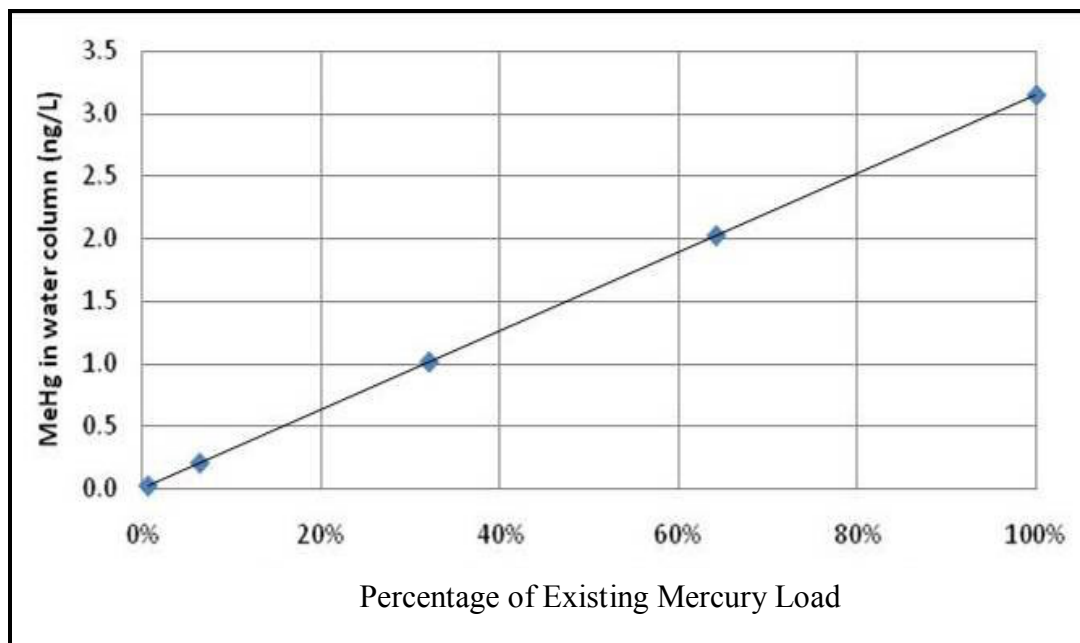


Figure 9.4 Concentration of methylmercury in the water column based upon multiple load reduction scenarios simulated In the WASP7 model for Parker Canyon Lake.

The response was linear as expected and indicates a direct correlation between mercury levels in the water column and mercury loading into the lake. This direct correlation has been observed in other mercury TMDLs conducted for lakes inside Arizona and other regions of the country. As can be seen in Figure 9.4, the existing mercury loading needs to be reduced by 83% to obtain the water quality goal of 0.56 ng/L in the water column. (NC DWQ 2004; USEPA 2006b)



## 10 Total Maximum Daily Load Summary

A TMDL is the total amounts of a pollutant that can be assimilated by a waterbody and still achieve water quality standards. The TMDL is the sum of allowed point sources, allowed non-point sources, and a margin of safety as seen in Equation 10.1.

$$TMDL = \Sigma WLA + \Sigma LA + MOS \quad (10.1)$$

Where      *TMDL*    Total Maximum Daily Load  
               *WLA*      Waste Load Allocation  
               *LA*        Load Allocation  
               *MOS*     Margin of Safety

Table 10.1 Summary of values resulting from mercury TMDL for Parker Canyon Lake.

<b>TMDL</b>	<b><math>\Sigma</math> WLA</b>	<b><math>\Sigma</math> LA</b>	<b>MOS</b>
3.82 g/yr	0 g/yr	3.44 g/yr	0.38 g/yr

### 10.1 Waste Load Allocation

Waste Load Allocation is the term that accounts for point sources of a pollutant. A review of USEPA emission inventories, industrial emission inventories, and historical records of mining in the area revealed no point sources for mercury inside of the Parker Canyon Lake Watershed. Without point sources the WLA was set to 0 g. (TetraTech 2005)

