ADEQ
Arizona Department of Environmental Quality

Total Maximum Daily Load For: Pena Blanca Lake

Parameters: Mercury in Fish Tissue

October 1999

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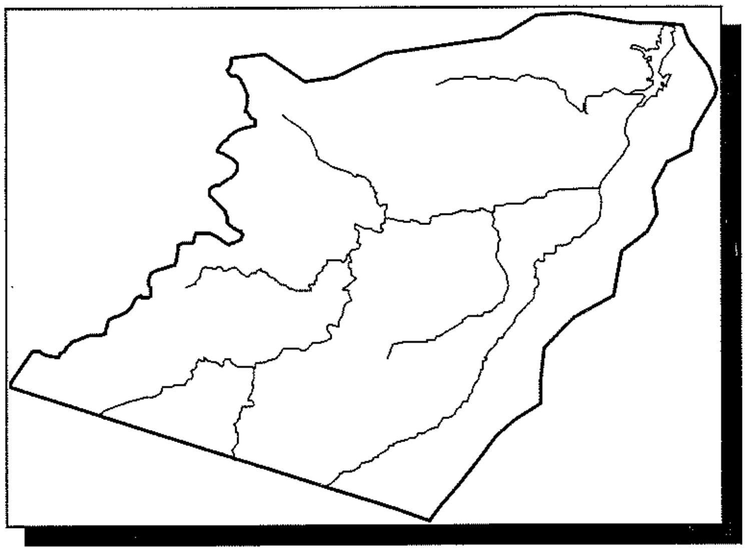
TOTAL MAXIMUM DAILY LOAD AND IMPLEMENTATION PLAN FOR MERCURY PEÑA BLANCA LAKE, ARIZONA



Arizona Department of Environmental Quality
U.S. Environmental Protection Agency, Region 9
Tetra Tech, Inc.

October 15, 1999

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TOTAL MAXIMUM DAILY LOAD AND IMPLEMENTATION PLAN FOR MERCURY IN PEÑA BLANCA LAKE, ARIZONA

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Executive Summary

The Arizona Department of Environmental Quality (ADEQ) has identified Peña Blanca Lake as not supporting its designated uses due to the presence of fish tissue concentrations of mercury in excess of criteria for issuing Fish Consumption Advisories. Ambient water quality criteria for concentrations of mercury in water have not been exceeded; however, the physical and chemical characteristics of this lake lead to a situation in which mercury readily builds up in fish tissue to levels that present a risk to human health. Because Peña Blanca Lake does not support its designated uses, ADEQ and U.S. EPA Region 9 (EPA) have developed a Total Maximum Daily Load (TMDL) for mercury loading to the lake. The TMDL is a mechanism established in the Clean Water Act for situations in which water quality impairment cannot be mitigated by imposition of technology-based effluent limits on permitted point sources. ADEQ included Arivaca Lake on its Clean Water Act Section 303(d) list of waters needing TMDLs beginning in 1996.

Pursuant to a consent decree entered to settle a TMDL lawsuit (*Defenders of Wildlife v. Browner*, consent decree approved April 22, 1997), EPA is required to ensure that a TMDL is established for all waters identified on Arizona's 1996 Section 303(d) list for mercury. Final TMDLs are required to be established for the first two listed waters by October 22, 1999. Establishment of TMDLs for Arivaca Lake and Peña Blanca Lake will meet this requirement

The TMDL consists of allocation of the available loading capacity of the lake (the maximum rate of loading that would be consistent with achieving designated uses) to point sources, nonpoint sources, and a margin of safety. This TMDL analysis estimates that the loading capacity of Peña Blanca Lake is approximately 145 grams of mercury per year. Within the Peña Blanca Lake watershed there are no permitted point sources of mercury discharge. There is, however, significant loading to the lake of mercury from a tailings pile associated with a past gold mining and processing operation. In addition, there are nonpoint or diffuse loads of mercury from naturally occurring background in local rocks, atmospheric deposition, and other sources. The contaminated mine tailings site is now owned by the U.S. Forest Service (Coronado National Forest), which has indicated a desire to remediate the site to Arizona Health Based Guidance Levels (HBGLs). This TMDL analysis indicates that the proposed remediation of the contaminated mine tailings will reduce mercury loading into the lake to a level sufficient to meet the criteria for Fish Consumption Guidelines within 10 years, with a significant unallocated reserve on the loading capacity.

Upon approval by EPA, the State is required to incorporate the TMDL into the State Water Quality Management Plan (WQMP). Although it is not a required component of a TMDL, States are required to identify implementation measures in the WQMP which are necessary to implement the TMDL. Therefore, this document also includes a proposed implementation plan to address mercury loading to Arivaca Lake. The plan includes provisions to 1) implement remedial actions at the St. Patrick Mine ball mill site and 2) monitor fish tissue mercury levels in order to review and, if necessary, revise the TMDL in the future.

Glossary

Acute toxicity. A stimulus severe enough to rapidly induce a toxic effect; in aquatic toxicity tests, an effect observed within 96 hours or less is considered acute.

Aerobic. Environmental condition characterized by the presence of dissolved oxygen; used to describe chemical or biological processes that occur in the presence of oxygen.

Algae. Any organisms of a group of chiefly aquatic microscopic nonvascular plants; most algae have chlorophyll as the primary pigment for carbon fixation.

Anaerobic. Environmental condition characterized by the absence of dissolved oxygen; used to describe chemical or biological processes that occur in the absence of oxygen.

Anoxic. Aquatic environmental conditions containing zero or minimal dissolved oxygen.

Benthic. Refers to material, especially sediment, at the bottom of an aquatic ecosystem.

Benthic organisms. Organisms living in, or on, bottom substrates in an aquatic ecosystem.

Bioaccumulation. The process by which a contaminant accumulates in the tissues of an organism.

Chronic toxicity. Toxic impacts that occur over relatively long periods of time, often one-tenth of the life span or more. Chronic effects may include mortality, reduced growth, or reduced reproduction.

Cinnabar. A compound of sulfide and mercury (HgS), also known as red mercuric sulfide, which is the primary naturally occurring ore of mercury.

Designated uses. Those beneficial uses of a water body identified in state water quality standards that must be achieved and maintained as required under the Clean Water Act.

Epilimnion. The surface water layer overlying the thermocline of a lake. This water layer is in direct contact with the atmosphere.

Eutrophication. Nutrient enrichment of a water body leading to accelerated biological productivity (growth of algae and weeds) and an accumulation of algal biomass.

Evapotranspiration. Water loss from the land surface by the combined effects of direct evaporation and transpiration by plants.

Hg. Chemical symbol for mercury.

Hydrophobic. A compound that lacks affinity for water and thus tends to have low solubility in water.

Hypolimnion. The bottom water layer underlying the thermocline of a lake. This layer is isolated from direct contact with the atmosphere.

Lipophilic. A compound that has a high affinity for lipids (fats and oils) and is thus prone to be stored in body tissues.

Load Allocation. The portion of a receiving water's loading capacity that is attributed either to one of its existing or future nonpoint sources of pollution or to natural background sources.

Loading capacity. The amount of contaminant load (expressed as mass per unit time) that can be loaded to a waterbody without exceeding water quality standards or criteria.

Macrophytes. Macroscopic, multicellular forms of aquatic vegetation, including macroalgae and aquatic vascular plants.

Margin of Safety. A required component of the TMDL that accounts for uncertainty in the relationship between the pollutant loads and the quality of the receiving water body.

Metalimnion. The water stratum between the epilimnion and hypolimnion containing the thermocline.

Methylation. The process of adding a methyl group (CH_3) to a compound, often occurring as a result of bacterial activity under anaerobic conditions.

Methylmercury (MeHg). A compound formed from a mercury ion and a methyl molecule, CH_3Hg, usually by bacterial activity. Methylmercury exhibits chemical behavior of an organic compound, and is the form of mercury most likely to be taken up and retained by organisms.

Morphometry. The shape, size, area, and volumetric characteristics of a water body.

Nonpoint source pollution. Pollution that is not released through pipes but rather originates from multiple sources over a relatively large area.

Oligotrophic. Water bodies characterized by low rates of internal production, usually due to the presence of low levels of nutrients to support algal growth.

pH. A measure of acidity and alkalinity of a solution that is a number on a scale on which the value of 7 represents neutrality and lower numbers indicate increasing acidity. pH is equivalent to the negative logarithm of hydrogen ion activity.

Photodegradation/Photolysis. Degradation of compounds by light energy.

Phytoplankton. Free-floating algae.

Piscivorous. Fish-eating.

Potential Evapotranspiration. An estimate of the evapotranspiration that would occur in response to available solar energy if water supply was not limiting.

Redox potential. A measure of the energy available for oxidation and reduction reactions, represented as the negative logarithm of electron activity in a solution.

Stratification (of water body). Formation of water layers with distinct physical and chemical properties that inhibit vertical mixing. Most commonly, thermal stratification occurs when warmer surface water overlies colder bottom water.

Tailings. Residue of raw material or waste separated out during the processing of mineral ores.

Thermocline. A lake water layer separating warmer surface waters from colder bottom waters, correctly defined as the plane of maximum rate of decrease of temperature with respect to depth.

Total Maximum Daily Load (TMDL). The sum of the individual wasteload allocations for point sources, load allocations for nonpoint sources and natural background, and a margin of safety as specified in the Clean Water Act. The TMDL must be less than or equal to the loading capacity and can be expressed in terms of mass per time, toxicity, or other appropriate measures that relate to a state's water quality standards.

Trophic level. One of the hierarchical strata of a food web characterized by organisms that are the same number of steps removed from the primary producers (such as photosynthetic algae). Animals that consume other animals are at higher trophic levels. Certain pollutants such as methylmercury tend to accumulate at higher concentrations in animals at higher trophic levels.

Wasteload Allocation. The portion of a receiving water's loading capacity that is allocated to one of its existing or future permitted point sources of pollution.

Watershed. The entire upstream land area that drains to a given waterbody.

1. Background

1.1 Description of TMDL Process

High-quality water is an extremely valuable commodity in Arizona. Water quality standards are established to protect the designated uses of Arizona's waters. When States and local communities identify problems in meeting water quality standards, a Total Maximum Daily Load (TMDL) can be part of a plan to fix the water quality problems. The purpose of this TMDL is to provide an estimate of pollutant loading reductions needed to restore the beneficial uses of Peña Blanca Lake and to guide the implementation of control actions needed to achieve these reductions.

Section 303(d) of the Clean Water Act (CWA) requires states to identify the waters for which the effluent limitations required under the National Pollutant Discharge Elimination System (NPDES) or any other enforceable limits are not stringent enough to meet any water quality standard adopted for such waters. The states must also rank these impaired waterbodies by priority, taking into account the severity of the pollution and the uses to be made of the waters. Lists of prioritized impaired water bodies are known as the "303(d) lists" and must be submitted to EPA every two years.

A TMDL represents the total loading rate of a pollutant that can be discharged to a waterbody and still meet the applicable water quality standards. The TMDL can be expressed as the total mass or quantity of a pollutant that can enter the waterbody within a unit of time. In most cases, the TMDL determines the allowable loading capacity for a constituent and divides it among the various contributors in the watershed as wasteload (i.e., point source discharge) and load (i.e., nonpoint source) allocations. The TMDL also accounts for natural background sources and provides a margin of safety. For some nonpoint sources it might not be feasible or useful to derive an allocation in mass per time units. In such cases, a percent reduction in pollutant discharge may be proposed.

TMDLs must include specific information to be approved by U.S. EPA Region 9. This information can be summarized in the following seven elements:

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

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

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

4. **Identify pollution reduction goals:** The TMDL plan includes pollutant reduction targets for all point and nonpoint sources of pollution.

5. **Describe the linkage between water quality endpoints and pollutants of concern:** The TMDL must explain the relationship between the numeric targets and the pollutants of concern. That is, do the recommended pollutant load allocations exceed the loading capacity of the receiving water?

6. **Develop margin of safety that considers uncertainties, seasonal variations, and critical conditions:** The TMDL must describe how any uncertainties regarding the ability of the plan to meet water quality standards that have been addressed. The plan must consider these issues in its recommended pollution reduction targets.

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

A plan to implement a TMDL is required by federal regulations (40 CFR 130.6) and is being established in this document pursuant to this requirement. EPA expects that this plan will provide a specific process and schedule for achieving pollutant reduction targets. A monitoring plan should also be included, especially where management actions will be phased in over time and to assess the validity of the pollutant reduction goals.

2. Problem Statement

2.1 Waterbody Name and Location

Peña Blanca Lake is a man-made impoundment located in Santa Cruz County, Arizona, on Peña Blanca Canyon in the Santa Cruz River watershed (HUC 15050301). The lake lies in southern Arizona, near the Mexican border, and is within the boundaries of the Coronado National Forest (Figure 1). Peña Blanca lake was impounded in 1958 and is managed by Arizona Department of Game and Fish (AZGF).

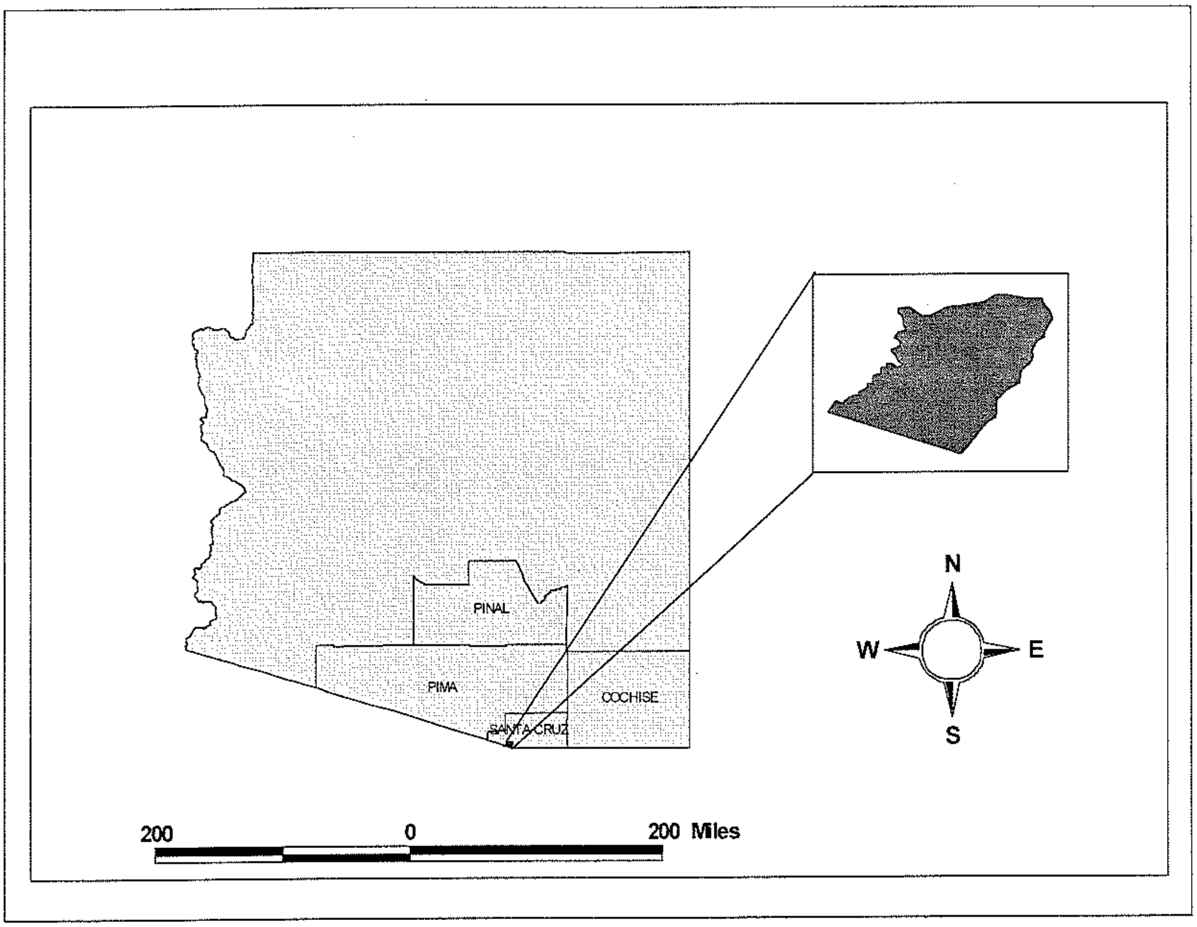


Figure 1. Location Map for Peña Blanca Watershed, Arizona

Information on the morphometry of Peña Blanca Lake was obtained from an as-built blueprint provided by the Arizona Game and Fish Department. This shows the spillway elevation at 160 feet above an approximate index contour of 3,800 feet mean sea level (MSL). At full pool, the lake has a surface area of 49.05 acres, a volume of 1070.75 acre-feet, a maximum depth of 60 feet, and an average depth of 21.8 feet. Depth-area-capacity information obtained from the table included on the plan is summarized in Figure 2. Note that area-capacity data are not

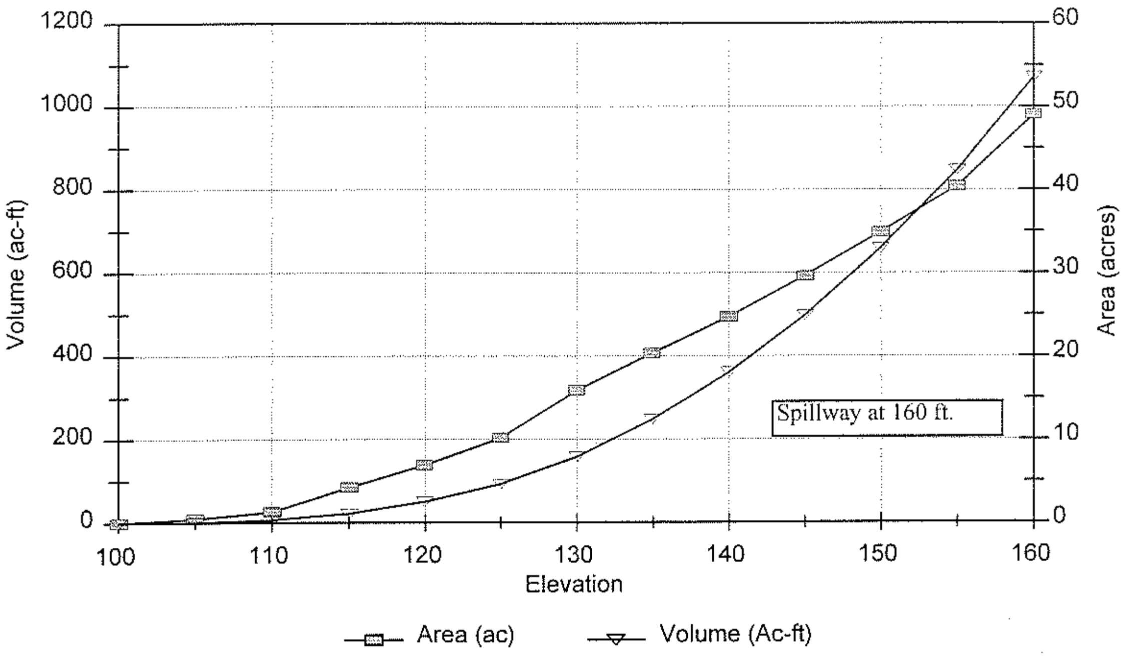


Figure 2. Depth-Area-Capacity Information for Peña Blanca Lake

provided above the spillway elevation. The lake does not have a downstream release requirement and outflow is not actively managed.

Since impoundment, the lake has lost some volume to sedimentation. A study in 1973 (NFS, 1973) estimated the loss of capacity to sedimentation at 8 acre-ft/yr. This rate of filling would have reduced the lake volume by over 20 percent by 1999; however, improved management practices since 1973 may have reduced sedimentation. No more recent data on lake morphometry was obtained; however, depths recorded during 1998 EPA sampling do suggest that significant filling may have occurred in some parts of the lake.