### 10.2 Load Allocation

Load Allocation is the term that accounts for non-point sources of a pollutant. The non-point sources of mercury loading are naturally occurring mercury in the watershed from soils and atmospheric deposition of distant sources of airborne mercury. A majority of the non-point sources of mercury enter the lake as a result of precipitation events either as runoff or rain scrubbing of airborne mercury. The remaining mercury enters the lake from dry deposition of airborne mercury onto the lake. In the case of Parker Canyon

Lake where the TMDL was determined with models and there are no WLA, the LA is the term that is found with Equation 10.1. (TetraTech 2005)

### **10.3 Margin of Safety**

The margin of safety is the term that accounts for uncertainty in the relation between pollutant loads and receiving water quality. The MOS can be determined explicitly or implicitly. The use of an explicit MOS requires that a specific portion of the TMDL calculations are set aside for uncertainties in the modeling by reserving a portion of the total load as a safety factor. Traditionally, this portion is 10 percent of the total loading; however, values as high as 75 percent have been used when there is great uncertainty in values. The use of explicit MOS is simple to understand and avoids the complication of additional statistics; however, the TMDL becomes more stringent since the load attributed to MOS is not permitted to come from point or non-point sources. The second approach is an implicit MOS which requires that each step of the TMDL use conservative values that account for uncertainties. An advantage of the implicit MOS is that loading is not reduced further since errors are already accounted for; however, the implicit MOS is often difficult to explain how the uncertainty was addressed. (CBP 2006; NC DWQ 2004)

A ten percent explicit MOS was chosen to be consistent with other mercury TMDLs and results in a MOS of 0.38 g/yr. An implicit MOS was not warranted due to the error that could exist in the models; however, a large explicit MOS was not used since conservative values were used when developing models. Additionally, the USEPA recommended fish consumption limit of 0.3 mg/kg has built-in ten fold conservative factor fold that accounts for most uncertainty in the analysis. (CBP 2006)

### **10.4 Total Maximum Daily Load**

The mercury TMDL for Parker Canyon Lake was developed from the results of the WCS spatial model, regional BAF factor, and WASP7 linkage analysis. The WCS model estimates an existing annual load of 22.5 g of mercury in various forms and sources enters Parker Canyon Lake. The WASP7 model revealed that the critical condition occurs

when the bioaccumulation of mercury is quickest during low lake levels after the large runoff events with a stratified lake. During an average year, the 22.5 g annual load of mercury causes the reference 40 cm Largemouth Bass to have 0.92 mg/kg of MeHg in tissue based on an estimated average concentration of 3.17 ng/L MeHg in the water column. Additionally, it was found that the water column should have less than 0.56 ng/L MeHg to meet USEPA recommend guidance of 0.3 mg/kg MeHg in fish tissue. A linkage analysis using the WASP7 water quality model showed that the loading would need to be reduced by 83 percent in order to obtain the level of 0.56 ng/L MeHg in the water column; therefore, reducing the estimated 22.5 g/yr currently entering the lake by 83 percent results in a TMDL of 3.82 g/yr. In other words, the lake can assimilate up to 3.82 g/yr of total mercury and still have resident fish mercury levels that are acceptable for human consumption.

## 11 Recommendations

After a TMDL is developed for an impaired waterbody, the USEPA recommends developing an implementation plan to meet water quality standards. Implementation of the TMDL could include policy changes, management strategies, or remediation techniques depending on the extent of the problem and source of contamination. The implementation plan is normally developed and administered by the responsible state or local authority. (USEPA 2002)

Prior to implementation, the Parker Canyon Lake mercury TMDL should be verified by additional testing. Water sampling should be performed under various conditions to better understand how mercury is transported in the lake. Ideal times to sample would be after large storm events and during low lake levels since they are identified as critical conditions that will cause the highest mercury concentrations in the lake. Mercury samples should be taken at various depths if stratification is suspected. In addition to lake sampling, it is recommended that runoff be analyzed for solids, organics, and mercury content which would help determine actual loading into the lake. Sediment coring of the lake could be used to observe mercury deposition trends and the impact of shutting down the Cananea and Douglas Smelters. Finally, sampling of the soils in the watershed would allow better classification of the soils and possibly reveal mercury hotspots which could be controlled. (NC DWQ 2004; TetraTech 1999)

In addition to sampling it is recommended that monitoring climate and mercury deposition occur in the watershed. The hydrology of the lake for the TMDL is based on an estimated water balance. Installing a simple weather station and monitoring lake levels would lead to a more accurate water balance and a better TMDL. Monitoring for both wet and dry mercury depositions would allow for calibration of values from the nearest MDN station. Ideally, an ambient monitoring station will be installed to continuously monitor lake chemistry and mercury content. Even if the monitor can not detect low levels of mercury, the station would record important contributing factors for

methylation such as pH and dissolved organic carbon concentrations. (NC DWQ 2004; TetraTech 1999)

No significant mercury point sources have been identified within the Parker Canyon Lake Watershed and it is assumed that almost all of the loading is a result of atmospheric deposition from distant sources on the watershed. To reduce the amount of atmospherically deposited mercury that enters Parker Canyon Lake, management techniques could be used and engineered structures built. Management techniques include soil conservation techniques such as requiring anti-erosion controls during construction and reducing the amount of grazing animals. Engineered systems include the installation of sediment traps in major drains into the lake. The peak flows experienced during infrequent high-intensity rain events may prevent sediment traps from being effective for every storm, but more common low-intensity storms should allow the sediment traps to effectively reduce the mercury loading into the lake. To assist in the design of sediment traps, estimated peak flow rates into Parker Canyon Lake for different return period storms are provided in Appendix C. (TetraTech 1999b)

Even with sediment controls, achieving the 83 percent reduction in watershed loading may be impossible to achieve under current atmospheric conditions. An estimated 28.9 percent of the mercury loading is directly deposited on the lake surface. In order to achieve the TMDL, massive restructuring of federal and international mercury emission standards are required. Alternatively, the rate of methylation and/or demethylation in the lake could be changed to reduce MeHg concentrations in the lake. (TetraTech 1999b)

There are several methods that have been successful on a laboratory scale to change methylation and demethylation rates in an aquatic system. One method is aeration or mixing of the waterbody. This method reduces anaerobic conditions in the lake and thus lowers the rate of methylation. It also disturbs or prevents the formation of the hypolimnion layer to allow even distribution of MeHg throughout the lake. The high costs of constant aeration or mixing of Parker Canyon Lake may prevent the method from being feasible. Another method is to alter the sulfur chemistry in the lake in order to promote the growth of demethylating bacteria and reduce the amount of dissolved

mercury in the water column. A problem with altering sulfur chemistry is that it may adversely impact other lake chemical parameters and lead to additional problems. Another proposed method to reduce mercury content in lakes is treatment with aluminum sulfate. Aluminum sulfate treatment causes scavenged particulate matter to form flocs that are removed from the lake. The treatment is similar to the process used to clean drinking water in conventional water treatment plants. While the treated water would contain less organic and suspended material, the cost of alum treatment may be excessive and there is also the danger of aluminum poisoning of the lake. (TetraTech 1999a)

If it is discovered that mercury in the sediment is the cause of high mercury levels in the fish, then remediation of the lake will need to occur. A method that has been successful for sediment remediation in the past is dredging. Dredging removes the source of contamination from the lake and if done correctly does not cause a large suspension of sediment. An advantage of dredging is that it may need to be conducted as part of a scheduled maintenance to recover reservoir volume and there may not be additional costs attributed only to remediation efforts. A danger exists with dredging when sediments that were previously isolated are exposed and release a higher concentration of contaminant into the water. Another remediation technique involves the addition of species, such as clams, to naturally absorb mercury from the lake. Alternatively, inorganic materials that absorb mercury could be placed in the lake. If the sediment is highly contaminated adding a layer of impervious material such as clay or a plastic lining to the bottom of the lake could prevent contact between the sediment and water and reduce mercury bioaccumulation in fish. This method is only a temporary solution and the problem would return after new mercury enters the lake from the watershed. (D'Itri, 1972; TetraTech 1999b)