Peña Blanca Lake experiences nuisance growths of aquatic macrophytes, as do many other Arizona lakes, and is described as having dense aquatic vegetation (Mitchell, 1995, 1996). AZGF conducts restoration activities at Peña Blanca to improve fishing and recreational opportunities through removal of aquatic macrophytes by mechanical harvesting. AZGF records show 15 periods of macrophyte harvesting between 1987 and 1998. Between 1987 and 1994, from 1 to 5 acres per year were harvested. Harvesting activities have increased in recent years: In 1997 a total of 900 tons of macrophytes were removed from the lake by harvesting in January, April - June, and October - December. In 1998, 600 tons were removed by harvesting in August - September and October - November. Harvesting is by cutting and removal (since 1995) and does not involve uprooting of macrophytes from sediments.

AZGF conducted aquatic wildlife surveys of Peña Blanca Lake in 1995 and 1996 (Mitchell, 1995, 1996). Sampling by electrofishing found that Peña Blanca supports a healthy fish community which is dominated by largemouth bass, bluegill sunfish, redear sunfish, and yellow bullhead, with lesser numbers of black crappie, rainbow trout, channel catfish, and green sunfish. The lake is stocked, and experiences a high number of angler hours.

2.2 Water Quality and 303(d) Status

The water quality standards applicable to a water body are associated with its designated uses as defined in regulation. Arizona has designated uses for Peña Blanca Lake as Aquatic and Wildlife (coldwater) (A&Wc), Full Body Contact (FBC), Fish Consumption (FC), Agricultural Irrigation (AgI), and Agricultural Livestock Watering (AgL).

Peña Blanca Lake was added to Arizona's CWA Section 303(d) list in 1994 following detection of elevated levels of mercury in fish tissue in samples collected by the Arizona Department of Environmental Quality (ADEQ) and Arizona Game and Fish Department (AZGF). Arizona's 1998 303(d) list shows Peña Blanca Lake as not supporting uses due to the presence of Fish Consumption Advisories for mercury. The criterion or guideline used by Arizona to establish Fish Consumption Advisories is an average concentration in target species of greater than 1 mg/kg (ppm). Relevant water quality standards for completing a TMDL for Peña Blanca Lake are discussed in more detail in Section 3 of this report.

Water and fish tissue quality in Peña Blanca lake have been sampled by both AZGF and US EPA. To date, mercury concentrations in the water column have not been detected in excess of ambient water quality standards for mercury. In fish tissue, sample average mercury concentrations in excess of the Fish Consumption Guideline have been reported from one or more sampling events for largemouth bass, bluegill sunfish, and black crappie. The highest concentrations have been observed in largemouth bass, consistent with their role as top predator within the lake ecosystem and the tendency of mercury to bioaccumulate within the food chain. Lower mercury concentrations are reported for fish species at lower trophic positions. Sampling results for Peña Blanca Lake are summarized by media below.

Fish Samples

Five largemouth bass were taken from Peña Blanca Lake in May of 1994. Samples were analyzed for metals concentrations at the EPA Superfund Contract Laboratory Program (CLP) lab in Region 9. Whole body concentrations averaging 1.0 mg/kg were measured.

On November 15, 1994, AZGF collected 13 largemouth bass and three redear sunfish from the lake. Analyses of fish filets (not whole body) were carried out at the Arizona Department of Health Services (ADHS) State Laboratory. The analytical approach was based on EPA 600/4-81-055, "EPA Research and Development's interim methods for the sampling and analysis of priority pollutants in sediment and fish tissue." All measurements of mercury were in mg/kg wet weight. Average concentrations from the November 1994 samples are summarized in Table 1.

Table 1. Mercury Concentrations in Fish from Peña Blanca Lake, November 1994

Species	Number of Fish Sampled	Average Mercury Burden (mg/kg wet weight)
Largemouth Bass	13	1.44
Redear Sunfish	6	0.47
All Species	16	1.25

The use of fish filets at the ADHS State lab may have contributed to the higher average concentrations observed in largemouth bass as compared to the EPA CLP lab, where whole body concentrations were measured.

The concentrations in largemouth bass exceeded the Arizona fish tissue criterion that triggers a Fish Consumption Advisory (1.0 mg/kg tissue concentration). The lake was subsequently listed as impaired in 305(b) assessment and a fishing advisory was issued.

On May 15, 1995, AZGF conducted extensive sampling of several species of fish. 30 largemouth bass were separated by age (using visualization of fish scales) and sampled for mercury content at AZGF's laboratory. The AZGF methodology uses fish filets, has a detection limit of 0.3 mg/kg wet weight, and is not certified by the State, although AZGF results have been consistent with results from certified labs. Results are shown in Table 2.

Table 2. Mercury Concentrations in Largemouth Bass, Peña Blanca Lake, 1995

Age (years)	Number of Fish	Average Mercury Concentration (mg/kg wet weight)
1	3	0.92
2	10	1.02
3	2	1.04
4	2	1.04
5	2	1.34
6	2	1.52
7	4	1.90
9	3	1.85
10	1	2.02

These measurements show a general increase in mercury body burden with increasing age of fish, a result consistent with findings in other studied waterbodies.

Four other species were also sampled in May 1995, as summarized in Table 3.

Table 3. Mercury Concentrations in Fish from Peña Blanca Lake, May 1995

Species	Number of fish sampled	Average Mercury Burden (mg/kg wet weight)
Largemouth Bass	29	1.31
Redear Sunfish	5	0.46
Yellow Bullhead	6	0.52
Bluegill Sunfish	4	1.14
Black Crappie	2	0.87
All species	46	1.08

On May 16, 1996, AZGF sampled fish from Peña Blanca Lake again. Analyses were again carried out at AZGF's lab, using the same methods as previously. Table 4 summarizes results:

Table 4. Mercury Concentrations in Fish from Peña Blanca Lake, May 1996

Species	Number of fish sampled	Average Mercury Burden (mg/kg wet weight)
Largemouth Bass	12	1.53
Redear Sunfish	4	0.51
Yellow Bullhead	4	0.63
Bluegill Sunfish	7	0.88
Black Crappie	1	1.26
Rainbow Trout	1	< 0.3
All species	29	1.05*

* Average calculated with non-detects set to one-half the detection limit of 0.3 mg/kg.

AZGF resampled Peña Blanca in May 1997, obtaining results similar to those found in 1996 (Table 5). The May 1997 samples were collected during a period in which macrophytes were being harvested, unlike earlier fish samples which were collected in non-harvest periods.

Table 5. Mercury Concentrations in Fish from Peña Blanca Lake, May 1997

Species	Number of fish sampled	Average Mercury Burden (mg/kg wet weight)	Average length (mm)	Average whole body weight (grams)
Largemouth Bass	13	1.49	399	1139
Redear Sunfish	6	0.46	200	123
Bluegill Sunfish	4	0.61	175	110
Yellow Bullhead	5	0.56	223	145

Water Column Sampling

A surface water sample was taken from Peña Blanca Lake on May 17, 1994, by staff of ADEQ. The sample was taken at one meter depth, close to the dam. It was analyzed for a range of parameters two days later at the ADHS State Laboratory. The lab followed EPA method 245.1 for analysis of mercury. Mercury in this sample fell below the method detection limit of 0.0005 mg/L.

During the same field trip, ADEQ staff conducted a vertical profile of several water quality parameters at the same site (near the dam). They found that dissolved oxygen fell from 8.9 mg/L at the surface to 0.17 mg/L at 15.6 meters, pH dropped from 8.89 to 7.0 over the same depth range, and redox potential dropped from 389 to -105. In addition, iron and manganese in the water column increased from nondetect levels at the surface to 0.63 mg/L iron and 1.18 mg/L manganese at 16 meters of depth.

These data indicate the presence of a nearly anaerobic, strongly reducing environment in the hypolimnion of Peña Blanca Lake. The low-oxygen conditions may favor the production of methylmercury by bacteria in the hypolimnion and bottom sediments.

In July 1998, EPA staff conducted a water column depth profile of Peña Blanca Lake at a site 50 feet from the dam. Field parameters (pH, dissolved oxygen, temperature, and conductivity) were measured at approximately 1 meter intervals, as shown in Figure 3. Samples were taken for laboratory analysis at three depths to represent the epilimnion, the oxic/anoxic boundary, and the hypolimnion. Results of the analyses of these samples are shown in Table 6.

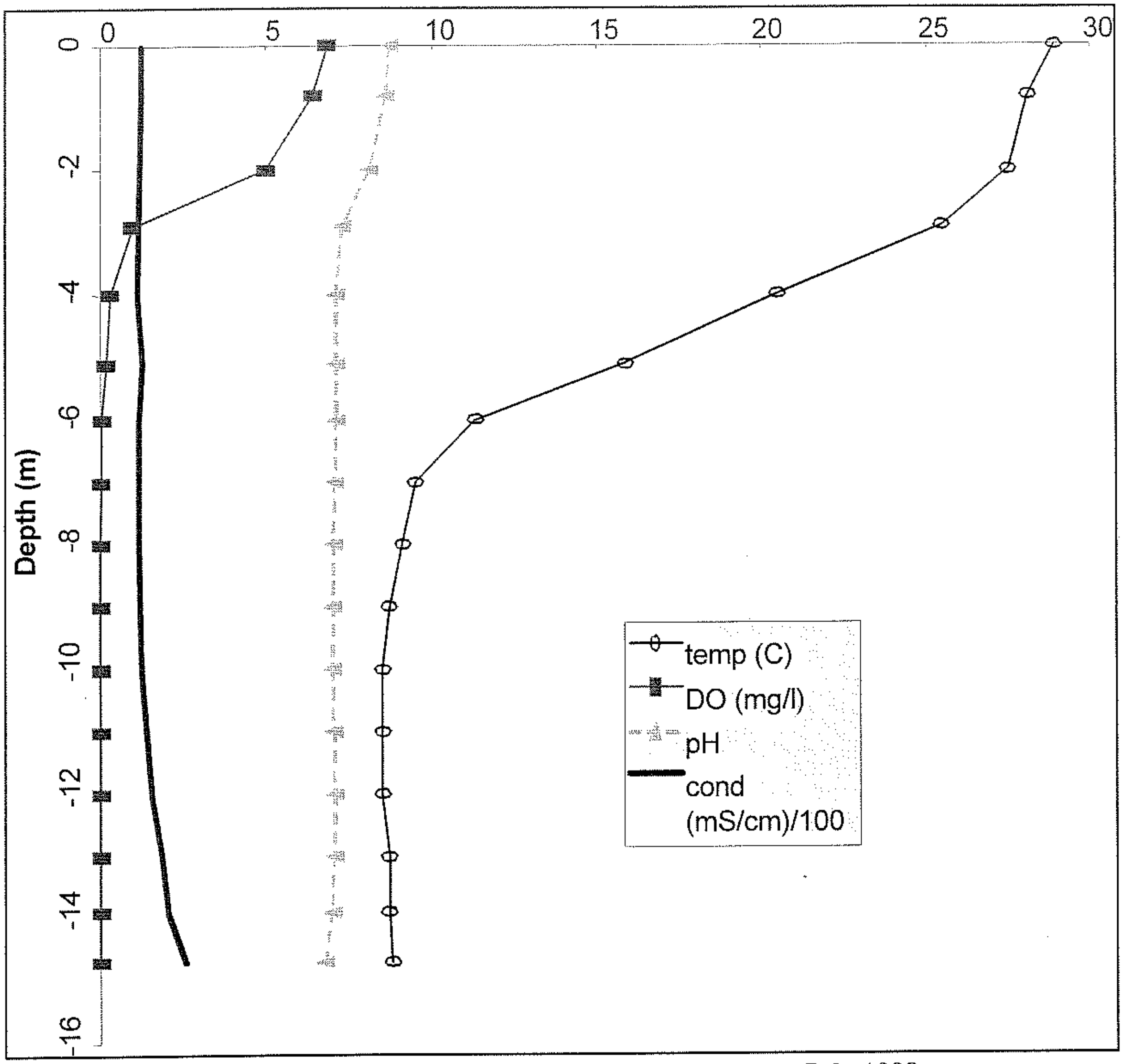


Figure 3. Depth Profiles of Peña Blanca Lake, Field Parameters, July 1998

Table 6. Water quality analyses (depth profile) from Pena Blanca Lake, July 1998

Sample ID	Sample description	Depth (m)	Total Hg ng/L (ppt)	Total MeHg ng/L (ppt)	TSS mg/L	Volatile Solids mg/L	TDS mg/L	DOC mg/L	alk. mg/L	SO_4^{-2} mg/L	Ca^{+2} mg/L	Mg^{+2} mg/L
W-10	sample depth = 0.8 m (epilimnion) No algal blooms, low turbidity sampling station: 50 ft from dam total water depth = 14.7 m (52 ft)	0.8	3.75		10.0	10.0	20.0	8.8	25.2	7.9	12.8	2.2
PB MeHg	sample depth = 8.0 m (just below oxic/anoxic boundary) same station as W-10	8.0	15.3	3.92								
W-11	sample depth = 11.0 m (hypolimnion) same station as W-10	11.0	19.6		10.0	10.0	122	9.7	85.7	6.5	12.7	2.4

Note: TSS = total suspended solids, TDS = total dissolved solids, DOC = dissolved organic carbon, alk = total alkalinity.

Table 7. In-Lake Sediment Analyses from Peña Blanca Lake , July 1998

Sample ID	Site Description	Total Hg (ppb dry weight)	MeHg (ppb dry weight)	pH	Redox (mV)	Sulfate (ppm)	Sulfide (ppm)	TOC (ppm dry weight)	Percent Clay	Longitude	Latitude
PBM20	300 feet in front of dam water depth = 50 ft sediment black with strong odor no apparent algal blooms in lake low turbidity	388.0	0.9	6.7	-133.0	510.0	350.0	23,000.0	39.4	-111.0852	31.4086
PBM21	mid-lake, water depth = 34 ft, odor but less than PBM-20	470.0	1.2	6.5	-118.0	320.0	1150.0	19,500.0		-111.0859	31.4056
PBM22	near boat ramp, water depth = 4 ft, odor but less than PBM-20	218.0	0.6	6.2	-116.0	280.0	38.0	39,100.0		-111.0870	31.4011
PBM24	mid-lake, water depth = 22 ft, odor but less than PBM-20	364.0	1.0	6.5	-130.0	42.0	43.0	23,200.0		-111.0866	31.4038

Note: TOC = total organic carbon.

Lake Sediment Sampling

A sediment sample was collected from close to the dam in Peña Blanca Lake on May 17, 1994. The sample was analyzed for metals concentrations at the EPA CLP lab in Region 9. This showed a mercury concentration of 560 ppb (0.56 mg/kg) in the sediment.

EPA staff collected lake sediment samples from four locations in Peña Blanca Lake in July 1998. Results of laboratory analysis of these samples are shown in Table 7 (above). Mercury concentrations in the sediment samples are shown graphically in Figure 4.

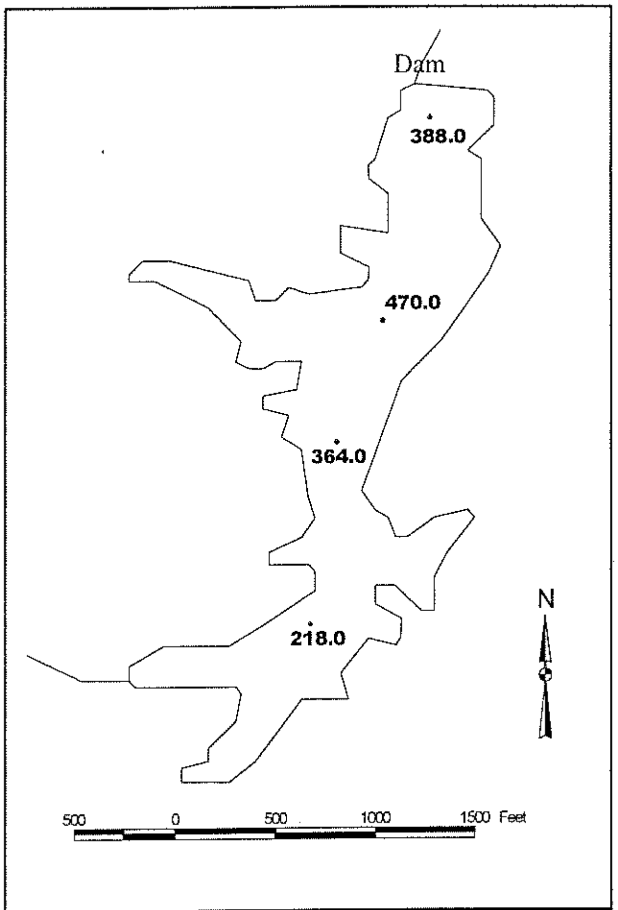


Figure 4. Mercury concentrations (ppb) in Peña Blanca Lake sediment, July 1998

Analytical Methods and Data Quality Concerns

Both the EPA CLP lab and the ADHS State lab used EPA-approved methodologies, and have strong quality assurance. The AZGF lab is not certified by ADHS to conduct mercury sampling, but their results have been consistent with ADHS and EPA results. Results from all sampling of fish mercury levels show good consistency, especially when differences between whole body and filet analyses are taken into account.

2.3 Watershed Description

The watershed of Peña Blanca Lake consists of approximately 8,821 acres. It is almost entirely rural and is mostly contained within the Coronado National Forest. A small portion of the watershed extends south into Mexico. The watershed was delineated for this study based on examination of topographic maps and the EPA Reach File 3 stream coverage.

The geology of the watershed is varied; however, the majority of the area is underlain by an interbedded extrusive igneous complex consisting of lava flows, tuffs, and agglomerates, and varying in composition for rhyolitic to basaltic (NFS, 1973). Much of the terrain is steep and rugged, with elevations ranging from 5,300' to 3,650'. Soils are generally shallow (less than 20 inches thickness), and there are significant areas of bare rock outcrops.

The watershed has a semi-arid climate, with abundant rainfall only in July and August. Most of the remainder of the annual precipitation occurs in the winter months. More detail on watershed climate is provided below in the description of the watershed model.

Vegetative cover in the watershed is a shrub-grassland complex, with low overstory density (NFS, 1973). The major shrub species are Mexican and Emory oaks, juniper, and manzanita. Land use/land cover (LU/LC) within the U.S. portion of the watershed was obtained from the BASINS Version 2.0 CD (Lahlou et al., 1998), which contains USGS GIRAS land use/land cover data. Coverage for the Peña Blanca watershed is taken from the Nogales L-157 1:100,000 LU/LC map, compiled in 1973 (USGS, 1990). This identifies land cover using an Anderson Level 2 classification (Anderson et al., 1976). Information on land use within the Mexican portion of the watershed was not available, although the topographic maps show it to be almost entirely vacant rural land. This small area (0.8 square miles) was assumed to represent a mix of forest and rangeland in the same proportions as found in the U.S. portion of the watershed. Given the rural nature of the watershed and the lack of newer land use digital coverages, the 1973 land use/land cover data were judged adequate for watershed modeling. The tabulation of land use/land cover is shown in Table 8 and Figure 5.

Table 8. Land Use/Land Cover for the Peña Blanca Lake Watershed, 1973.

Anderson Level 2 Classification	Acres
Evergreen Forest Land	7,906.7
Urban or Built-Up Land	33.2
Reservoirs	34.8*
Shrub and Brush Rangeland	845.9
Total	8,820.6

* Reservoir surface area is less than the full pool area of Peña Blanca Lake (49 acres), suggesting that the lake was below full pool when the coverage was taken. In addition, narrow arms of the lake are likely omitted from the aerial photo interpretation.

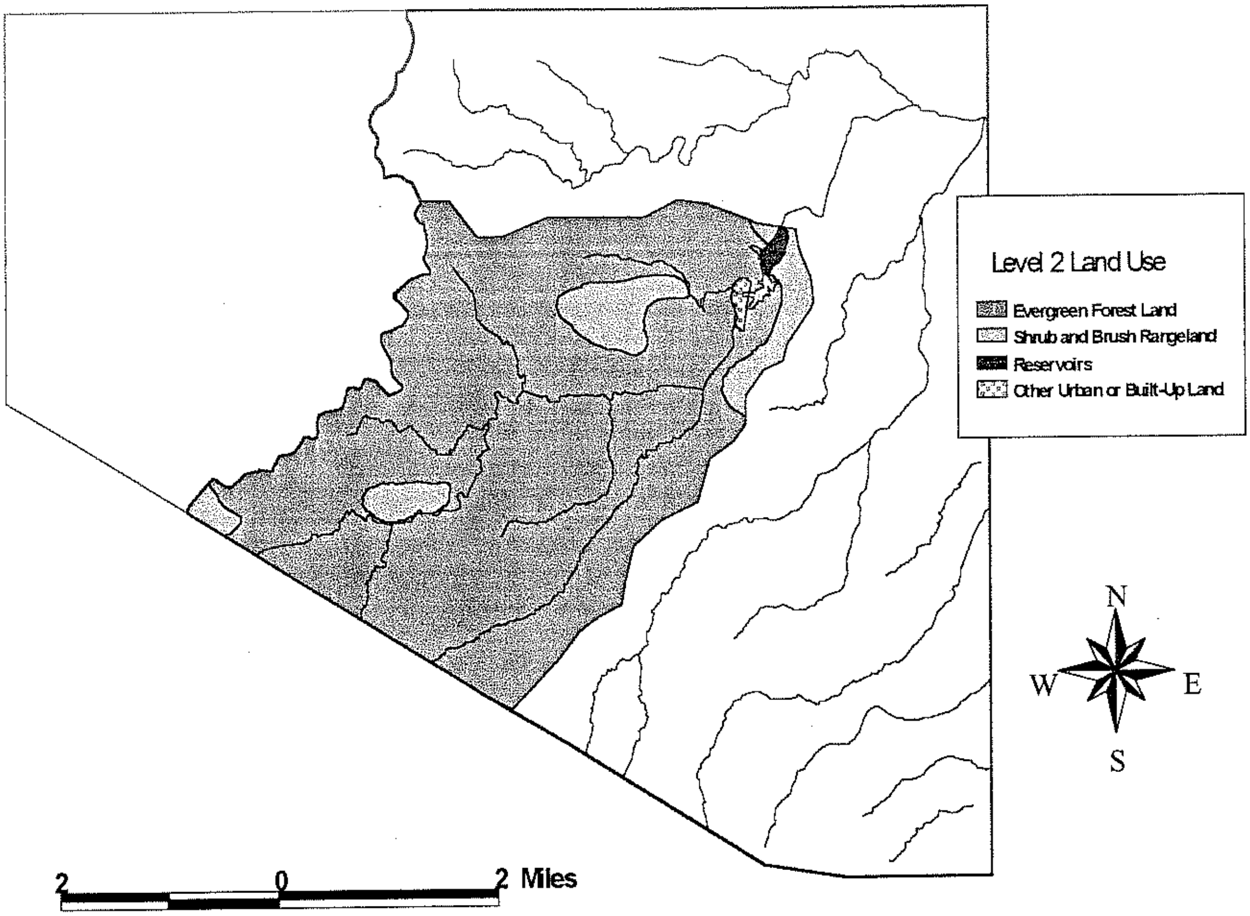


Figure 5. 1973 GIRAS Land Use, Peña Blanca Lake Watershed (U.S. Portion)

3. Numeric Targets

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

3.1 Numeric Water Quality Standards

Arizona has adopted water quality standards for mercury that apply to a number of the designated uses specified for Peña Blanca Lake (*Arizona Administrative Code*, R-18-11, Appendix A). The standards for the protection of aquatic life and wildlife are expressed in terms of the dissolved, rather than total recoverable mercury concentration, as recommended by U.S. EPA (FR 60(86): 22229-22237, May 4, 1995). Numeric water quality criteria for mercury applicable to human and agricultural uses are expressed in terms of total recoverable mercury. These water quality standards are summarized in Table 9. None of the mercury criteria are hardness-dependent.

Table 9. Arizona Water Quality Standards for Mercury

Designated Use	Criterion (µg/l)	Chemical Form
Aquatic and Wildlife (Coldwater) (A&Wc)	acute: 2.4 chronic: 0.01	dissolved dissolved
Full Body Contact (FBC)	42.0	total recoverable
Fish Consumption (FC)	0.6	total recoverable
Agricultural Irrigation (AgI)	No numeric criterion	
Agricultural Livestock Watering (AgL)	10.0	total recoverable

The most stringent applicable standard for total recoverable mercury is 0.6 µg/L (FC). The dissolved standards for protection of aquatic life and wildlife include both an acute standard, applicable to short-term exposures, with compliance determined from grab samples, and a chronic standard, applicable to longer-term exposures, with compliance determined from the arithmetic mean of consecutive daily samples collected over a 4-day period (*Arizona Administrative Code*, R-18-11-120.C). To date, mercury concentrations in water in Peña Blanca Lake (total or dissolved) have not been determined to be in excess of the applicable water quality standards, and Peña Blanca Lake is listed as not supporting its designated uses based on the presence of a Fish Consumption Advisory, rather than an excursion of ambient water quality standards for mercury.

3.2 Narrative Standards

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

> A *surface water shall be free from pollutants in amounts or combinations that:*
>
> 1. *Settle to form bottom deposits that inhibit or prohibit the habitation, growth, or propagation of aquatic life or that impair recreational uses;*
>
> ...
>
> 5. *Are toxic to humans, animals, plants, or other organisms;*
>
> ...

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

3.3 Fish Consumption Guidelines

Arizona has a Fish Consumption Guideline for mercury of 1.0 mg/kg (ppm) wet weight tissue concentration in the edible portion, as recommended by the U.S. Food and Drug Administration (FDA). Fish Consumption Advisories are issued when the average concentration in sport fish is found to exceed this guideline.

U.S. EPA (1995, Table 5-2) recommended a screening value for Fish Consumption Guidelines of 0.6 mg/kg tissue concentration total mercury, based on the following assumptions:

- Reference Dose (RfD) for methylmercury of 3×10^{-4} mg/kg/day for adults, reduced by a factor of 5 to estimate an RfD of 6×10^{-5} mg/kg/day for developmental impacts in fetuses and nursing infants.
- Total mercury concentration can be considered approximately equal to methylmercury concentration in fish.
- Average adult consumption rate of 6.5 g/day.
- Average adult body weight of 70 kg.

Since release of the 0.6 mg/kg screening value, the RfD for methylmercury has been revised in EPA's Integrated Risk Information System (IRIS) to 1×10^{-4} mg/kg/day for both developmental and chronic system effects (U.S. EPA, 1997c). U.S. EPA (1997c) did not recalculate a screening value; however, use of the revised RfD in the calculations used for the screening value in U.S. EPA (1995) would also result in a screening value of approximately 1 mg/kg in fish tissue.

Tables 4-8 through 4-10 in U.S. EPA (1997) use the revised RfD to provide recommended monthly consumption limits for chronic systemic health endpoints for the general population, for developmental health endpoints for women of reproductive age, and for developmental health endpoints for children, as a function of methylmercury concentration in fish tissue and average meal size. Calculation of a site-specific standard for Peña Blanca Lake would require an analysis of the exposed population, including meal size and frequency of consumption. Although the majority of sport fishermen are likely to consume fish from the lake only occasionally, consumption rates might be higher for some local residents.

Although data are not available at this time to compute site-specific, risk-based standards for the protection of human health, the 0.6 and 1.0 mg/kg tissue concentrations lead to the risk-based consumption limits shown in Table 10 (U.S. EPA, 1997c).

Table 10. Recommended Consumption Limits for Methylmercury in Fish (US EPA, 1997c)

	0.6 mg/kg fish tissue	1.0 mg/kg fish tissue
General Population, 12-oz meal size	1 meal per month	6 meals per year
Women of Reproductive Age, 12-oz meal size	1 meal per month	6 meals per year
Children, 4-oz meal size	6 meals per year	NONE

3.4 Wildlife Protection Considerations in Numeric Target Selection

In addition to posing a human health risk through consumption of contaminated fish, mercury can also cause wildlife health effects to predators that are high in the food chain as result of eating mercury-contaminated fish. Mercury is believed to bioaccumulate to levels of potential concern for wildlife only in larger, older fish (e.g. largemouth bass who are several years old). The only fish eating birds present in Arizona which are believed to be capable of catching such large fish are bald eagles (personal communication with Sam Rector, ADEQ, August 25, 1999). ADEQ and Arizona Department of Game and Fish report that bald eagles are not regularly found in the Peña Blanca Lake watershed; nor are nesting bald eagles found nearby (personal communication with Sam Rector, ADEQ, August 25, 1999). Therefore, ADEQ and EPA conclude that potential risk to wildlife from eating mercury contaminated fish from Peña Blanca Lake is minimal and need not be further addressed in the TMDL.

3.5 Selected Numeric Target for Completing the TMDL

The applicable numeric targets for the Peña Blanca TMDL are the Arizona water quality standard of 0.2 μg/L total mercury in the water column and the Fish Consumption Guideline of 1 mg/kg total mercury concentration in fish tissue. Water column mercury concentrations have not been found in excess of the ambient water quality standard; however, tissue concentrations in largemouth bass have consistently exceeded the guideline value. Fish in Peña Blanca Lake accumulate unacceptable tissue concentrations of mercury even though the ambient water quality standard appears to be met. The most binding regulatory criterion is the fish tissue concentration criterion of 1 mg/kg total mercury, which is selected as the primary numeric target for calculating the TMDL.

Mercury bioaccumulates in the food chain. Within a lake fish community, top predators usually have higher mercury concentrations than forage fish, and tissue concentrations generally increase with age class. Top predators (such as largemouth bass) are often target species for sport fishermen. Arizona's Fish Consumption Guideline is based on average concentrations in a sample of sport fish. Therefore, the criterion should not be applied to the extreme case of the most-contaminated age class of fish within a target species; instead, the criterion is most applicable to an average-age top predator. Within Peña Blanca Lake, the top predator sport fish is the largemouth bass. The lake water quality model (see Section 5.7) is capable of predicting mercury concentrations in fish tissue for each age class at each trophic level. Average mercury concentrations in fish tissue of target species are assumed to be approximated by average concentration in 5-year-old largemouth bass. In the May 1995 sampling of Peña Blanca Lake, the average mercury tissue concentration in largemouth bass (1.31 mg/kg) was slightly lower than the average concentration in 5-year old bass (1.35 mg/kg), and the average concentrations in all other sampled species were lower than those in largemouth bass. **Therefore, the selected target for the TMDL analysis is an average tissue concentration in 5-year old largemouth bass of 1.0 mg/kg or less.**

4. Source Assessment

There are no permitted point source discharges and no known sources of mercury-containing effluent in the Peña Blanca watershed,. External sources of mercury load to the lake include natural background load from the watershed, nonpoint loading from past mining activities, and atmospheric deposition.

4.1 Watershed Background Load

The watershed background load of mercury derives from mercury in the parent rock and from the net effects of atmospheric deposition of mercury onto the watershed. Because no significant near-field sources of mercury deposition were identified, mercury from atmospheric deposition onto the watershed is treated as part of a general watershed background load in this analysis.

Atmospheric deposition of mercury occurs throughout the world, and mercury is input to the Peña Blanca watershed through both wet deposition (precipitation) and dry deposition. As described in Section 4.3, atmospheric deposition is estimated to contribute more than 12 micrograms of mercury per square meter per year ($\mu g/m^2/yr$). This atmospheric loading rate is greater than the total load of mercury from the watershed to the lake estimated in Section 5.5; however, portions of the atmospheric mercury deposition are recycled to the atmosphere or sequestered within the watershed.

Some mercury is also present within the parent rock formations of the Peña Blanca watershed, although no concentrated ore deposits are known (Keith, 1975). Cinnabar (HgS), the primary naturally-occurring ore of mercury, typically consists of 86.2 percent mercury and 13.8 percent sulfide by weight. Cinnabar occurs as impregnations and as vein fillings in near surface environments from solutions associated with volcanic activity and hot springs. Cinnabar can also occur in placer-type concentrations produced from the erosion of mercury-bearing rocks. In the Peña Blanca watershed, cinnabar has been reported to occur as traces in irregular and lensing fissure veins in association with argentiferous galena, pyrite, marcasite, and chalcopyrite (Keith, 1975).

EPA collected 14 sediment samples from dry tributaries in the Peña Blanca watershed in July 1998 and analyzed them for total mercury. Mercury concentrations (in parts-per-billion [ppb] dry weight) are shown in Figure 6 (including two blind duplicate samples). Sediment mercury concentrations were below 100 ppb except for samples at and just downstream of the tailings pile site near the St. Patrick Mine ball mill site. The sample just below the tailings pile showed an extremely elevated concentration of 555,000 ppb. Results are summarized in Table 11.

In October 1997, EPA collected 3 background sediment samples from just outside of the nearby Arivaca Lake watershed, in areas expected to be relatively uncontaminated by anthropogenic sources of mercury. These samples had mercury concentrations of 197, 54 and 12 ppb dry weight. Adriano (1986) found that the normal mercury concentration in soils ranged from 30 to 200 ppb dry weight. Based on these data, most of the sediment samples from the Peña Blanca watershed may be considered at or near background mercury levels. Excluding the two samples at the St. Patrick Mine and assuming a lognormal distribution, the minimum variance unbiased small-sample estimate (Gilbert, 1987) of the arithmetic mean concentration in Peña Blanca tributaries is 47.9 ppb.

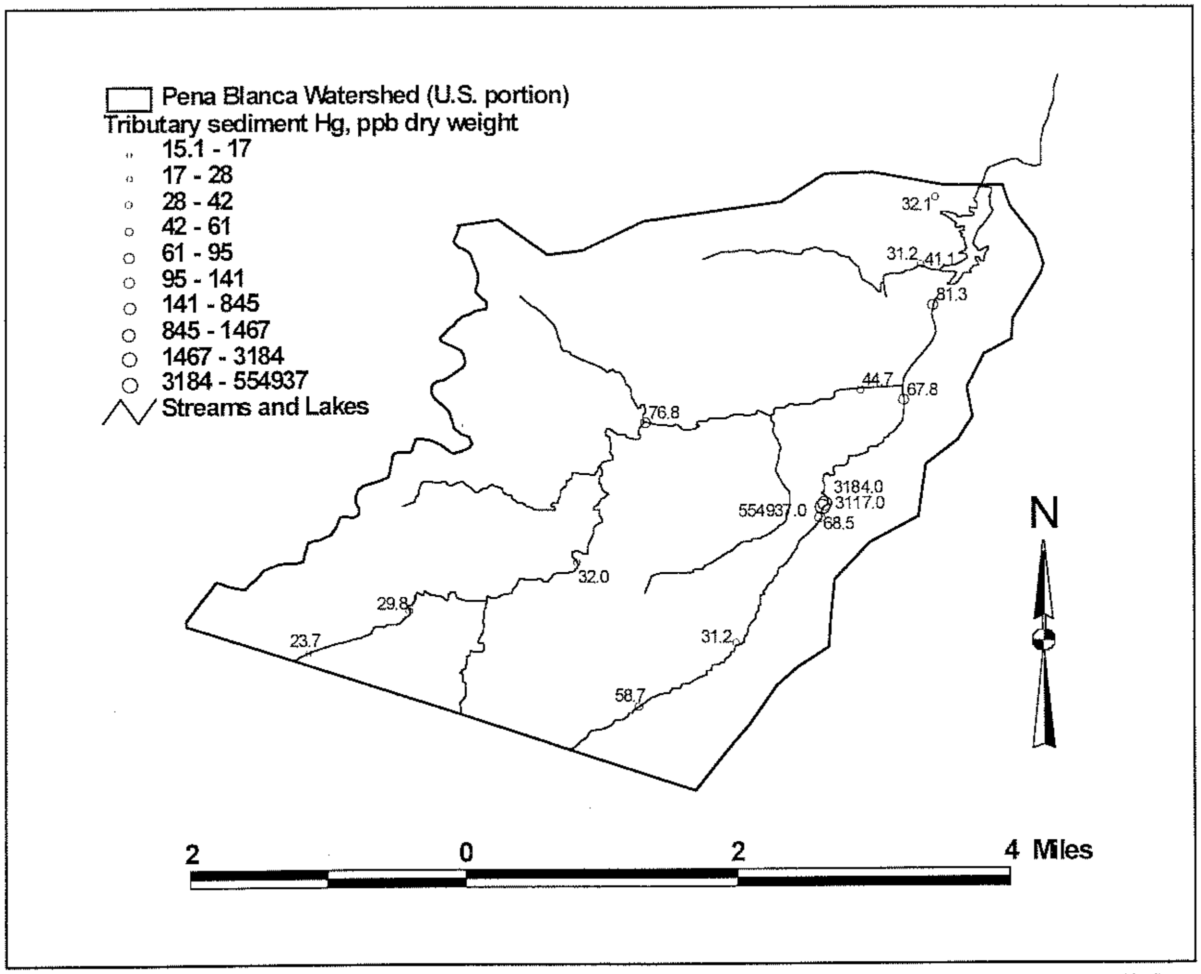


Figure 6. Tributary Sediment Mercury Concentrations, Peña Blanca Watershed, July 1998

Table 11. EPA Sediment Analyses from Peña Blanca Watershed, July 1998

Site Description	Total Hg, ppb dry weight	Percent Clay
Upper Pena Blanca Canyon @ Tinker Dam	58.7	2.2
Upper P. Blanca Cyn--upstream of St. Patrick Mine	31.2	
P. Blanca Cyn--200 feet upstream of St. Patrick Mine mill site	68.5	
St. Patrick Mine, P. Blanca Cyn--just below the gravity bed tailings, on right side of wash	554,937.0	30.6
P. Blanca Cyn--200 feet downstream of St. Patrick Mine mill site	3,184.0	3.6
blind duplicate	3,117.0	
Lower P. Blanca Cyn, near campground	67.8	
Lower P. Blanca Cyn, just above lake's parking lot	81.3	
Lowest Alamo Cyn wash location, 1/4 mile from P. Blanca Cyn junction	44.7	
Alamo Cyn, section 33 on topo, silty sand	76.8	6.6
Alamo Cyn, near peak (4992), sandy	32.0	
Alamo Cyn, downstream of Coyote tank, near USMM, silty soil	29.8	
Upper Alamo Cyn	23.7	5.5
small drainage close to PB lake, Rock Water Spring, pebbly/sandy-silt	32.1	11.4
small drainage close to PB lake, near sewage pond, silty-sand	31.2	
blind duplicate	41.1	

4.2 Nonpoint Load from Past Mining Activities

The mining of precious metals such as gold and silver was common in the Parajitto mining area surrounding Peña Blanca Lake. The U.S. Bureau of Mines Mineral Availability System/Mineral Industry Location System (MILS) CD-ROM (last updated in 1995) identifies three exploratory prospects and four past producer mines in the Peña Blanca watershed (Table 12 and Figure 7).