Probably the most effective method to reduce the hazard of mercury in fish is not to consume the fish. This can be achieved by preventing fishing at the lake, promoting a catch-and-release policy, or not stocking undesirable fish species. Since the Parker Canyon Lake was originally created as a recreation facility these methods may be unwarranted. (USEPA 2006)

## 12 Summary and Conclusion

The 50 ha Parker Canyon Lake located in southern Arizona has an average mercury concentration of 0.92 mg/kg in a reference 40 cm fish. This concentration exceeds the USEPA recommended concentration of 0.3 mg/kg MeHg in fish tissue resulting in the lake being listed in Arizona's 303(d) list of impaired water. ADEQ water analysis shows that existing mercury related water quality standards have not been exceeded indicating that the fish are accumulating low levels of mercury located in the water column. As a result of the listing as impaired waterbody, a mercury TMDL for Parker Canyon Lake was developed. (USEPA 2006)

The first step in the development of the Parker Canyon Lake TMDL was determining the amount of mercury that enters the lake. It was assumed that all loading was a result of naturally occurring mercury in watershed soils and atmospheric deposition of mercury. Quantitative mercury loading was found using the GIS based WCS model which used soil characteristics, atmospheric deposition rates, and climate parameters to estimate that the annual mercury loading in the lake was 22.5 g.

The second step in the development of the TMDL was constructing a water balance for Parker Canyon Lake. The water balance used rainfall rates, evaporation rates, visual evidence that the spillway for Parker Canyon Lake was rarely utilized, and evidence of seepage through Parker Canyon Dam to find losses and gains into Parker Canyon Lake. The water balance was then used to determine lake volumes for the period of 1990-2002.

The next step in the development of the TMDL was establishing a water quality goal using BAFs. A regional logarithmic BAF was chosen after exploring the validity of multiple bioaccumulation techniques. The regional logarithmic BAF showed that the average MeHg concentration in the water column should remain below 0.56 ng/L in order to ensure less than 0.3 mg/kg MeHg in resident fish tissue.

The final step in the development of the TMDL was performing a water quality model with WASP7. The model was built as a four layer system to determine the fate of  $\text{Hg}^0$ ,  $\text{Hg(II)}$ , and  $\text{MeHg}$  in Parker Canyon Lake for the period of 1990-2002. The model was calibrated using ADEQ water analysis results. The model took into account the critical condition of low lake volumes coupled with high runoff rates by finding average mercury loading in the lake over time. The average loading is appropriate since the fish intake mercury over several years prior to being consumed. The WASP7 model revealed that total mercury loading needs to be reduced 83 percent to achieve the water quality goal of 0.56 ng/L  $\text{MeHg}$  in the water column. (TetraTech 1999a)

The TMDL of 3.82 g/yr was found by multiplying the WCS estimated loading of 22.5 g by the 83 percent reduction factor. A 10 percent explicit MOS was used resulting in 3.4 g/yr LA into Parker Canyon Lake. In other words, up to 3.4 g/yr of mercury compounds are allowed to enter Parker Canyon Lake and still meet USEPA recommended limit of 0.3 mg/kg  $\text{MeHg}$  in fish tissue.

Since an estimated 6.5 grams of total mercury enters Parker Canyon Lake as a result of direct atmospheric deposition on the water, practical engineered systems and watershed management practices cannot achieve sufficient reduction in mercury loading. The only way that the reduced loading could be achieved is by reducing worldwide emission levels by implementing stricter mercury emission standards. It should be noted that even though mercury concentrations exceed USEPA recommended values, occasional and reduced consumption of the fish is not considered excessively hazardous to human health and a complete ban on fish consumption is not warranted. Regardless of the policies and management approaches chosen to implement the mercury TMDL for Parker Canyon Lake, fish consumption advisories and continued monitoring should continue. (USEPA 2001; USEPA 2006)



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**Appendix A**

**Watershed Characterization System (WCS)**  
**Inputs and Results**

Table A1 Databases and shape files used by WCS mercury module for Parker Canyon Lake. Additional database files were required in the local folder to complete a run of the WCS model but the non-listed files were not used by the model.