Table 12. Mining Operations in the Peña Blanca Watershed Identified in MILS

Name	Type	Status	Elevation	River	Company	Minerals
Joe Parker 5	Unknown	Exp Prospect	1554	San Simon Wash	Sigler AJ and Porter HW	Uranium
Midnight	Underground	Past Producer	1295	Santa Cruz River	Herbert; Sirgo Joseph	Silver Lead Copper Zinc
Morning and Evening Group	Surf-underg	Past Producer	1280	Santa Cruz River	Kimmel	Silver Lead Gold Copper
Old Bextrum Mine	Underground	Past Producer	1386	Santa Cruz River	Carson	Lead Silver
Reactor and Opaline Groups	Unknown	Exp Prospect	1646S	Santa Cruz River	Cog Mines	Uranium Aluminum
St. Patrick	Underground	Past Producer	1250	Santa Cruz River	Clarke Phil	Silver Lead Gold Copper
Silver Mine	Unknown	Exp Prospect	1295	San Simon Wash	Laughlin a B	Uranium Aluminum

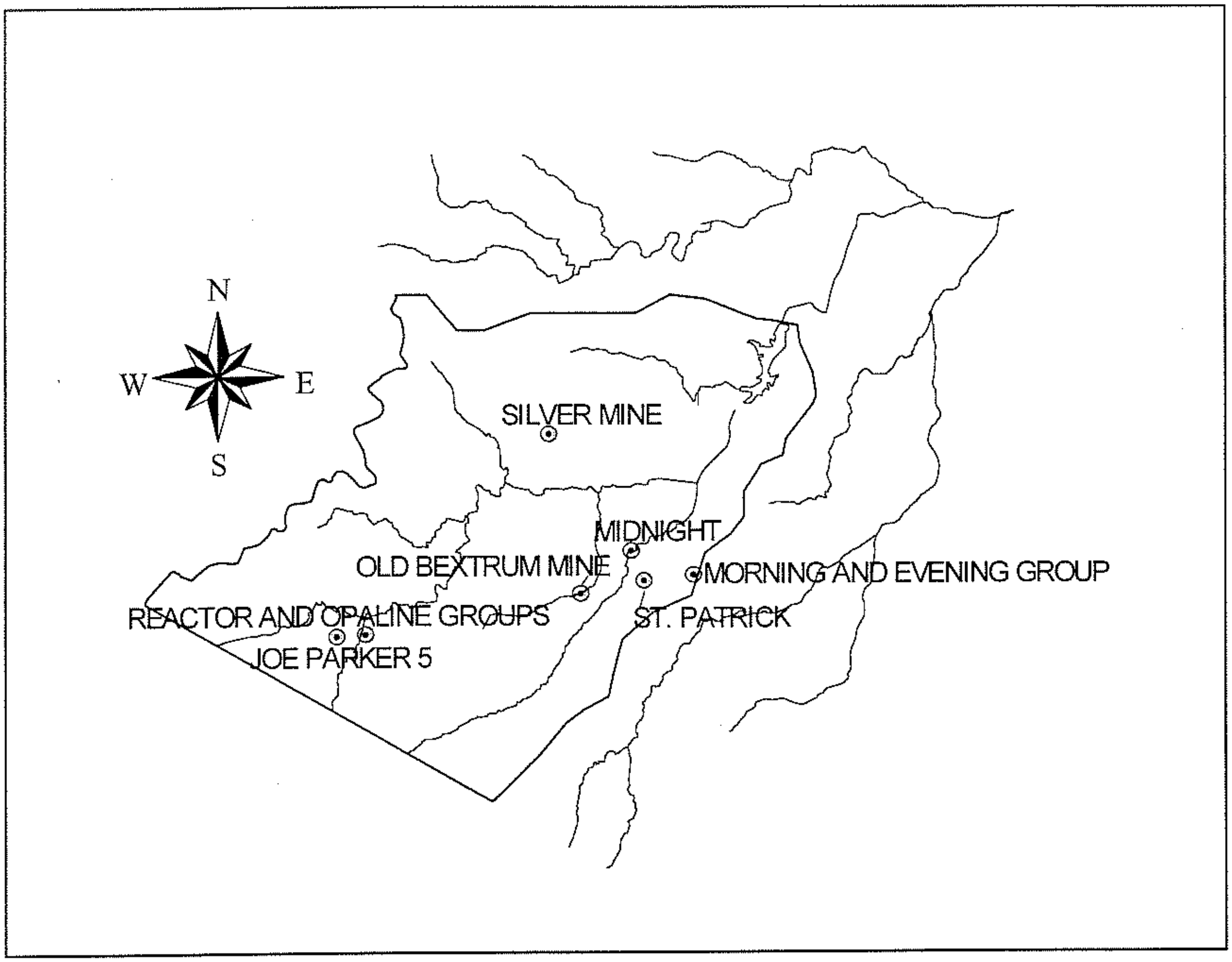


Figure 7. Location of Mining Operations in the Peña Blanca Watershed

Mercury itself is not known to have been mined in the watershed. Mining activities for minerals other than mercury can nonetheless affect watershed mercury load in two distinct ways. First, mining activity produces tailing residues of crushed rock. If the parent material contains mercury ore, the conversion of rock to tailings increases the amount of mercury ore present in readily erodible form. Second, mercury may be directly used in the gold mining process: Before the introduction of cyanidation technology at the beginning of the 20th century, mercury amalgamation of precious metal ores was used throughout the western United States. It was common practice to use mercury to amalgamate gold ore in ball mills. In the ball mill process, the raw ore was crushed to a talc consistency and placed into a settling trough with water and elemental mercury. The gold amalgamated with the mercury and settled out. The excess water and overburden were washed out of the trough onto the ground, and the amalgam was collected and placed in a furnace, where the mercury was evaporated off, recondensed into a retort, and saved for reuse. Some loss of mercury occurred in many steps in this metallurgical process. Most of the gold-mercury amalgam settled out and was recovered, but some was inevitably washed out of the trough with the fine overburden. The amalgam furnace might also have elevated local soil concentrations through short-range atmospheric deposition. Ball mill process mercury is likely to be of greater concern for environmental impact because the residue is more likely to contain soluble species of mercury than low-solubility cinnabar outcrops. Studies of the highly contaminated Carson River area in Nevada (Lechler, 1998) demonstrate that the dominant form of mercury present in amalgamation-process tailings is still elemental mercury, approximately a century after peak mining activity, whereas stream sediments in the tailings area were dominated by elemental and exchangeable forms of mercury. Significant conversion to relatively insoluble cinnabar occurs only when these materials are transported to more anoxic, reducing environments with concentrations of labile sulfur in excess of 0.1 percent by weight. Thus, the mercury contained in ball mill tailings is likely to be more mobile and more bioavailable than the mercury contained in cinnabar in the watershed soils background and tailings residue from hard rock mines, which has not been processed by mercury amalgamation.

There were two past producers of gold in the Peña Blanca watershed, the Morning and Evening Group and the St. Patrick Mine. One ball mill site has been identified in the Peña Blanca watershed, associated with the St. Patrick Mine and with a tailings pile adjoining an intermittent stream bed (Figure 7). ADEQ analyzed a sample from this tailings pile in March 1995, and reported a concentration of 1,370 ppm. Subsequently, the U.S. Forest Service (USFS) has commenced a CERCLA (Superfund) investigation of the site. In June 1999, 30 samples were collected from the tailings pile, mill site, and adjacent stream bed site by the USFS' contractor and analyzed for mercury at Aspen Analytical. Preliminary results were provided by Eli Curiel (Coronado National Forest) to U.S. EPA Region 9. Samples from outside of the tailings pile generally revealed low levels of contamination (from non-detectable up to 15 mg/kg). Seven samples collected from the tailings pile gave higher results, ranging from 63 to 460 mg/kg total mercury. These results confirm that the tailings pile is a mercury hotspot, although the concentrations reported are lower than those detected by ADEQ in 1995.

The extent of the hotspot area with concentrations greater than 35 mg/kg was originally estimated at approximately 2,500 square feet, based on personal communication from Gregg Olson (U.S. EPA Region 9) and from examination of a field sampling map provided by the USFS delineating the approximate area with concentrations in excess of 35 ppm total mercury. Recently, the contractor for the USFS remediation indicated that "the estimated area of levels over 35 ppm is approximately 120' x 60' " (e-mail from Jim Moots, GES Environmental to Gregg Olson, US EPA Region 9, July 23, 1999) – or 7,200 square feet; however, depths of the tailings hot spot deposits ranged from 6 inches to 3 feet. Concentrations within the tailings are assumed to exhibit a log-normal distribution, as is commonly found for environmental contamination samples (Gilbert, 1987). The seven USFS samples were combined with the single ADEQ sample and the EPA sample taken immediately below the gravity beds and a minimum variance unbiased estimator (MVUE) of the arithmetic mean of 287.38 mg/kg was estimated using the method of Aitchison and Brown (1969). A larger downstream area of the stream bed also appears to have somewhat elevated concentration levels, extending at least as far as the EPA sample 200 feet downstream with concentration greater than 3 mg/kg. Five USFS samples from the bed downstream of the hottest area (ranging from 0.15 to 8 mg/kg) were combined with this EPA sample, and an MVUE of the arithmetic mean of 2.22 mg/kg was estimated. The downstream extent of elevated concentrations is not clearly determined by existing sampling, and this concentration was conservatively assumed to apply to an area of 400 x 50 = 20,000 square feet.

4.3 Atmospheric Deposition

Near-Field Atmospheric Deposition

Significant atmospheric point sources of mercury often cause locally elevated areas of near-field atmospheric deposition downwind. Mercury emitted from man-made sources usually contains both gaseous elemental mercury (Hg(0)) and divalent mercury (Hg(II)). Hg(II) species, because of their solubility and their tendency to attach to particles, are redeposited relatively close to their source (probably within a few hundred miles), whereas Hg(0) remains in the atmosphere much longer, contributing to long-range transport.

The fact that there is relatively low precipitation in Arizona means that less mercury is likely to be deposited near the source; i.e., Hg(II) forms of mercury probably have time to migrate farther from their source before being scavenged by precipitation or dry depositing as particle-attached mercury. This diminishes the impact of near-field sources relative to the regional background. It is still possible, however, that individual atmospheric point sources might contribute to elevated mercury levels in nearby waterbodies.

Significant potential point sources of airborne mercury include coal-fired power plants, waste incinerators, cement and lime kilns, smelters, pulp and paper mills, and chlor-alkali factories. Based on a review of *Mercury Study Report to Congress* (U.S. EPA, 1997a) and a search of the EPA AIRS database of permitted point sources, there are no significant U.S. sources of airborne mercury within or near the Peña Blanca watershed.

The prevailing wind direction in the Peña Blanca watershed is from the southwest, the direction of the Gulf of California. Most nearby parts of Mexico immediately to the southwest of the watershed are sparsely populated. Information provided by Gerardo Monroy and Edna Mendoza of ADEQ (personal communication to Peter Kozelka, U.S. EPA Region 9, April 27, 1999) summarizes what is known of potential Mexican and border mercury emissions:

- The city of Nogales, Sonora, is a few miles southeast of the lake at the U.S. border. A study entitled *Air Emission Rate Summary for Stationary Sources in Nogales, Sonora* compiled by Powers Engineering in 1996 estimated the total mercury emission rate for all stationary mercury sources in Nogales, Sonora as less than 4 pounds per year. During the Ambos Nogales air quality study some of the teflon filters that were used in collecting particulate matter samples were analyzed for mercury, and mercury emissions "were not considered significant."
- The nearest lime kiln plants are in Paul Spur, Arizona, just west of Douglas, and south of Aqua Prieta, Sonora, across the border from Douglas. These are all to the east of the watershed and not in the direction of the prevailing wind.
- The Nacozari smelter in Sonora is approximately 150 miles distant from the watershed, to the southeast. A smelter was located at Cananea, Sonora, about 50 miles away (again to the southeast) and is now shut down. There was also a smelter at Douglas, AZ, which was shut down around 1986-87.
- The nearest coal-fired electric utility is in the Sulphur Springs Valley, north of Douglas, AZ, approximately 80 miles east of the watershed.

Based on the lack of major nearby sources, particularly sources along the axis of the prevailing wind, near-field atmospheric deposition of mercury attributable to individual emitters is not believed to be a major component of mercury loading to the Peña Blanca watershed.

Long-Range Atmospheric Deposition

Long range atmospheric deposition (regional atmospheric background) is a major source of mercury in many parts of the country. In a study of trace metals contamination of reservoirs in New Mexico, it was found that perhaps 80 percent of mercury found in surface waters was coming from atmospheric deposition (Popp et al., 1996; Steve Hansen, personal communication, June 13, 1997). In other remote areas (e.g., in Wisconsin, Sweden, and Canada), atmospheric deposition has been identified as the primary (or possibly only) contributor of mercury to waterbodies (Watras et al., 1994; Burke et al., 1995; Keeler et al., 1994).

The Mercury Deposition Network (MDN) has measured wet deposition of mercury. In its first year of operation (February 1995–February 1996), the MDN found a volume-weighted average concentration of 10.25 ng/L total mercury in precipitation at 17 stations located mainly in the upper Midwest, Northeast, and Atlantic seaboard (http://nadp.nrel.colostate.edu/NADP/mdn/mdn.html). Volume-weighted average concentration of mercury did vary by station, ranging from 3.62 ng/L at Acadia National Park, Maine, to 13.56 ng/L at Bondville, Illinois. Average weekly wet deposition rates at the 17 stations ranged from 63 ng/m^2 to 280 ng/m^2.

Only limited monitoring of atmospheric deposition of mercury is available in the Southwest, and none from Arizona. Dry and wet deposition were measured in the Pecos River basin of eastern New Mexico in 1993–1994 (Popp et al., 1996). Average weekly deposition rates were calculated to be 140 ng/m^2-wk of mercury from dry deposition and 160 ng/m^2-wk of mercury from wet deposition. These data demonstrate the importance of both dry and wet deposition as sources of mercury.

In May 1997, the MDN began collecting deposition data at a new station in Caballo, in the southwestern quadrant of New Mexico. This station is still approximately 200 miles east of Peña Blanca watershed, but it is about 150 miles closer to the subject lake than the Pecos River basin. Original data files for the Caballo station for May 1997 through December 1998 were obtained from the MDN Coordinator. These show an average wet deposition rate of 99 ng/m^2-wk over the period of record, but this estimate is skewed upward by omission of the relatively low-deposition January to April period in 1997. For the complete year of 1998, the deposition rate was 78 ng/m^2-wk. Both estimates are at the lower end of the range seen for other MDN stations due to low precipitation.

It appears that the Caballo MDN station provides the most relevant estimate of mercury deposition at Peña Blanca Lake. Lack of geographically closer monitoring introduces considerable uncertainty; however, as shown below, direct atmospheric deposition appears to account for only a small portion of the total mercury load to the lake. Even if the direct atmospheric loading rate is underestimated by a significant amount, it would have only a minor effect on the predicted lake response. The Caballo data were therefore selected to characterize mercury wet deposition to the lake surface. The short period of record available was extrapolated to provide estimates across the period of simulation. Two approaches were considered to make this extrapolation: development of a relationship between mercury concentration and rainfall volume and calculation of average deposition rates. The first approach is based on the observation that mercury wet deposition concentrations are typically inversely related to rainfall volume. There is considerable scatter in this relationship in the Caballo data, particularly at low precipitation volumes. Given this scatter and the short period of record available, the concentration approach was rejected. Instead, it was assumed that cumulative deposition mass was a more robust estimator than concentration. To make maximum use of the available data, the series of all possible running 12-month sums were calculated and then averaged, yielding an annual wet deposition rate of 4.125 $\mu g/m^2$-yr (79 ng/m^2-wk). This annual sum was then apportioned to months based on the observed deposition pattern from May 1997 through April 1998, yielding a scaled pattern of deposition which replicates the average annual total. The observed and scaled wet deposition rates are shown in Figure 8.

The Caballo station does not measure dry deposition. Although there are few direct measurements to support well-characterized estimates, dry deposition of mercury often is assumed to be approximately equal to wet deposition (e.g., Lindberg et al., 1991), as is reported in the Pecos River basin. Throughfall studies in a coniferous forest indicate that dry deposition beneath a forest canopy could be on the order of 50 percent of the wet deposition signal (Lindqvist et al., 1991). Estimated global mercury budgets suggest that dry and wet deposition rates for mercury in deserts are roughly equivalent (Lindqvist et al., 1991). Mercury accumulation rates in wetlands (Delfino et al, 1994) and a seepage lake in Florida (Sigler, 1998) indicate that dry deposition rates are highly uncertain, and could range from negligible to three times wet deposition rates. In wet climates, such as Florida, where scavenging of reactive gaseous mercury (RGM) and aerosol mercury is extensive, the ratio of dry to wet deposition is likely smaller than would occur in more arid environments. Given the low annual rainfall at Caballo, a ratio of dry to wet deposition greater than 1 is appropriate, and it was conservatively assumed that dry deposition at this station is approximately twice wet deposition. This estimate is consistent with the estimate supplied by the local university cooperator at the Caballo station (Colleen Caldwell, personal communication to Peter Kozelka, U.S. EPA Region 9, cited in Kozelka memo dated April 22, 1999). With this assumption, total atmospheric deposition of mercury (wet and dry) at Caballo was estimated to be 12.4 $\mu g/m^2/yr$, which is close to the total (wet and dry) deposition rate estimated for the Pecos River basin of 15.6 $\mu g/m^2/yr$.

The total mercury deposition rate at Caballo is assumed to apply to Peña Blanca Lake. Because the climate at Peña Blanca is wetter than at Caballo, the distribution of wet and dry deposition is likely to be different. Monthly wet deposition rates at Peña Blanca were estimated as the product of the volume-weighted mean concentration for wet deposition at Caballo times the rainfall depth at Peña Blanca. This approach was used because volume-weighted mean concentrations are usually much more stable between sites than wet deposition rates, which are sensitive to rainfall amount. Dry deposition at Peña Blanca was then calculated as the difference between the total deposition rate at Caballo and the estimated Peña Blanca wet deposition rate. The estimates derived for Peña Blanca are 5.1 $\mu g/m^2/yr$ by wet deposition and 7.3 $\mu g/m^2/yr$ by dry deposition. In sum, total mercury deposition at Peña Blanca is assumed to be equivalent to that estimated for Caballo, New Mexico, but Peña Blanca is estimated to receive greater wet deposition and less dry deposition than Caballo because more of the particulate mercury and reactive gaseous mercury that contribute to dry deposition will be scavenged at a site with higher rainfall.

In comparison, US EPA's (1997b) national-scale RELMAP modeling estimates total mercury deposition for this part of Arizona to be on the order of 1 to 3 μg/m²/yr, which is in the lower end of the simulated range for the continental United States of 0.02 to 80.3 μg/m²/yr. The RELMAP modeling is not, however, considered reliable for the border area due to uncertainty as to Mexican emissions.

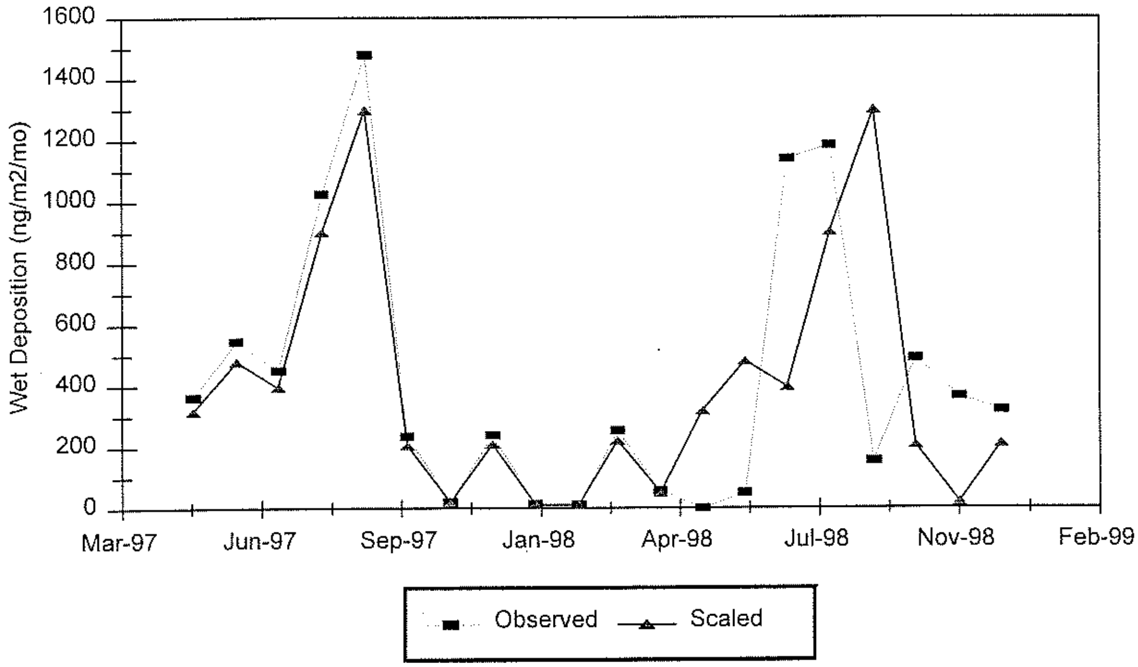


Figure 8. Observed and Scaled Mercury Wet Deposition at Caballo, NM.

5. Linkage Analysis

The linkage analysis defines the connection between numeric targets and identified sources. The linkage is defined as the cause-and-effect relationship between the selected indicators, the associated numeric targets, and the identified sources. This provides the basis for estimating total assimilative capacity and any needed load reductions. Specifically, models of watershed loading of mercury are combined with a model of mercury cycling and bioaccumulation in the lake. This enables a translation between the numeric target (expressed as a fish tissue concentration of mercury) and mercury loading rates. The loading capacity is then determined via the linkage analysis as the mercury loading rate that is consistent with meeting the target fish tissue concentration.

The linkage analysis is first expressed qualitatively in the form of a risk hypothesis. Based on the conceptual form of the risk hypothesis, quantitative tools are then developed to complete the linkage.

5.1 The Mercury Cycle

Development of the risk hypothesis requires an understanding of how mercury cycles in the environment. Mercury chemistry in the environment is quite complex: mercury has the properties of a metal (including great persistence due to its inability to be broken down), but also has some properties of a hydrophobic organic chemical due to its ability to be methylated through a bacterial process. Methylmercury is easily taken up by organisms and tends to bioaccumulate; it is very effectively transferred through the food web, magnifying at each trophic level. This can result in high levels of mercury in organisms high on the food chain, despite nearly unmeasurable quantities of mercury in the water column. In fish, mercury is not usually found in levels high enough to cause the fish to exhibit signs of toxicity, but wildlife that habitually eat contaminated fish are at risk of accumulating mercury at toxic levels, and the mercury in sport fish can present a potential health risk to humans.

Selected aspects of the lake and watershed mercury cycle are summarized schematically in Figure 9. The boxes represent stores of mercury, and the arrows represent fluxes. The top of the diagram summarizes the various forms of mercury that may be loaded to a lake. It is important to recognize that mercury exists in a variety of forms, including elemental mercury (Hg(0)), ionic mercury (Hg(I) and Hg(II)), and compounds in which mercury is joined to an organic molecule. In the figure, Hg(I) is ignored because Hg(II) species generally predominate in aquatic systems. Mercuric sulfide (HgS or cinnabar) is a compound formed from Hg(II), but is shown separately because it is the predominant natural ore. Organic forms of mercury include methylmercury (CH_3Hg or "MeHg"), and also other organic forms, including natural forms such as dimethylmercury and man-made compounds such as organic mercury pesticides. (Where sorption and desorption are indicated in the model diagram, "Hg(II)" and "MeHg" refer to the same common pools of water column Hg(II) and MeHg shown in the compartments at the top of the diagram.)

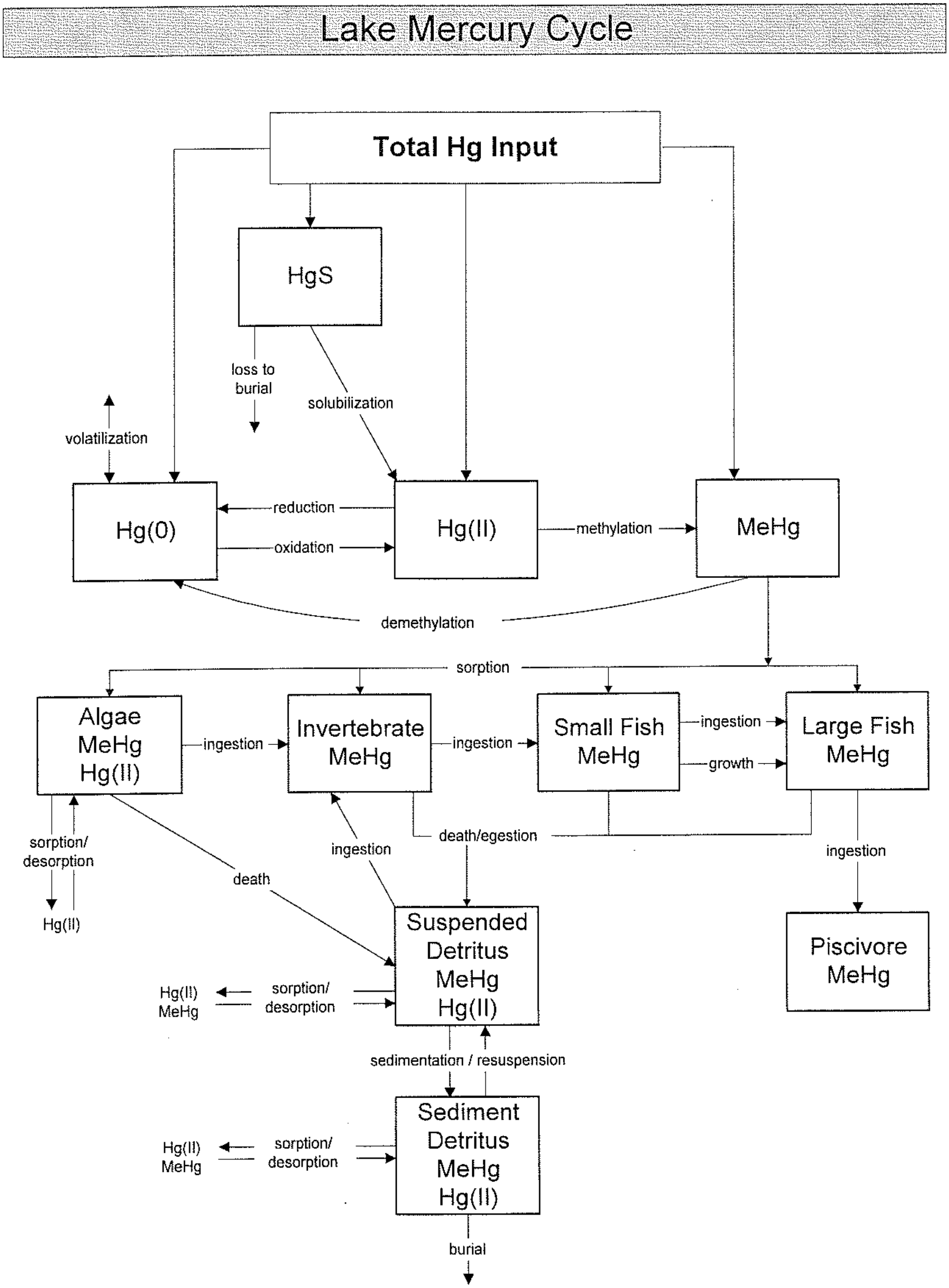


Figure 9. Conceptual Diagram of Lake Mercury Cycle

In the lake mercury cycle, it is critical to consider the distribution of mercury load between the various forms. The major forms reaching a lake from the watershed can have different behavior:

- Mercuric sulfide (HgS), which can be washed into the lake as a result of weathering of natural cinnabar outcrops. HgS has low solubility under typical environmental conditions and would be expected to be settle out to the bottom sediments of the lake. Under aerobic conditions, however, Hg(II) may be liberated by a bacteria-mediated oxidation of the sulfide ion. This Hg(II) would then be much more bioavailable and would be available for methylation. Alternatively, under anaerobic conditions, HgS may be formed from Hg(II).
- Methylmercury (MeHg), which is found in rainfall and may be found in small amounts in mine tailings or wash sediments. It is more soluble than HgS and has a strong affinity for lipids in biotic tissues.
- Elemental mercury (Hg(0)), which may remain in mine tailings, as has been noted in tailings piles from recent gold mining in Brazil. Elemental mercury tends to volatilize into the atmosphere, though some can be oxidized to Hg(II).
- Other mercury compounds that contain and may easily release ionic Hg(II). Such compounds are found in the fine residue left at abandoned mine sites where mercury was used to draw gold or silver out of pulverized rock.

Note that dimethyl mercury (CH_3-Hg-CH_3) is ignored in the conceptual model shown in Figure 9, because this mercury species seems to occur in measurable quantities only in marine waters. Organic mercury pesticides also have been ignored in this TMDL study since such pesticides are not currently used in this country and past use is probably insignificant because there is no cropland in the Peña Blanca watershed.

Mercury and methylmercury form strong complexes with organic substances (including humic acids) and strongly sorb onto soils and sediments. Once sorbed to organic matter, mercury can be ingested by invertebrates, thus entering the food chain. Some of the sorbed mercury will settle to the lake bottom; if buried deeply enough, mercury in bottom sediments will become unavailable to the lake mercury cycle. Burial in bottom sediments can be an important route of removal of mercury from the aquatic environment.

Methylation and demethylation play an important role in determining how mercury will accumulate through the food web. Hg(II) is methylated by a biological process that appears to involve sulfate-reducing bacteria. Rates of biological methylation of mercury can be affected by a number of factors. Methylation can occur in water, sediment, and soil solution under anaerobic conditions, and to a lesser extent under aerobic conditions. In lakes, methylation occurs mainly at the sediment-water interface and at the oxic-anoxic boundary within the water column. The rate of methylation is affected by the concentration of available Hg(II) (which can be affected by the concentration of certain ions and ligands), the microbial concentration, pH, temperature, redox potential, and the presence of other chemical processes. Methylation rates appear to increase at lower pH. Demethylation of mercury is also mediated by bacteria.

Note that both Hg(II) and methylmercury (MeHg) sorb to algae and detritus, but only the methylmercury is assumed to be passed up to the next trophic level (inorganic mercury is relatively easily egested). Invertebrates eat both algae and detritus, thereby accumulating any MeHg that has sorbed to these. Fish eat the invertebrates and either grow into larger fish (which have been shown to have higher body burdens of mercury) or are eaten by larger fish. These are then prey for bald eagles and other piscivores. At each trophic level, a bioaccumulation factor must be assumed to represent the magnification of mercury concentration that occurs as one steps up the food chain.

Typically, almost all of the mercury found in fish (greater than 95 percent) is in methylmercury form. Studies have shown that fish body burdens of mercury increase with increasing size or age of the fish, with no signs of leveling off.

Although it is important to identify sources of mercury to the lakes, there may be fluxes of mercury within the lake that would continue nearly unabated for some time even if all sources of mercury to the lake were eliminated. In other words, compartments within the lake are probably currently storing a significant amount of mercury, and this mercury can continue to cycle through the system (as shown in the conceptual diagram, Figure 9) even without an ongoing outside source of mercury. The most important store of mercury within the lake is likely to be the bed sediment. Mercury in the bed sediment may be cause exposure to biota by being

- Resuspended into the water column, where it is ingested or it adsorbs to organisms that are later ingested.
- Methylated by bacteria. The methylmercury tends to attach to organic matter, which may be ingested by invertebrates and thereby introduced to the lake food web. It is methylmercury that poses the real threat to biota due its strong tendency to accumulate in biota and magnify up the food chain.

5.2 Cross-Sectional/Reference Site Approach to Linkage Analysis

The complex nature of mercury cycling in the environment can introduce considerable uncertainty into linkage analysis modeling. From examination of a single waterbody, it is difficult to determine the relative contributions of gross mercury loading, internal mercury cycling, and rates of mercury methylation and food chain accumulation to observed body burdens in fish.

Additional constraints on the analysis can be developed by examination of several lakes within the same region simultaneously (cross-sectional approach). Explaining the differences in mercury load, cycling, and bioaccumulation among several lakes provides a robust basis on which to develop the conceptual model. Therefore, the linkage analysis for Peña Blanca Lake has been developed simultaneously with analyses for Arivaca Lake and Patagonia Lake. A mercury TMDL is also required for Arivaca Lake, submitted in a companion to this document. Patagonia Lake is within the same region and was also sampled by EPA, yet it has acceptable fish tissue mercury concentrations. Patagonia Lake thus serves as an unimpaired reference site for the cross-sectional analysis. The basic physical characteristics of the three lakes and their watersheds are compared in Table 13.

Table 13. Cross-Sectional Comparison of Studied Lakes

	Peña Blanca Lake	Arivaca Lake	Patagonia Lake
Surface area (acres)	49	90	200
Volume at full pool (acre-feet)	1,071	1,050	11,000
Average depth (ft)	21.8	11.7	29.1
Maximum depth (ft)	60	25	86
Estimated hydraulic residence time (yr), 1985-98 average	0.36	0.33	0.16
Watershed area (ac)	8,820.6	12,696.4	145,904
Rangeland (ac)	845.9	5,761.3	55,509.7
Evergreen Forest (ac)	7,906.7	6,421.1	88,503.8
Cropland and Pasture (ac)	0	420.3	1,204.2
Urban and Residential (ac)	33.2	26.5	408.2
Producing mines identified in MILS	4 inactive	none	88 inactive 6 active
Mines producing gold	2 inactive	none	51 inactive 1 active

Notes: "Active" mines include those on temporary shutdown as of the 1995 MIL.
Prospects are omitted from the tabulation.

All three lakes lack known point source discharges of mercury and have a fairly similar distribution of rural rangeland and forest land uses. The Patagonia watershed has more historical gold mining operations (within a much larger watershed area), but highly contaminated ball mill sites have not been documented. EPA has not detected elevated mercury concentrations in streambed sediment in the Patagonia watershed. Physically, Patagonia differs from Peña Blanca and Arivaca in having a much larger volume, a larger contributing watershed, and a shorter hydraulic residence time. Patagonia is also the deepest of the three lakes.

EPA collected data from all three lakes and their watersheds in July 1998, which provides a valuable basis for cross-sectional comparison. All three lakes were strongly stratified with anoxic hypolimnia at the time of sampling.

At the time of the July sampling, all three lakes had similar total mercury concentrations in the sediment but very different concentrations in the water column. Lake sediment concentrations in Peña Blanca were somewhat elevated relative to Arivaca and Patagonia. All three lakes showed significant amounts of methylmercury in sediment, but Patagonia, unlike Arivaca and Peña

Blanca, did not have much methylmercury in the water column. This seems to explain why fish have unacceptable levels of mercury contamination in Arivaca and Peña Blanca, but not in Patagonia.

The July data emphasize that there may be little correlation between the total mercury mass stored in lake sediments and mercury concentration in fish tissue. Sediment concentrations in Patagonia Lake of both total mercury and methylmercury were higher than those in Arivaca (Table 14), yet Patagonia has acceptable fish tissue concentrations, while Arivaca does not. Sediment concentrations of total mercury in Peña Blanca were three times those in Arivaca, but total mercury concentrations in the water column are about twice as high in Arivaca as in Peña Blanca. These observations—indicating that total mercury concentrations in sediment are not linearly related to fish body burden—suggest that the linkage analysis requires a model that can describe the relationship between external mercury load and methylmercury generation.

Why are mercury levels in the water column higher in Arivaca and Peña Blanca than in Patagonia, despite rather similar sediment concentrations? Some clues are present in the water column chemistry results from the July sampling. As shown in Table 14, sulfate is strongly elevated in the hypolimnion of Patagonia relative to the other lakes, while alkalinity and pH are also elevated and DOC is somewhat depressed.

Table 14. Comparison of Summer Hypolimnetic Water Chemistry between Studied Lakes

	Patagonia	Arivaca	Peña Blanca
Sulfate (mg/L)	185	0.2	7
Alkalinity (mg/L)	156	91	86
pH	7.5	6.6	7
DOC (mg/L)	7	24	10
MeHg (ng/L)	0.8	14.3	3.9
Total Hg (ng/L)	2	37	20
Total Hg in sediment (ppb dry weight)	148	129	360
MeHg in sediment (ppb dry weight)	0.45	0.30	0.95

These observations suggest that relatively high sulfate concentrations (under alkaline conditions) promote precipitation of cinnabar in Patagonia, thus reducing water column concentrations. Differences in sediment chemistry might also play an important role. The sediment of Patagonia Lake has a stronger reducing environment and lower organic carbon content than the other two lakes. Finally, Patagonia is the deepest lake, which might reduce growth of algae and photosynthetic bacteria at the sediment interface.

5.3 Risk Hypothesis

In sum, the key differences between the lakes appear to be in water chemistry and in consequent effects on mercury speciation and cycling, rather than in gross total mercury load (as indicated by sediment concentration). Prior to model development, this understanding was summarized in a risk hypothesis as follows:

- Mercury concentrations in fish are driven by summer methylmercury concentrations in the epilimnion (surface water).
- Summer methylmercury concentrations in the epilimnion are driven by mixing from methylmercury concentrations in the hypoxic zone just below the thermocline.
- Methylmercury concentrations below the thermocline are determined primarily by water chemistry and its effect on mercury methylation in the anoxic portion of the water column and/or the cycling between the water and sediment, and only secondarily by mercury concentration in the sediment or gross mercury loads.
- Total mercury concentration in the sediments is driven by watershed loads but reflects accumulation over relatively long periods of time and changes only slowly.

The linkage analysis components described in the following sections are designed to provide a quantitative investigation of this risk hypothesis. The linkage tools are separated into several general components. The first two components address the watershed, while the third and fourth address the lake itself. First is a watershed hydrologic and sediment loading model (Section 5.4), which represents the movement of water and sediment from the watershed to the lake. This model supports an analysis of watershed loading of mercury to the reservoir (Section 5.5). A lake hydrologic model is presented in Section 5.6. Finally, a model of lake mercury cycling and bioaccumulation (Section 5.7) is used to address the cycling of mercury in the lake among and between abiotic and biotic components. When combined, these components enable completion of the TMDL linkage analysis.

5.4 Watershed Hydrologic and Sediment Loading Model

An analysis of watershed loading could be conducted at many different levels of complexity, ranging from simple export coefficients to a dynamic model of watershed loads. Data are not, however, available at this time to specify parameters or calibrate a detailed representation of flow and sediment delivery within the watersheds. Therefore, a relatively simple, scoping-level analysis of watershed mercury load, based on an annual mass balance of water and sediment loading from the watershed, is used for the TMDL. Uncertainty introduced in the analysis by use of a simplified and uncalibrated watershed loading model must be addressed in the Margin of Safety.

Watershed-scale loading of water and sediment was simulated using the Generalized Watershed Loading Function (GWLF) model (Haith et al., 1992). The complexity of this loading function model falls between that of detailed simulation models, which attempt a mechanistic, time-dependent representation of pollutant load generation and transport, and simple export coefficient models, which do not represent temporal variability. GWLF provides a mechanistic, simplified simulation of precipitation-driven runoff and sediment delivery, yet is intended to be applicable without calibration. Solids load, runoff, and ground water seepage can then be used to estimate particulate and dissolved-phase pollutant delivery to a stream, based on pollutant concentrations in soil, runoff, and ground water.

GWLF simulates runoff and streamflow by a water-balance method, based on measurements of daily precipitation and average temperature. Precipitation is partitioned into direct runoff and infiltration using a form of the Natural Resources Conservation Service's (NRCS) Curve Number method. The Curve Number determines the amount of precipitation that runs off directly, adjusted for antecedent soil moisture based on total precipitation in the preceding five days. A separate Curve Number is specified for each land use by hydrologic soil grouping. Infiltrated water is first assigned to unsaturated zone storage, where it may be lost through evapotranspiration. When storage in the unsaturated zone exceeds soil water capacity, the excess percolates to the shallow saturated zone. This zone is treated as a linear reservoir that discharges to the stream or loses moisture to deep seepage, at a rate described by the product of the zone's moisture storage and a constant rate coefficient.

Flow in rural streams may derive from surface runoff during precipitation events or from ground water pathways. The amount of water available to the shallow ground water zone is strongly affected by evapotranspiration, which GWLF estimates from available moisture in the unsaturated zone, potential evapotranspiration, and a cover coefficient. Potential evapotranspiration is estimated from a relationship to mean daily temperature and the number of daylight hours. In the arid Southwest, evapotranspiration often exceeds moisture supply, so stream runoff occurs sporadically in response to precipitation exceeding infiltration capacity. All the streams feeding Peña Blanca Lake are classified by USGS as intermittent and lack a consistent base flow component.

Monthly sediment delivery from each land use is computed from erosion and the transport capacity of runoff, whereas total erosion is based on the universal soil loss equation (Wischmeier and Smith, 1978), with a modified rainfall erosivity coefficient that accounts for the precipitation energy available to detach soil particles (Haith and Merrill, 1987). Thus, erosion can occur when there is precipitation, but no surface runoff to the stream; delivery of sediment, however, depends on surface runoff volume. Sediment available for delivery is accumulated over a year, although excess sediment supply is not assumed to carry over from one year to the next.

GWLF Model Input

GWLF application requires information on land use, land cover, meteorology, and parameters that govern runoff, erosion, and nutrient load generation.

Land Use/Land Cover. The development of the watershed delineation and land use/land cover is described above under Watershed Description (Section 2.3). The watershed delineation was overlain on the STATSGO soil coverage to identify soil groups and associated hydrologic soil groups. Major soil groups for the Peña Blanca watershed are summarized in Table 15.