Theme	Data Source Name	Source
Cataloging Unit Boundaries	Cat.dbf Cat.sh Cat.shx	U.S. Geological Survey(USGS)
Climate Stations	clim_sta.dbf clim_sta.shp clim_sta.shx	Western Regional Climate Center (WRCC)
Climate Data	clim_dat.dbf	WRCC
County Boundaries	Cnty.dbf Cnty.shp Cnty.shx	U.S. Census Bureau (USCB)
DEM (CU NUMER)	<CU NUMBER>.dbf <CU NUMBER>.shp <CU NUMBER>.shx	USGS
Forest Operations	forest.dbf	U.S. Forest Service (USFS)
Landuse (L_Tilename)	l_tilename.dbf l_tilename.shx l_tilename.shp	USGS
MRLC codes	Mrlccode	USGS
Mines	Mines.dbf Mines.shx Mines.shp	U.S. Bureau of Mines (USBOM)
PCS Data	pcsload.dbf	US Environmental Protection Agency (USEPA)
PCS Parameters	pcs_prm.dbf	USEPA
Permit compliance system	pcs.dbf pcs.shp pcs.shx	USEPA
Permitted Dischargers Parameters Table	Pcs_prm.dbf	USEPA
Population Data	pop.dbf	USCB
Populated Places	ppl.dbf ppl.shx ppl.shp	USCB
Reach File, V1	rf1.dbf rf1.shp rf1.shx	USGS
Reach File, V3 (CU NUMER)	<CU NUMBER>.dbf <CU NUMBER>.shp <CU NUMBER>.shx	USGS
Soil Component and Layer Data	statsgoc.dbf statsgol.dbf Statsgo.dbf Statsgo.shp Statsgo.shx	U.S. Department of Agriculture (USDA) State Soil Geographic (STATSGO) Database
STORET Surface Stations	s_stations.dbf s_stations.shp s_stations.shx	USEPA
State Boundaries	st.dbf st.shp st.shx	USCB
STORET Agencies	Storetag.dbf	USEPA
USLE Parameters	usle.dbf	USDA



Table A2 Inputs for WCS mercury module for Parker Canyon Lake.

Description	Value
Grid Cell Size (m)	10
Slope Length (m)	10
Soil Layer	Surface layer
Stream Grid Value	5000
USLE R Factor	Weighted R_factor
LS Factor Grid Theme	Ls_factor
C Factor Grid Theme	C_factor
P Factor Grid Theme	P_factor
Start Year	1902
End Year	2002
Growing Season Start Month	6
Growing Season End Month	8
Growing Season Average Rain Days (/month)	4
Non-Growing Season Avg. Rain Days (/month)	1
Annual Irrigation for Cropland (cm/gr. season)	0
Dry Deposition Rate (g/m <sup>2</sup> -yr)	0.0000092
Wet Deposition Rate (g/m <sup>2</sup> -yr)	0.0000046
Deposition Period (yr)	100
Soil-water Partition Coefficient (ml/g)	58000
Soil Loss Degrading Constant [/yr]	0
Soil Base Reduction Rate (1/day)	0.0005
Soil Base Reduction Depth (cm)	0.5
Watershed Incorporation Depth (cm)	1
Pollutant Enrichment Factor	2
Base Soil Mercury Concentration (ng/g)	40
Dry/Wet Deposition (user input)	true
Dry Deposition Map Multiplier	1
Wet Deposition Map Multiplier	1

Table A3 Detailed output from WCS mercury module regarding USLE for Parker Canyon Lake.