Table 15. STATSGO Soil Groups for Peña Blanca Watershed

Soil ID	Predominant Soil Groups	Soil Hydrologic Group
AZ272	Lithic, Rock Outcrop	D
AZ251	Fluentic Lithic, Typic	B/C

Rainfall and Runoff Input Data and Parameters

Meteorology. Hydrology in GWLF is simulated by a water-balance calculation, based on daily observations of precipitation and temperature. Precipitation in southern Arizona shows considerable local geographic variability, primarily due to orographic (elevation) effects, with higher precipitation at higher elevations. The nearest first-order weather surface meteorological station is at Tucson International Airport; however, this is well to the northeast and at a lower elevation (2,548 ft MSL) than the Peña Blanca watershed (lake elevation 3,832 ft MSL with much of the watershed above 4,200 ft). A search was made of available NOAA Cooperative Summary of the Day (SOD) reporting stations, as well as daily stations reporting to the AZMET network. Based on this review, the most appropriate available meteorological data appear to be those from the SOD station Nogales 6N (Coop ID 025924), located at elevation 3,559 feet MSL at 31°27' N, 110°58'W. This station supplies both daily precipitation and maximum/minimum temperatures.

The Nogales 6N station is at a slightly lower elevation than the Peña Blanca watershed. To assess the importance of local orographic effects, a double mass analysis was used to compare Nogales precipitation to records from Canelo 1 NW (Coop ID 021231), located at elevation 5,009 feet MSL, but further from the Peña Blanca watershed at 31°34' N, 110°32' W. Comparison of the Nogales and Canelo records did not reveal any consistent trends in precipitation, so Nogales records were used.

Online data for Nogales 6N were obtained for January 1985–November 1997 from the Arizona Climate Center (http://climate.usu.edu/free/USA_AZ.HTM), while data for December 1997–December 1998 were purchased from the National Climatic Data Center. No data are missing within the 1985–1998 time period. Precipitation is primarily in the form of rain, with rare snow events. For one snow event, only snow depth is reported. This was converted to an equivalent depth of water using a conversion factor of 10% (Dunne & Leopold, 1978).

Average total precipitation and mean daily temperature by month for the 1985–1998 time period are summarized in Table 16. Monthly precipitation is variable from year to year, as shown in Figure 10; however, there are typically two wetter seasons, one in July–August, and one in December–February.

Table 16. Climate Normals for Nogales 6N, 1985-1998.

Month	Average Total Precipitation (inches)	Average Air Temperature (Fahrenheit)	Maximum Air Temperature (Fahrenheit)	Minimum Air Temperature (Fahrenheit)
January	1.42	45.90	83	13
February	1.45	49.13	85	14
March	0.99	53.40	93	18
April	0.74	59.35	99	25
May	0.28	66.45	103	29
June	0.37	75.03	112	39
July	3.52	79.30	109	47
August	4.95	78.26	107	49
September	1.38	72.75	100	38
October	1.04	63.47	98	24
November	0.78	52.34	87	14
December	1.68	45.99	81	10
FULL YEAR	18.6	61.78	112.00	10.00

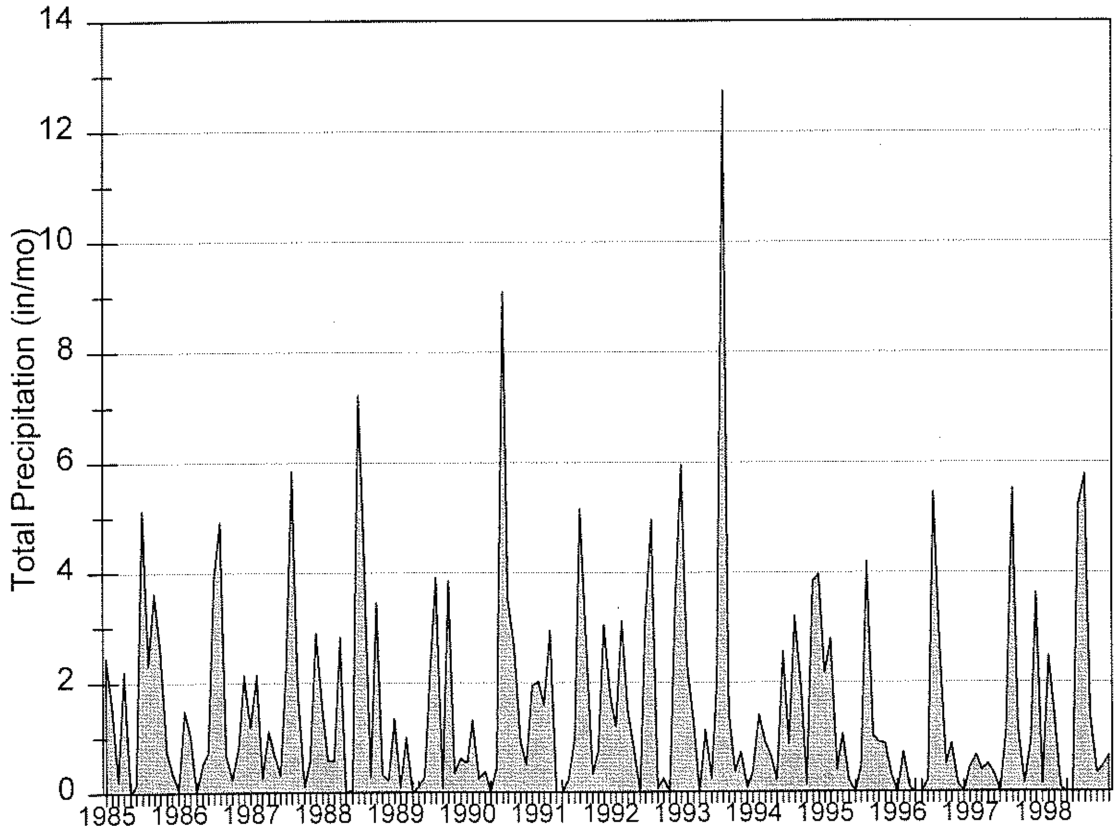


Figure 10. Nogales 6N Monthly Precipitation, 1985–1998

Runoff Curve Numbers. The direct runoff fraction of precipitation in GWLF is calculated using the curve number method from the U.S. Soil Conservation Service (now NRCS) TR55 method literature based on land-use and soil hydrologic group (SCS 1986). Curve numbers can vary from 25 for undisturbed woodland with good soils, to 100, for completely impervious surfaces. Weighted curve numbers were calculated for each land-use category based on soil distribution among hydrologic groups. Curve numbers assigned for the Peña Blanca watershed are summarized in Table 17.

Table 17. Runoff Curve Numbers for the Peña Blanca Watershed

Anderson Level 2 Classification	Acres	Curve Number
Evergreen Forest Land	7906.7	88.0
Urban or Built-Up Land	33.2	96.0
Shrub and Brush Rangeland	845.9	90.0

Evapotranspiration Cover Coefficients. The portion of rainfall returned to the atmosphere is determined by GWLF based on temperature and the amount of vegetative cover. Cover coefficients were set to 0.8 for the growing season and 0.3 for the nongrowing season. These relatively low numbers reflect the sparse vegetative coverage in the watershed

Soil Water Capacity. Water stored in soil may evaporate, be transpired by plants, or percolate to ground water below the rooting zone. The amount of water that can be stored in soil—the soil water capacity—varies by soil type and rooting depth. Based on soil water capacities reported in the STATSGO database, soil types present in the watershed, and GWLF user's manual recommendations, the GWLF default soil water capacity of 10 cm was used. Given the low precipitation and high temperatures in the watershed, the capacity is rarely exceeded, and almost all streamflow is simulated as surface runoff. Thus, the simulation is insensitive to this parameter.

Recession and Seepage Coefficients. The GWLF model has three subsurface zones: a shallow unsaturated zone, a shallow saturated zone, and a deep aquifer zone. Behavior of the second two stores is controlled by a ground water recession and a seepage coefficient. Because the model simulation yields almost no shallow ground water flow, results are insensitive to specification of these parameters. The recession coefficient was set to 0.15 per day, and the seepage coefficient to 0.

Erosion Parameters

GWLF simulates rural soil erosion using the Universal Soil Loss Equation (USLE). This method has been applied extensively, so parameter values are well established. This computes soil loss per unit area (sheet and rill erosion) at the field scale by

$$A = RE \cdot K \cdot (LS) \cdot C \cdot P$$

where

A = rate of soil loss per unit area,
RE = rainfall erosivity index,
K = soil erodibility factor,
LS = length-slope factor,
C = cover and management factor, and
P = support practice factor.

It should be noted that use of the USLE approach will underestimate total erosion within a watershed of this type. This is because the USLE addresses only sheet and rill erosion, whereas mass wasting (landslides) and gullying are probably the dominant components of the total sediment budget within the watershed (see NFS, 1973). It was reasoned, however, that the mercury from the watershed that is likely to become bioavailable in the lake would be the mercury associated with the fine sediment fraction. The USLE approach should provide a reasonable approximation of the finer sediment load, even though movement of larger material by other processes is omitted, and can thus serve as a basis for evaluation of mercury loading from watershed sediments to the lake.

Soil loss or erosion at the field scale is not equivalent to sediment yield since substantial trapping may occur, particularly during overland flow or in first-order tributaries or impoundments. GWLF accounts for sediment yield by (1) computing transport capacity of overland flow and (2) employing a sediment delivery ratio (DR) which accounts for losses to sediment redeposition.

Rainfall Erosivity (RE). Rainfall erosivity accounts for the impact of rainfall on the ground surface, which can make soil more susceptible to erosion and subsequent transport. Precipitation-induced erosion varies with rainfall intensity, which shows different average characteristics according to geographic region. The factor is used in the USLE and is determined in the model as follows:

$$RE_t = 64.6 \cdot a_t \cdot R_T^{1.81}$$

where

RE_t = rainfall erosivity (in megajoules mm/ha-h),
a_t = location- and season-specific factor, and
R_t = rainfall on day t (in cm).

Erosivity was assigned a constant value of 0.3, based on the assumption that values for southern Arizona should be similar to values reported for west and central Texas (Wischmeier and Smith, 1978; Haith and Merrill, 1987).

Soil Erodibility (K) Factor. The soil erodibility factor indicates the propensity of a given soil type to erode, and are a function of soil physical properties and slope. Soil erodibility factors were extracted from the STATSGO soil coverage. Values for individual land use varied from 0.08 for rangeland to 0.19 for forest.

Length-Slope (LS) Factor. Erosion potential varies by slope as well as soil type. Length-slope factors were calculated by measuring representative slopes from topographic maps for upland and bottomland land-use categories. The LS factor is calculated following Wischmeier and Smith (1978):

$$LS = (0.045 \cdot x_k)^b \cdot (65.41 \cdot \sin^2\phi_k + 4.56 \cdot \sin\phi_k + 0.065)$$

where

ϕ_k = $\tan^{-1}(ps_k/100)$, where ps_k is percent slope
x_k = slope length (m)

LS values for Peña Blanca are 0.75 for forest and 5.0 for rangeland, based on average slopes of 5.2% and 17.6% respectively, and an assumed slope length of 100 meters.

Cover and Management (C) and Practice (P) Factors. The mechanism by which soil is eroded from a land area and the amount of soil eroded depends on soil treatment resulting from a combination of land uses (e.g., forestry versus row-cropped agriculture) and the specific manner in which land uses are carried out (e.g., no-till agriculture versus non-contoured row cropping). Land use and management variations are represented by cover and management factors in the USLE and in the erosion model of GWLF. Cover and management factors were drawn from several sources (Wischmeier and Smith, 1978; Haith et al., 1992; Novotny and Chesters, 1981). Cover factors were 0.04 for forest and 0.11 for rangeland, and reflect the relatively sparse cover typical of this landscape. Practice (P) factors were all set to 1, consistent with recommendations for non-agricultural land.

Sediment Delivery Ratio. The sediment delivery ratio (DR) indicates the portion of eroded soil carried to the watershed mouth from land draining to the watershed. The soil can be water-column suspended sediment or bed load, depending on the total size of the subwatershed. Values for DR were estimated from an empirical relationship of DR to watershed area (ASCE, 1975). ASCE's graphical relationship is approximated by the following empirical equation:

$$\text{Log}_{10}(DR) = -0.301\ \text{Log}_{10}(\text{Area}) - 0.400$$

For lakes, it is not usually appropriate to calculate a DR based on total watershed area, since the watershed drains to the lake as a number of smaller, independent watersheds. The sediment delivery ratios were therefore calculated by delineating major subwatersheds for the lake, calculating DR for each, then forming an area-weighted average.

Sediment delivery ratios and KLSCP factors for rural land uses in the Peña Blanca watershed are summarized in Table 18.

Table 18. Erosion and Sediment Yield Parameters for the Peña Blanca Watershed Model

Land Use	K	LS	C	P	KLSCP	DR
Rangeland	0.08	5	0.11	1	0.044	0.184
Forest	0.19	0.75	0.04	1	0.0057	0.184

Watershed Model Results

Application of the GWLF model to the period from October 1985 through September 1998 yields an average of 9.9 cm/year runoff and 1,220,000 kg sediment yield by sheet and rill erosion. The sediment yield estimate is considerably less than the average yield rate estimated by NFS (1973); however, most of the difference is apparently due to the inclusion of mass wasting loads in the NFS calculation. As noted above, mass wasting loads are thought to be of minor significance for loading of bioavailable mercury to the lake. GWLF model results are summarized in Figure 11.

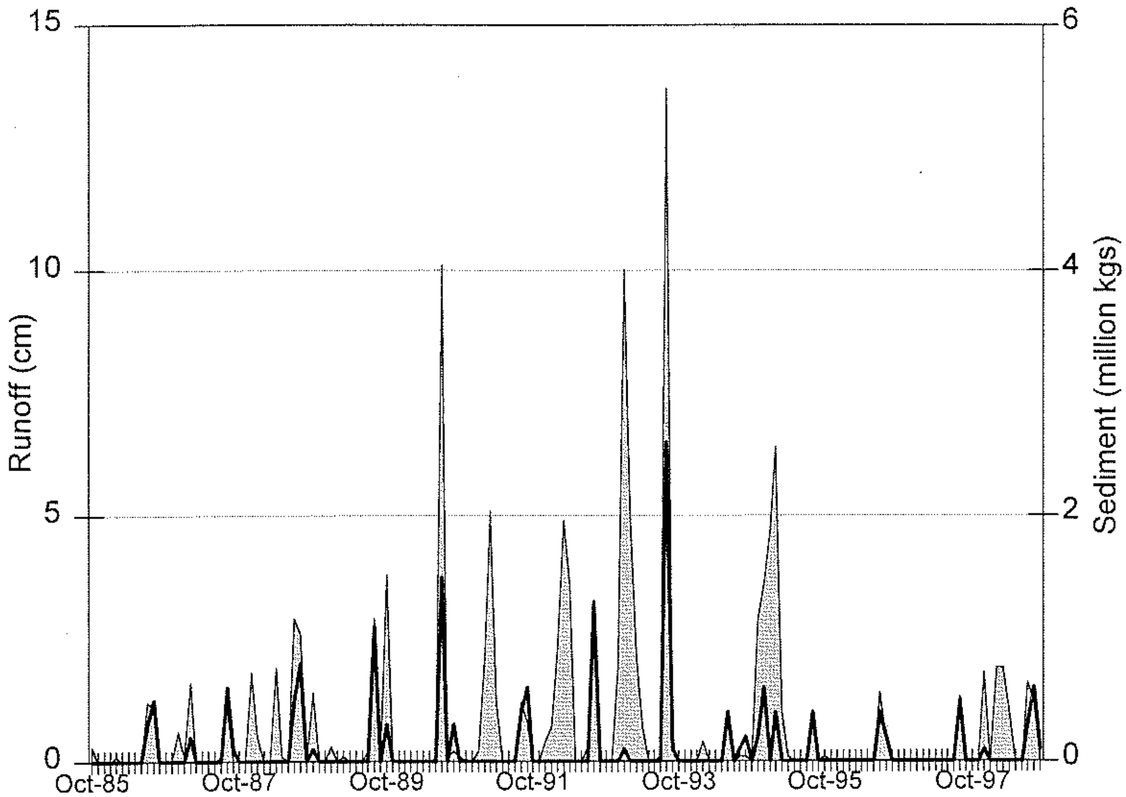


Figure 11. GWLF Watershed Model Predictions for Monthly Runoff (shaded area) and Sediment Yield (heavy line) in Peña Blanca Lake Watershed

5.5 Watershed Mercury Loading Model

Estimates of watershed mercury loading are based on the sediment loading estimates generated by GWLF through application of a sediment potency factor expressing the mass of mercury per mass of sediment. A background loading estimate was first calculated, then combined with estimates of loads from individual hot spots.

The majority of the EPA sediment samples in the watershed showed no clear spatial patterns, with the exception of the "hot spot" area identified at the St. Patrick Mine ball mill tailings pile. Therefore, background loading was calculated using the central tendency of sediment concentrations from all samples excluding those at or near the St. Patrick mine ball mill site. The background sediment mercury concentrations were assumed to be distributed lognormally, as is typical for environmental concentration samples, and an estimate of the arithmetic mean of 47.9 ppb was calculated from the observed geometric mean and coefficient of variation (Gilbert, 1987). Applying this assumption to the GWLF estimates of sediment transport yields an estimated rate of mercury loading from watershed background of 58.6 g/yr. This load is ultimately derived from a combination of atmospheric deposition to the watershed, naturally occurring mercury in rocks underlying the watershed, and dispersed human activities. For comparison, the estimated rate of gross atmospheric mercury loading to the watershed is 441 g/yr. This gross atmospheric load is well in excess of the estimated rate of net loading from the watershed to the lake, but is balanced by re-emission to the atmosphere through volatilization and wind erosion, and by infiltration and sequestration in upland soils.

Loading from the St. Patrick mine ball mill tailings is calculated separately, but is also based on the GWLF estimate of sediment load generated per hectare of "rangeland" (the land use surrounding the hot spots), as reduced by the sediment delivery ratio for the watershed. The extent of the "hot spot" and the average mercury concentrations assigned to the tailings pile and downstream area are described in the Source Assessment (Section 4.2). Sediment load per hectare from the hot spot is assumed to be four times greater than that for normal rangeland, due to the fine consistency of tailings. This sediment load multiplier factor may be thought of in terms of the USLE equation (RE·K·LS·C·P), which predicts sediment loss. As discussed in section 5.4, the K factor for rangeland in the watershed was set to 0.08, based on data in the STATSGO soil coverage. This K factor is indicative of a sandy soil. The consistency of the mine tailings, however, as been compared to that of "talcum powder" (Sam Rector, ADEQ, personal communication). A typical K factor for very fine sand with low organic content is 0.42, which is 5.2 times the K factor for rangeland soil (and would therefore increase sediment loading estimates by 5.2 times). This factor is compensated somewhat by the fact that sediment at the ball mill site is likely to be a mixture of native sandy soil and the finer tailings, and by lower slopes at the ball mill site than the average for rangeland soils in the watershed (because the site is located in the bottom of the canyon). Therefore, a multiplier of 4 was selected as a reasonable estimate. With these assumptions, the estimated rate of mercury loading associated with the St. Patrick Mine ball mill hotspot and contaminated downstream sediments is 133 μg-Hg/yr, or almost 70 percent of the total external mercury load to the lake. This large percentage is a result of the high average concentration reported for the tailings (287,000 ppb) relative to the average mercury concentration in sediments in the remainder of the watershed (48 ppb).

Given the uncertainties in estimation of erosion rates and the incomplete status of the USFS characterization of the St. Patrick Mine ball mill tailings, the assessment of mercury loading from this area should be judged to be only a rough, order of magnitude estimate. The estimate of the importance of the St. Patrick Mine ball mill hotspot depends in part on the assumption of the sediment load multiplier–it will increase if this multiplier is larger than 4, and decrease if it is actually lower than 4. Table 19 summarizes the results of a sensitivity analysis of the percent of load associated with the St. Patrick Mine ball mill to variations in the sediment load multiplier.

Table 19. Sensitivity Analysis to Sediment Load Multiplier of St. Patrick Mine Ball Mill Source

Sediment Load Multiplier	Percent of Load Attributed to St. Patrick Mine Source
2	52.2%
4	68.6%
8	76.6%

The direct deposition of mercury from the atmosphere onto the Peña Blanca Lake surface was calculated by multiplying the estimated atmospheric deposition rates (Section 4.3) times the lake surface area.

A similar approach to estimate watershed loads was applied to Arivaca Lake (see separate TMDL submission) and Patagonia Lake (where no mercury hot spots or unacceptable fish tissue concentrations have been identified). A cross-sectional comparison of watershed mercury loading rates to the three lakes is included in Table 20. Although Patagonia Lake has a higher total annual mercury load, the load per volume of inflow is much lower than those in the two impaired lakes. *Direct* atmospheric deposition onto the lake surface does not appear to be a major source of total mercury load, as it is estimated to account for only about 1 percent of the total annual load to the lake. Atmospheric deposition to the watershed could, however, constitute a significant portion of the net loading from the watershed.

Table 20. Watershed Mercury Loading to Pena Blanca Lake

	Mercury loading to lake (grams per year)			
Water Year (Oct-Sept)	**From watershed**	**From hot spots**	**From direct atmos. dep. to lake**	**Total**
1986 Total	38.32	87.02	2.27	127.61
1987 Total	43.11	97.90	2.27	143.28
1988 Total	62.27	141.41	2.27	205.95
1989 Total	57.48	130.53	2.27	190.28
1990 Total	100.59	228.43	2.27	331.29
1991 Total	47.90	108.78	2.27	158.95
1992 Total	62.27	141.41	2.27	205.95
1993 Total	134.12	304.58	2.27	440.97
1994 Total	33.53	76.14	2.27	111.94
1995 Total	76.64	174.05	2.27	252.96
1996 Total	28.74	65.27	2.27	96.28
1997 Total	23.95	54.39	2.27	80.61
1998 Total	52.69	119.66	2.27	174.62
Grand Total	761.61	1729.57	29.51	2520.69
Annual Average	**58.59**	**133.04**	**2.27**	**193.90**

Lake Comparison	**Mercury Load (g/yr)**	**Average Inflow (ac-ft/yr)**	**Annual avg loading/inflow (g/ac-ft)**
Pena Blanca Lake	193.90	2,716	0.071
Arivaca Lake	183.78	3,153	0.058
Patagonia Lake	503.24	50,926	0.010

5.6 Lake Hydrologic Model

No monitoring data for inflow, water stage, or outflow are available for Peña Blanca Lake. The lake level is not actively managed, and releases occur when storage capacity is exceeded. Therefore, lake hydrology was represented by a simple monthly water balance, using the following assumptions:

1. Inflow from the watershed is given by monthly predictions from the GWLF model application.
2. Direct precipitation on the lake surface is estimated from Nogales 6N monthly precipitation depth times the lake surface area at the beginning of the month.
3. Evaporation from the lake surface is estimated from pan evaporation data and a pan coefficient of 0.7. This represents the ratio between mean annual lake surface evaporation (Kohler et al., 1959, as cited in Dunne and Leopold, 1978) and average annual evaporation from Class A evaporation pans for this area of southern Arizona (Kohler et al., 1959, as cited in Dunne and Leopold, 1978), and is within the range recommended by Dunne and Leopold (1978). A pan coefficient of 0.69 has also been reported for Nogales 6 N (NFS, 1973).
4. Net gain from or loss to groundwater seepage through the lake bed is assumed to be zero for Peña Blanca, lacking any evidence to the contrary.
5. Potential storage at the end of the month is calculated as the sum of initial storage plus inflow plus direct precipitation minus evaporation.
6. The stage-area-discharge curve is used to estimate the surface area and elevation of the lake surface corresponding to the potential storage at the end of the month. No corrections were made for potential losses of storage volume due to sedimentation since lake construction. If the lake surface elevation is computed to be higher than the spillway elevation, the excess volume is assumed to spill downstream.
7. Actual storage at the end of the month is the smaller of potential storage and full-pool storage.
8. Surface area and elevation of the lake surface at the end of the month are updated to reflect actual storage.

Application of the water balance model requires pan evaporation data as an input in addition to the watershed meteorological data described above. As no evaporation data were available from the Nogales Cooperative Summary of the Day meteorological station, pan evaporation data for Tucson were used. Pan evaporation for 1980 through 1995 was obtained from the BASINS 2.0 Region 9 CD-ROM and are summarized in Table 21. Later pan evaporation data were not available for Tucson, so monthly averages were used for the 1996 through 1998 water balance. Use of Tucson data may result in an overestimation of evaporative losses from the lake, since an average pan evaporation rate of 94 inches per year has been reported for Nogales (NFS, 1973).

Table 21. Pan Evaporation Data for Tucson, AZ (inches)

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Annual Total
1980	5.20	6.30	9.20	13.18	15.67	17.81	15.22	13.45	11.40	10.79	7.72	6.93	132.87
1981	5.35	6.67	7.95	12.72	14.84	16.88	13.57	15.06	11.78	9.46	7.39	5.73	127.42
1982	4.92	5.72	8.18	12.42	15.45	17.30	14.26	12.05	11.41	10.24	5.88	4.36	122.20
1983	5.94	5.18	7.73	11.23	16.27	17.16	15.17	12.34	10.48	7.59	5.44	4.72	119.25
1984	5.54	7.52	11.52	12.66	16.72	15.65	13.16	11.82	12.24	8.30	6.76	3.93	125.82
1985	4.97	5.80	9.16	12.82	15.29	17.75	15.78	13.53	11.39	8.58	5.92	5.15	126.13
1986	7.60	6.00	9.69	12.54	16.29	16.89	13.25	12.08	11.95	8.93	5.72	4.05	124.97
1987	5.47	6.12	9.31	12.59	13.46	16.49	15.91	12.95	11.32	9.24	6.50	4.32	123.66
1988	5.27	6.93	10.91	12.13	17.02	16.65	14.67	12.16	13.23	10.10	7.30	6.49	132.84
1989	5.91	7.81	11.91	15.34	17.70	19.13	16.91	14.57	15.04	9.92	7.29	6.20	147.72
1990	5.77	6.08	9.63	12.84	15.94	18.41	13.28	12.94	11.44	10.89	7.66	4.99	129.84
1991	4.62	6.64	8.08	13.09	16.88	16.23	15.07	12.18	11.24	11.03	6.99	4.54	126.59
1992	5.58	5.89	7.88	12.41	13.46	16.41	14.31	11.93	12.68	11.11	7.36	3.66	122.68
1993	4.11	4.83	9.09	13.28	16.15	18.18	15.16	11.41	13.12	9.91	6.36	5.47	127.05
1994	6.68	6.75	9.56	13.33	14.38	16.63	15.66	13.68	11.53	9.68	6.14	4.66	128.66
1995	4.31	6.31	8.89	12.06	14.10	17.25	16.19	12.40	12.61	10.82	6.89	5.58	127.38
Ave.	5.48	6.29	9.46	12.95	15.51	17.27	15.11	12.71	12.32	10.02	6.74	5.01	128.87

The water balance model was run for the period 1985 through 1998. This water balance approach provides a rough approximation of the seasonal cycle of changes in volume and surface area of Peña Blanca Lake, and of the amount of water released downstream over the spillway. It cannot capture daily or event scale movement of water in and out of the lake. Estimates for individual months are subject to considerable uncertainty in the rainfall-runoff model as well.

Similar water balance models were constructed for Arivaca Lake and Patagonia Lake. These are similar to the Peña Blanca application, except that controlled releases from Patagonia Lake are accounted for. Average end-of-month depth for Peña Blanca is compared to predictions for Arivaca and Patagonia Lake in Figure 12.

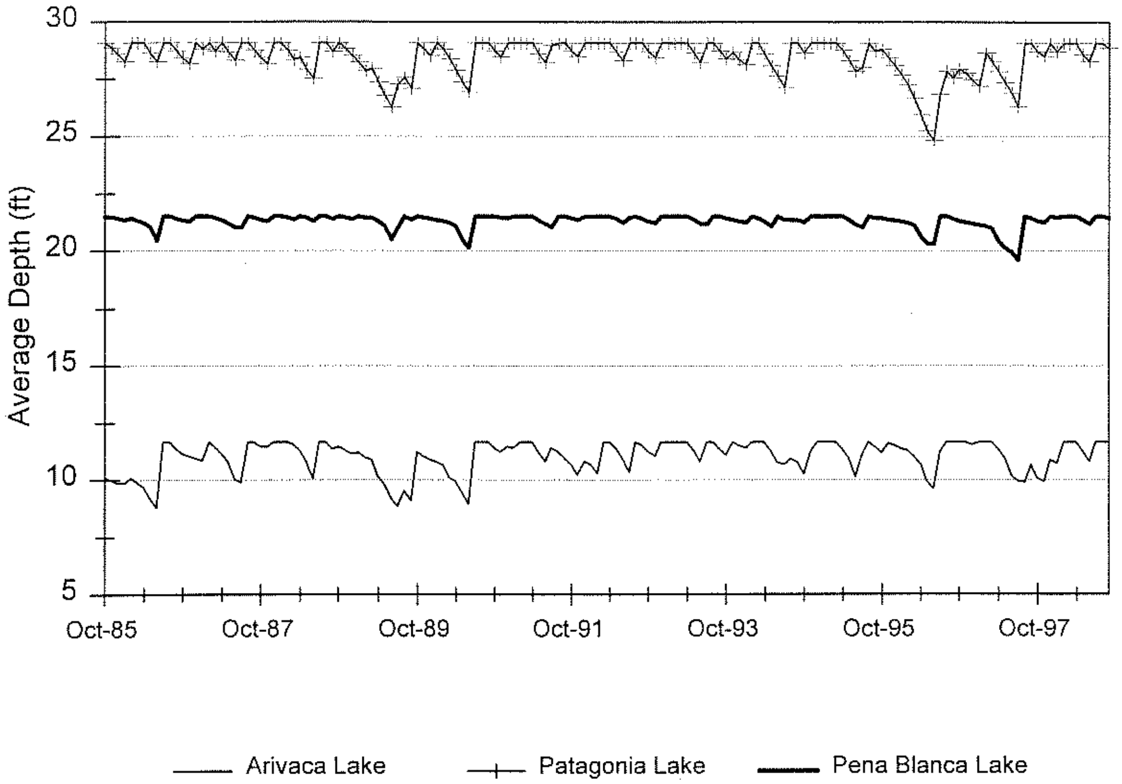


Figure 12. Average Depths (Volume over Surface Area) from Water Balance Model

5.7 Lake Mercury Cycling and Bioaccumulation Model

Cycling and bioaccumulation of mercury within the lake were simulated using the Dynamic Mercury Cycling Model (D-MCM; Tetra Tech, 1999). D-MCM is a Windows 95/NT-based simulation model that predicts the cycling and fate of the major forms of mercury in lakes, including methylmercury, Hg(II), and elemental mercury. D-MCM is a time-dependent mechanistic model, designed to consider the most important physical, chemical, and biological factors affecting fish mercury concentrations in lakes. It can be used to develop and test hypotheses, scope field studies, improve understanding of cause/effect relationships, predict responses to changes in loading, and help design and evaluate mitigation options.

A schematic overview of the major processes in D-MCM is shown in Figure 13. These processes include inflows and outflows (surface and ground water), adsorption/desorption, particulate settling, resuspension and burial, atmospheric deposition, air/water gaseous exchange, industrial mercury sources, in situ transformations (e.g. methylation, demethylation, MeHg photodegradation, Hg(II) reduction), mercury kinetics in plankton, and bioenergetics related to methylmercury fluxes in fish.

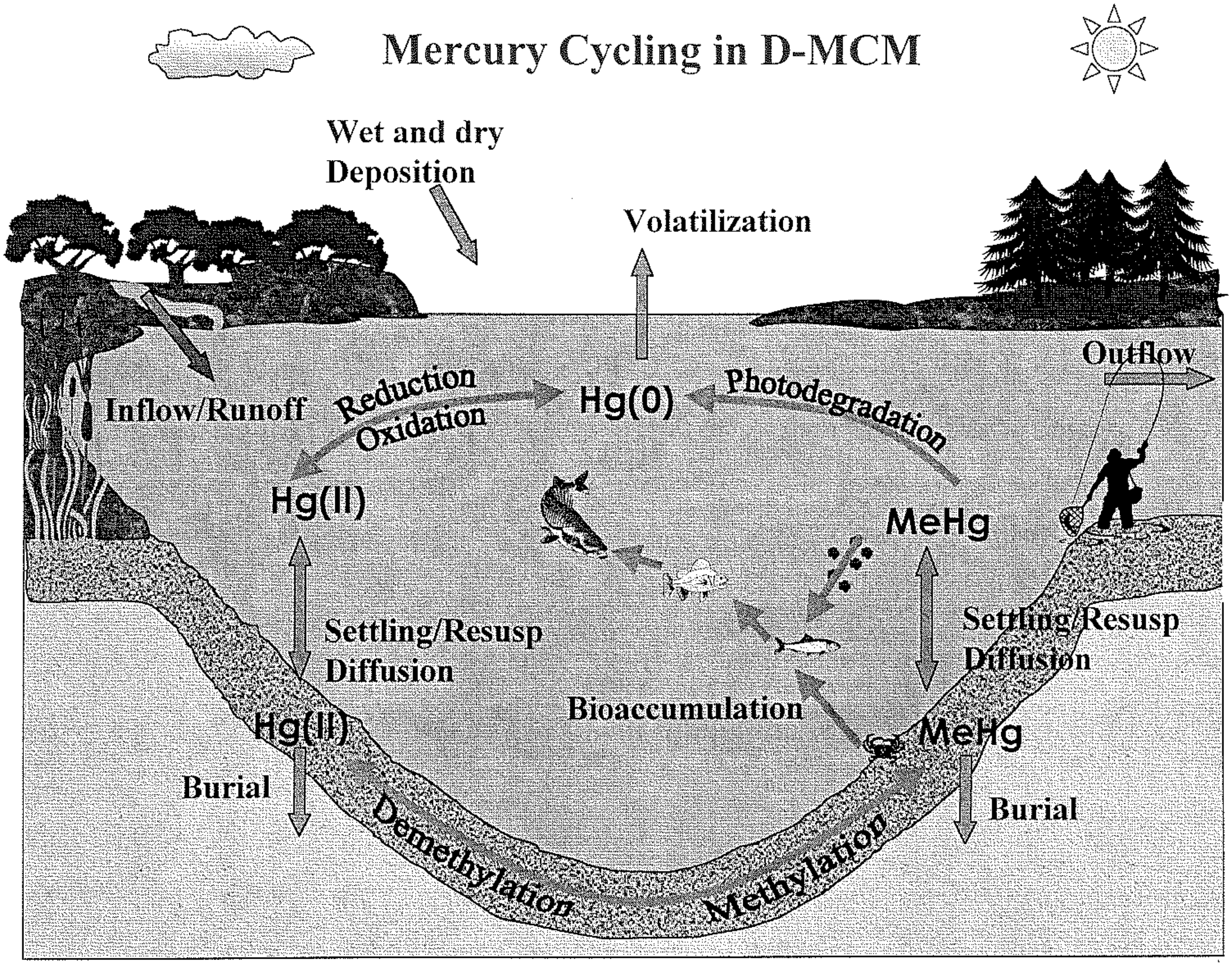


Figure 13. Major Processes in the D-MCM Model

Model compartments include the water column, sediments, and a food web that includes three fish populations. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous exchange, wet deposition, dry deposition). Similarly, watershed loadings of Hg(II) and methylmercury are input directly as time-series data. The user provides for hydrologic inputs (surface and ground water flow rates) and associated mercury concentrations, which are combined to determine the watershed mercury loads.

The food web consists of six trophic levels (phytoplankton, zooplankton, benthos, non-piscivorus fish, omnivorous fish, and piscivorus fish). Fish mercury concentrations tend to increase with age and thus are followed in each year class. Bioenergetics equations for individual fish (Hewitt and Johnson 1992) have been adapted to simulate year classes and entire populations.

The Electric Power Research Institute (EPRI) has funded development of the D-MCM model. It is an extension of previous mercury cycling models developed by Tetra Tech, including the original Macintosh-based MCM models developed during the EPRI-sponsored Mercury in Temperate Lakes Project in Wisconsin (Hudson et al. 1994) and the subsequent steady-state Regional Mercury Cycling Model (R-MCM) (Tetra Tech 1996). The original model was developed for a set of seven oligotrophic Wisconsin seepage lakes. R-MCM has been applied to 21 lakes in Wisconsin; Lake Barco, Florida; and Lake 240 at the Experimental Lakes Area, Ontario. Performance of the model on the large data sets available for Wisconsin is summarized in Figure 14.

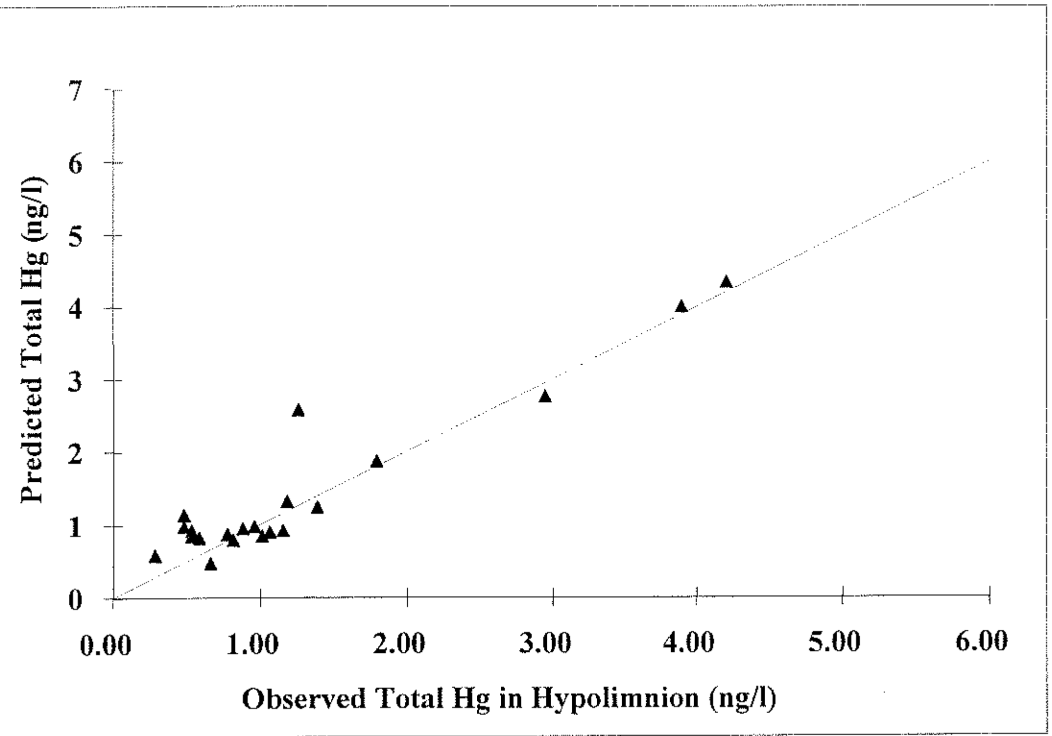
The present version of D-MCM has updated mercury kinetics and an enhanced bioenergetics treatment of the food web. The predictive capability of D-MCM is evolving but is currently limited by some scientific knowledge gaps, which include:

- The true rates and governing factors for methylation and Hg(II) reduction;
- Factors governing methylmercury uptake at the base of the food web; and
- The effects of anoxia and sulfur cycling.

For example, there is evidence that anoxia and sulfides can affect mercury cycling and influence water column mercury concentrations in lakes (e.g. Benoit et al., 1999; Driscoll et al., 1994; Gilmour et al., 1998; Watras et al., 1994), but the underlying mechanisms and controlling factors have not been quantified.

Another important assumption in the current version of D-MCM is that all of the Hg(II) on particles is readily exchangeable. This results in longer predicted response times for lakes to adjust to changing conditions or mercury loads than likely would occur. It is quite plausible that a significant fraction of Hg(II) on particles is strongly bound, reducing the pool size of Hg(II) available to participate in mercury cycling and the time required for fish mercury concentrations to adjust to changes in mercury loadings. The magnitude of this error potentially can be quite large for oligotrophic lakes with very low sedimentation rates and very long particulate Hg residence times in the surficial sediments. For systems that have very high sedimentation rates, such as is found in many reservoirs, the practical consequence of this assumption could be quite small. D-MCM modifications are planned to include both rapid and slow exchange of Hg(II) on particles. Experimental work is also proposed to develop the associated input values for the model.