Data Layer	Minimum	Maximum	Standard Deviation	Mean
Total Atmospheric Deposition (mg)	1.38	1.38	0	1.38
Total Mercury Load (mg)	0.004	1.38	0.196	0.095
Load from Point Sources (mg)	0	0	0	0
Load from Imp. Deposition (mg)	0	1.173	0.009	0
Load from Runoff (mg)	0	0.007	0.001	0.005
Load from Sediment (mg)	0	1.303	0.07	0.064
Load from Deposition on Water (mg)	0	1.38	0.193	0.027
Soil Hg Concentration (mg/kg)	0.002	0.051	0.005	0.035
Source Sediment in kg/km <sup>2</sup> -yr	0	3.30x10 <sup>6</sup>	18821.2	9782.96
Total Infiltration (cm)	1.81	15.182	2.816	8.892
Total ET (cm)	8.382	35.12	2.88	28.387
Total Runoff (cm)	7.654	26.919	0.193	7.932
Total Water (cm)	45.211	45.211	0	45.211
Weighted R_factor	81.603	81.603	0	81.603
K_factor	0.1	0.19	0.026	0.178
Ls_factor	0.044	29.448	3.901	4.175
C_factor	0	0.02	0.002	0.004
P_factor	1	1	0	1

Table A4 Additional output from WCS mercury module for Parker Canyon Lake.

From Atmosphere (mg)	Total Hg Load (mg)	Load (mg /ha)	From Impervious Surface (mg)	From Sediment (mg)	From Runoff (mg)	From Deposition on Water (mg)	From Point Source (mg)
326297	22482.5	9.46	35.56	14846.8	1116.91	6483.24	0

## **Appendix B**

### **Water Quality Analysis Simulation Program (WASP7) Model Parameters and Reaction Rates**

Table B1 WASP7 Global Constants for Parker Canyon Lake Model.

Variable	Value	Source
Waterbody Type; 0=lentic (flowing streams, rivers), 1=lotic (e.g., ponds, lakes)	1	Known Variable
Latitude of water body, degrees	31.43	Google Earth! 2006
Air temperature, degrees C, or multiplier for air temperature time function	1	Multiplication Rate

Table B2 WASP7 Divalent Mercury Hg(II) Constants for Parker Canyon Lake Model.

Variable	Value	Source
Molecular Weight for Divalent Mercury, Hg(II)	200.6	USEPA 1997a
Partition Coefficient of Hg(II) to Silts and Fines (L/kg)	200000	NC DWQ 2004
Partition Coefficient of Hg(II) to Sands (L/kg)	48000	NC DWQ 2004
Partition Coefficient of Hg(II) to Organic Solids (L/kg)	20000	NC DWQ 2004
Log DOC Partition Coefficient for Hg(II)	4	USEPA 2006f
Photolysis option for photoreduction of Hg(II) (Use Option 2)	2	Model Variable
Latitude at which surface photoreduction rate was measured (degrees and tenths)	31.43	Google Earth! 2006
Measured surface photoreduction rate constant for Hg(II), (1/day)	0.05	NC DWQ 2004
Reaction Yield Coefficient for Photoreduction of Divalent Mercury to Elemental Mercury	1.07	USEPA 2006f
Quantum Yield for Dissolved Divalent Mercury	1	USEPA 2006f
Quantum Yield for DOC-Complexed Divalent Mercury	1	USEPA 2006f
Quantum Yield for Sediment-Sorbed Divalent Mercury	1	USEPA 2006f
Methylation Rate Multiplier for Dissolved Divalent Mercury	1	USEPA 2006f
Temperature Correction Factor for Methylation of Dissolved Divalent Mercury	2	USEPA 2006f
Volatile Option: 1 = input K <sub>V</sub> as parameter, 2-5 = calculate K <sub>V</sub> from formulas	4	NC DWQ 2004
Atmospheric Concentration of Divalent Mercury, (g/m <sup>3</sup> )	9.7x10 <sup>-5</sup>	NADP 2006
Henry Law's Constant for divalent mercury, atm- m <sup>3</sup> /mole	7.1 x10 <sup>-10</sup>	USEPA 1997a

Table B3 WASP7 Methylmercury Constants for Parker Canyon Lake Model.

Variable	Value	Source
Molecular Weight Methyl Mercury, MeHg	215.6	USEPA 1997
Partition Coefficient of MeHg to Silts and Fines (L/kg)	200000	NC DWQ 2004
Partition Coefficient of MeHg to Sands (L/kg)	2000	NC DWQ 2004
Partition Coefficient of MeHg to Organic Solids (L/kg)	200000	NC DWQ 2004
Log DOC Partition Coefficient for MeHg	6	NC DWQ 2004
Bacterial Demethylation Rate Multiplier for Dissolved Methylmercury	1	Multiplication Rate
Bacterial Demethylation Rate Multiplier for DOC Sorbed Methylmercury	1	Multiplication Rate
Bacterial Demethylation Rate Multiplier for Sediment Sorbed Methylmercury	1	Multiplication Rate
Temperature Correction Factor (activation energy) for Demethylation, (kcal/mole)	10	USEPA 2006f
Yield Coefficient for Bacterial Demethylation of Hg(II) to MeHg, (g/g)	0.93	USEPA 2006f
Photolysis option for photo-demethylation of MeHg (Use Option 2)	2	Model Variable
Latitude at which surface photolysis rate was measured (degrees and tenths)	31.43	Google Earth! 2006
Photolytic Surface Demethylation Rate Constant, (1/day)	0.0027	USEPA 1997a
Wavelength of maximum absorption for photo-demethylation of MeHg	900	NC DWQ 2004
Yield Coefficient for photoreduction of MeHg to Hg <sup>0</sup> , (g/g)	0.93	USEPA 2006f
Quantum Yield for Dissolved Methylmercury	1	USEPA 2006f
Quantum Yield for DOC-Complexed Methylmercury	1	USEPA 2006f
Volatile Option: 1 = input K <sub>V</sub> as parameter, 2-5 = calculate K <sub>V</sub> from formulas	4	USEPA 2006f
Atmospheric Concentration of Methylmercury, (g/m <sup>3</sup> )	1.6 x10 <sup>-11</sup>	NADP 2006
Henry's Law Constant for Methylmercury (atm-m <sup>3</sup> /mole)	4.7 x10 <sup>-7</sup>	USEPA 1997a

Table B4 WASP7 Elemental Mercury Constants for Parker Canyon Lake Model.

Variable	Value	Source
Molecular Weight of Elemental Mercury, $Hg^0$	200.6	USEPA 1997a
Photolysis option for photooxidation of $Hg^0$ (use option 2)	2	Model Variable
Latitude at which photooxidation was measured (degrees)	31.43	Google Earth! 2006
Surface photooxidation rate constant for $Hg^0$ (1/day)	0.1	NC DWQ 2004
Wavelength of maximum absorption for photooxidation of $Hg^0$	900	USEPA 1997a
Volatile Option: 1 = input $K_V$ as parameter, 2-5 = calculate $K_V$ from formulas	4	
$Hg^0$ Volatilization Exchange Rate Constant (1/day)	0.1	USEPA 1997a
Atmospheric Concentration of $Hg^0$ , (g/m <sup>3</sup> )	0	NADP 2006
Henry's Law Constant for Elemental Mercury (atm-m <sup>3</sup> /mole)	0.0071	USEPA 1997a

Table B5 Additional WASP7 Parameters for Parker Canyon Lake Model.

Variable	Value	Source
Depth of surficial sediment layers (cm)	10	NC DWQ 2004; USEPA 2002
Sediment-water column diffusion coefficient	$10 \times 10^{-5}$	NC DWQ 2004
Sand bulk density (g/ml)	0.5	NC DWQ 2004
Sand particle density (g/ml)	2.7	NC DWQ 2004
Silt settling rate (m/day)	0.3	NC DWQ 2004; USEPA 2002
Resuspension (m/day)	0.006	NC DWQ 2004; USEPA 2002
Methylation in water (1/day)	0.001	NC DWQ 2004
Methylation in sediment (1/day)	0.00004	NC DWQ 2004
Oxidation rate (1/day)	0.001	NC DWQ 2004
Demethylation to $Hg(II)$ (1/day)	0.0001	NC DWQ 2004
Demethylation to $hg^0$ (1/day)	0.1	NC DWQ 2004
Depth of surficial sediment layers	10	NC DWQ 2004

**Sources and References used for WASP7 Model Parameters and Reaction Rates**

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## **Appendix C**

### **TR-20 Calculated Peak Flowrates**



Table C1 Peak flow rates from NRCS's GEO-Hydro TR-20 GIS Model.

Subwatershed	Area	Peak Flow Rates (m <sup>3</sup> /s)						
	(ha)	1 yr	2 yr	5yr	10 yr	25 yr	50 yr	100 yr
<b>1</b>	608.7	3.1	7.0	12.9	18.2	26.3	32.9	41.2
<b>2</b>	779.6	6.5	12.3	20.3	27.2	37.6	45.8	55.8
<b>3</b>	699.3	6.8	12.5	20.5	27.2	37.5	45.7	55.4
<b>4</b>	88.1	1.2	2.0	3.0	3.9	5.1	6.1	7.3
<b>5</b>	178.7	2.7	4.6	7.0	9.0	12.0	14.3	17.1
<b>Total</b>	2354.3	20.4	38.3	63.6	85.4	118.5	144.9	176.8

Channel geometry: Depth exponent = 0.28, Width exponent = 0.39,  
 Depth coefficient = 1.48, Coefficient = 14.04, and NRCS Lag  
 method assuming no infiltration.

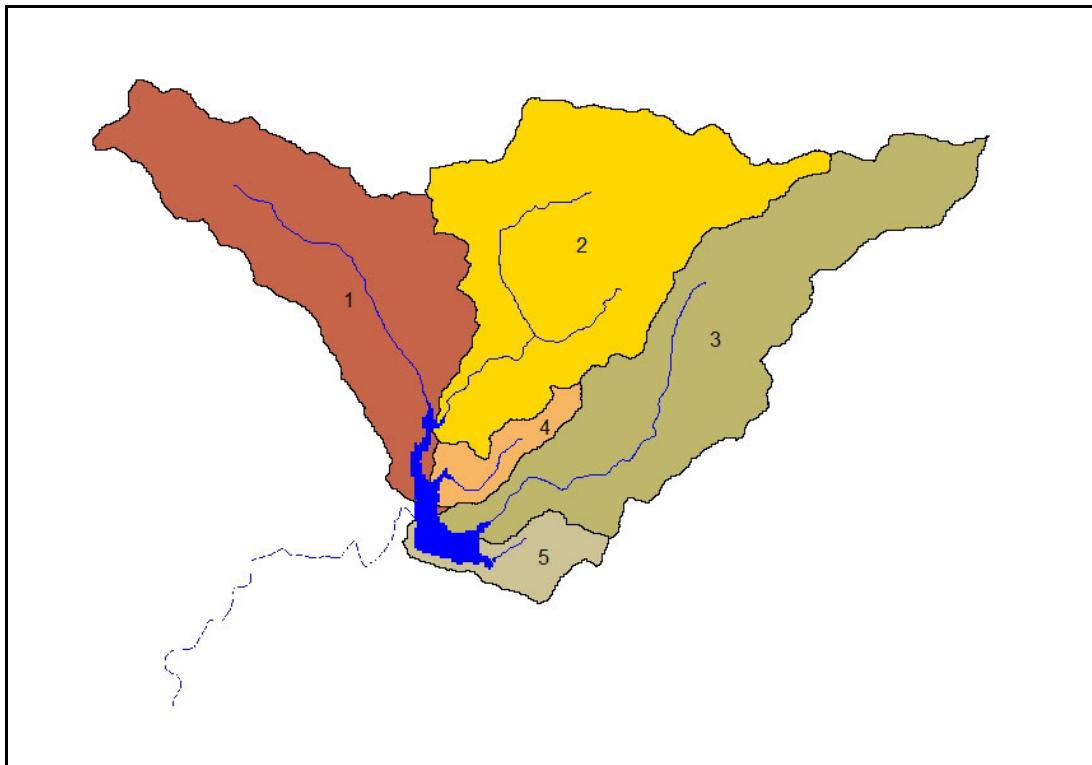


Figure C1 Subwatershed delineated by NRCS's GEO-Hydro TR-20 GIS Model.