Because strong anoxia in the hypolimnion is a prominent feature during summer stratification for the Arizona lakes simulated in this study, D-MCM was modified to explicitly allow significant methylation to occur in the hypolimnion. In previous applications of D-MCM, the occurrence of methylation was restricted to primarily within surficial sediments. That the locus of methylation likely includes or is even largely within the hypolimnion (at least for Arivaca and Pena Blanca lakes) is supported by (1) the detection of significant very high methylmercury concentrations in the hypolimnia of Arivaca and Pena Blanca lakes and (2) almost complete losses of sulfate in Arivaca Lake in the hypolimnion resulting from sulfate reduction. An input was added to the model to specify the rate constant for hypolimnetic methylation, distinct from sediment methylation.



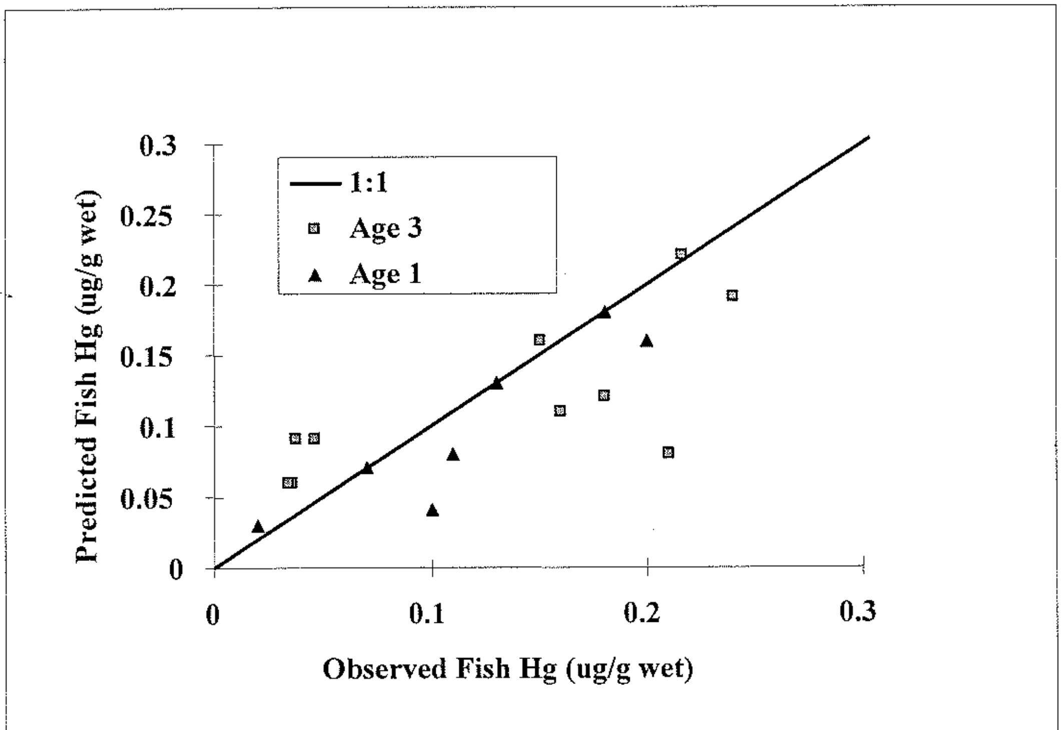


Figure 14. Summary of Mercury Cycling Model Applications to Wisconsin Lakes

5.8 Lake Model Application

Model Input Parameters

The D-MCM model was calibrated to the three study lakes by compiling and inputting into the model data specific to each lake on

- Hydrology and lake physical characteristics (morphometry, stratification);
- External loading rates of mercury (from the atmosphere, watershed, and St. Patrick Mine ball mill);
- Thermodynamic and kinetic rate constants;
- Water and sediment chemistry; and
- Biotic data.

Data specific to each of the three lakes were input into the model first, followed by data derived from calibrations for other lakes where site-specific data were lacking for Peña Blanca. For instance, thermodynamic and kinetic rate constants specific to Peña Blanca are not available and were obtained from previous calibrations of D-MCM to lakes in other regions.

Calibration proceeded by running the model with a daily time step for 10 years and adjusting the model so that concentrations of mercury in largemouth bass matched observed averages for each lake. Because the hydrology of these lakes is so dynamic and "flashy", more weight was placed on matching largemouth bass Hg concentrations than on trying to match predicted and observed water chemistry data precisely. This decision was based on the following:

1. Limited water chemistry data that indicate that chemistry in these systems varies rapidly;
2. Hydrologic budgets that show the average hydraulic residence time of all three lakes is relatively short (less than 0.4 years);
3. The lack of truly local atmospheric loading data adequate for resolving and validating short-term dynamics in any of the lakes; and
4. The fact that mercury concentrations in older cohorts of largemouth bass reflect dietary intake throughout their life history and are rather insensitive to short-term variations in water column chemistry and Hg loading dynamics.

The calibrations used the same kinetic (rate constant) assumptions for all three lakes, letting only differences in loading, hydrology, and chemistry dictate differences in response. The following paragraphs give a brief overview of how the input data were assembled and input to the model.

Hydrologic Inputs. D-MCM requires that the user compute all aspects of the hydrologic balance. Inputs include surface water inflow, direct precipitation, surface water outflow, subsurface seepage inflow and outflow, and change in storage. Inputs for all three systems were derived from monthly water balances compiled for October 1985 through September 1998, and computing the average monthly flows during that entire period. An "average" monthly budget was then computed from the hydrologic balance continuity equation, using the computed inflows, precipitation, evaporative losses, and outflow volumes to derive monthly changes in storage. Changes in monthly surface area related to changes in lake volume were computed from hypsographic curves empirically determined for each lake. Looping the monthly inputs for this average year back-to-back resolved discontinuities between the beginning-of-year and end-of-year changes in storage within 2 years. This "resolved" 12-month hydrologic budget was then input into the model.

Atmospheric Inputs. Development of estimates of direct atmospheric input of mercury to the lakes is described in Section 4.3.

Thermodynamic and Kinetic Rate Data. Thermodynamic data and rate kinetics data were derived from previous calibrations performed on multiple lakes in Wisconsin, and Lake Barco, a sub-tropical seepage lake in north-central Florida (Hudson et al., 1995; personal communication from Reed Harris, Tetra Tech). Thermal time series data were derived from measured in-lake thermal profiles and from long-term monthly average air temperature measurements measured at Nogales, Arizona, from 1952 through 1998.

Water and Sediment Chemistry Data. Water chemistry from the July 1998 sampling period for chlorine, dissolved organic carbon (DOC), pH, suspended sediment concentrations, dissolved oxygen and mercury species (particulate and dissolved total mercury and total methylmercury) were used to characterize epilimnetic and hypolimnetic conditions in the model for each lake. Additional data for Arivaca Lake collected during October 1997 were used to establish conditions for Arivaca Lake when the lake is isothermal. Sediment chemistry inputs (total mercury and total organic carbon [TOC]) for the model were developed by computing geometric mean concentrations for samples for each lake measured as a function of location within the lake (epilimnetic vs. hypolimnetic). Although no data were available for porosity and density, it was assumed that the porosities of epilimnetic and hypolimnetic sediments were 0.80 and 0.92, respectively. These values are consistent with porosities often measured in erosional (epilimnetic) and depositional (hypolimnetic) sedimentary environments (cf. Håkanson and Janson, 1983).

Biotic Data. Three trophic levels of fish were simulated in D-MCM: herbivorous fish, omnivorous fish, and piscivorous fish. Because the greatest concentrations of mercury in aquatic food webs develop in piscivorous fish, the focal point of the simulations was on largemouth bass. The rate at which fish feed and grow (bioenergetics) is a critical variable in determining rates of uptake of mercury. For example, all other factors being equal, fish that grow slowly will incorporate higher concentrations of mercury into their tissue than fish that grow more rapidly and efficiently. Measured ages, weights, and lengths from 30 largemouth bass collected in Pena Blanca Lake in May 1995 were used to calibrate age-weight and length-weight relationships. Dietary preferences for each trophic level were based on data developed for the Wisconsin R-MCM lakes.

Calibration

Several assumptions were used to guide the calibrations for the three study lakes. First, it was assumed that there were no good *a priori* reasons to use differing rate or thermodynamic constants for each lake to account for differing mercury behavior. As an example, there may be geochemical differences between the eroded sedimentary material and their ability to adsorb mercury between the Peña Blanca and Arivaca watersheds, but no data are available to substantiate and describe those differences and use of identical values provides a more robust cross-sectional calibration. As a result, binding constants (partition coefficients) for all three lakes were considered identical. A second assumption was that primary locus of methylation was the hypolimnion and that the rates of methylation in each lake were dependent upon the delivery of Hg(II) and the hypolimnetic methylation rate constant. This assumption was invoked after initial simulations that restricted methylation solely to the sediments resulted in severely under-predicted mercury concentrations in biota. This assumption is also consistent with the stable thermal stratification and anoxic conditions that develop in these lakes, the consumption of sulfate observed in Pena Blanca Lake and particularly Arivaca Lake, and the comparatively high concentrations of methylmercury that develop in the hypolimnia and metalimnia of Pena Blanca and Arivaca lakes.

Initial application of D-MCM to Arivaca and Pena Blanca resulted in large overestimates of the amount of mercury predicted in 5-year-old largemouth bass. In a highly parameterized model like D-MCM, a number of possibilities and combinations exist to change rate or thermodynamic constants to yield a more appropriate calibration. However, because the majority of the rate constant and thermodynamic data has been derived from regional calibrations and direct empirical observations from experimental and calibrated lake studies, it was elected not to manipulate any of those parameters to yield a better calibration. First, the particle-Hg(II) partition coefficients were adjusted for particles in the sediment and water column to yield stronger particulate binding, thus reducing the dissolved pool available for methylation. Higher partition coefficients are appropriate for the epilimnion because the hypolimnion becomes seasonally anoxic, which can reduce the ability of inorganic particles to sorb trace elements. Changing the partition coefficient from 5×10^{10} m^3/g-particle (dry weight), the value used for Wisconsin and Florida lakes, to a maximum of 1.6×10^{12} m^3/g for epilimnetic waters and 5×10^{11} m^3/g for hypolimnetic sediments yielded only modest improvements in the calibration.

To further improve the model calibration, focus was placed on one feature of the model known to be potentially inadequate--the ability of the model to predict the amount of labile Hg truly available for desorption. Previous simulations with D-MCM have illustrated that, although initial sorption of Hg to particles may be well characterized by conventional sorption models such as the Freundlich and Langmuir isotherms, desorption of "aged" Hg bound to particles may not follow the same models. In others, some Hg may become irreversibly bound after adsorption has initially occurred, and the amount of mercury ultimately available for desorption is less than the initial sorption models would predict. Stable isotope research to explicitly explore this so-called sorption "hysteresis" phenomenon for watersheds in Canada likely will be conducted in late 1999.

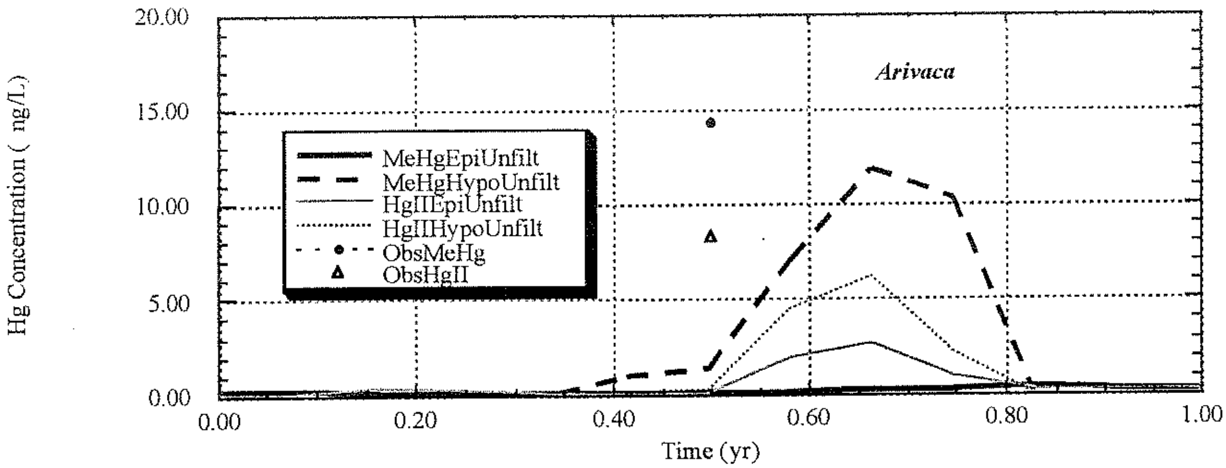
One attractive aspect of this hypothesis is that it could readily explain D-MCM's over prediction of mercury in largemouth bass in both Pena Blanca and Arivaca lakes, which receive the vast majority of their mercury loads through watershed transport of particulates. In calibrating the model to Pena Blanca and Arivaca lakes, it was assumed that the effective loading (i.e., the relative or fractional amount of the load truly available and not irreversibly bound) of mercury from watershed sources in both lakes were equivalent. Loads derived from ball mill tailings at the St. Patrick Mine (Peña Blanca Lake) and from waste disposal at Ruby Dump (Arivaca Lake) were considered wholly available. Using this approach, an effective watershed loading coefficient of 0.62 (i.e., an assumption that 38 percent of the watershed non-point source load is unavailable for desorption) provided very good calibrations for predicted mercury concentrations in largemouth bass (Table 22). Figure 15 presents the temporal dynamics predicted by D-MCM for total Hg(II) and methyl Hg in the hypolimnia and epilimnia of the three study lakes under long-term average conditions. Included in the plots are the results from the July 1997 sampling of the hypolimnia (the only location where both methyl and total mercury were sampled in the water column) for both chemical species. Although the timing of the peak concentrations for the observed and the modeled concentrations do not agree well, the predicted temporal dynamics and ranges in concentrations are quite consistent with the observed values, and the difference in timing very likely reflects the fundamental problem of comparing an "average" year with a single point in time.

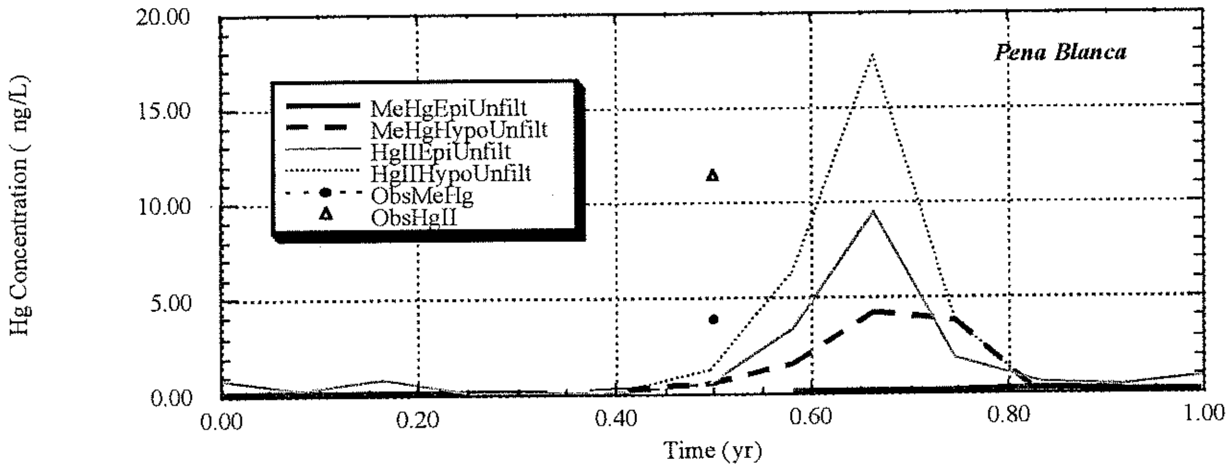
Table 22. D-MCM Calibration results for Pena Blanca, Arivaca, and Patagonia Lakes. Estimates are predicted annual ranges after model has reached steady state. Observed concentrations from July 1997.

Lake	Parameter Type	Methyl Hg (ng/L)	$Hg(II)_{total}$[1] (ng/L)	5-year Largemouth Bass Hg (mg/kg wet)
Pena Blanca	Observed	3.92	11.38	1.42
	Predicted	0.00 - 4.26	0.00 - 17.69	1.40
Arivaca	Observed	14.3	1.46 - 8.3	1.18
	Predicted	0.00 - 12.07	0.00 - 6.28	1.18
Patagonia	Observed	0.78	1.14	0.14
	Predicted	0.00 - 0.12	0.00 - 11.38	0.05

[1] Defined as the difference between measured total $Hg_{unfiltered}$ and $CH_3Hg^+_{unfiltered}$.

Mass balance summaries for inputs, outputs, and internal fluxes in the three lakes are compared in Table 23, expressed in micrograms per square meter of lake surface area. The key difference between Patagonia versus Peña Blanca and Arivaca is in the rate of hypolimnetic methylation. Relationships between mercury concentrations in the various biotic compartments simulated by the model are shown in Figure 16.





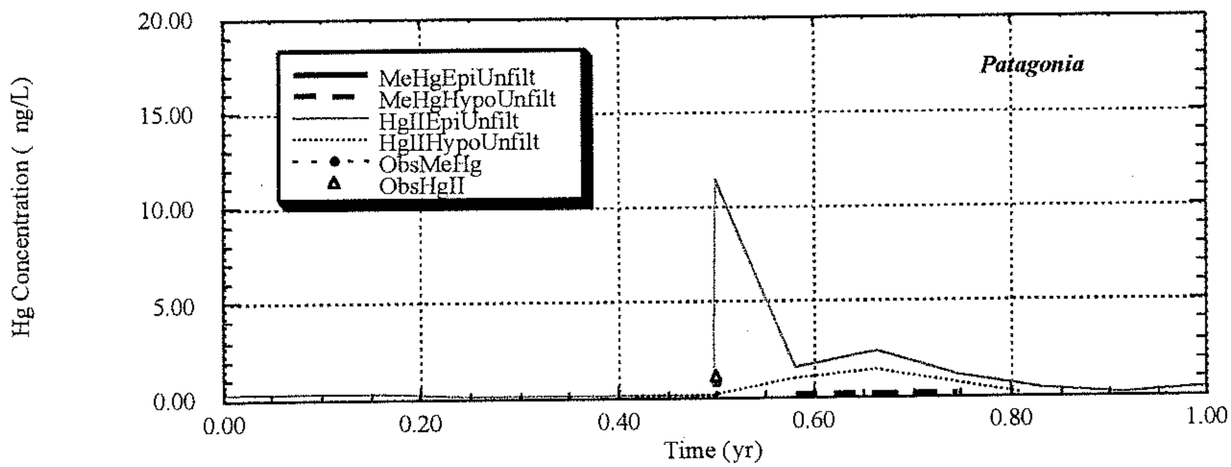


Figure 15. Calibrated D-MCM Predicted Average Annual Dynamics for Unfiltered Concentrations of MeHg and Hg(II) in Peña Blanca, Arivaca, and Patagonia Lakes. Also shown are sampling results from the hypolimnia of all three lakes collected in July 1997.

Table 23. Summary of Average Annual Mercury Fluxes for Peña Blanca, Arivaca, and Patagonia Lakes Predicted by the D-MCM Model. Rates are shown in micrograms per square meter of lake surface area.

	Peña Blanca Lake	Arivaca Lake	Patagonia Lake
Inputs			
Hg(II), Atmosphere	12.4	12.8	12.8
Hg(II), Watershed	193.3	326.3	278.2
Hg(II), Hot Spots	706.8	1.0	0.0
MeHg, Atmosphere	0.02	0.02	0.02
Outputs			
Hg(0), Volatilization	8.8	26.3	11.4
Hg(II), Sediment Burial	809.2	267.7	219.7
Hg(II), Outflow	49.7	9.2	43.4
MeHg, Sediment Burial	36.8	24.1	3.5
MeHg, Outflow	1.0	1.5	0.04
Internal Transformations			
Methylation in Sediment	4.3	7.3	0.7
Methylation in Hypolimnion	43.0	51.8	3.1
Demethylation, Water Column	0.7	2.0	0.006
Demethylation, Sediment	6.1	28.6	0.1
Hg(II) Reduction	4.7	2.1	15.4

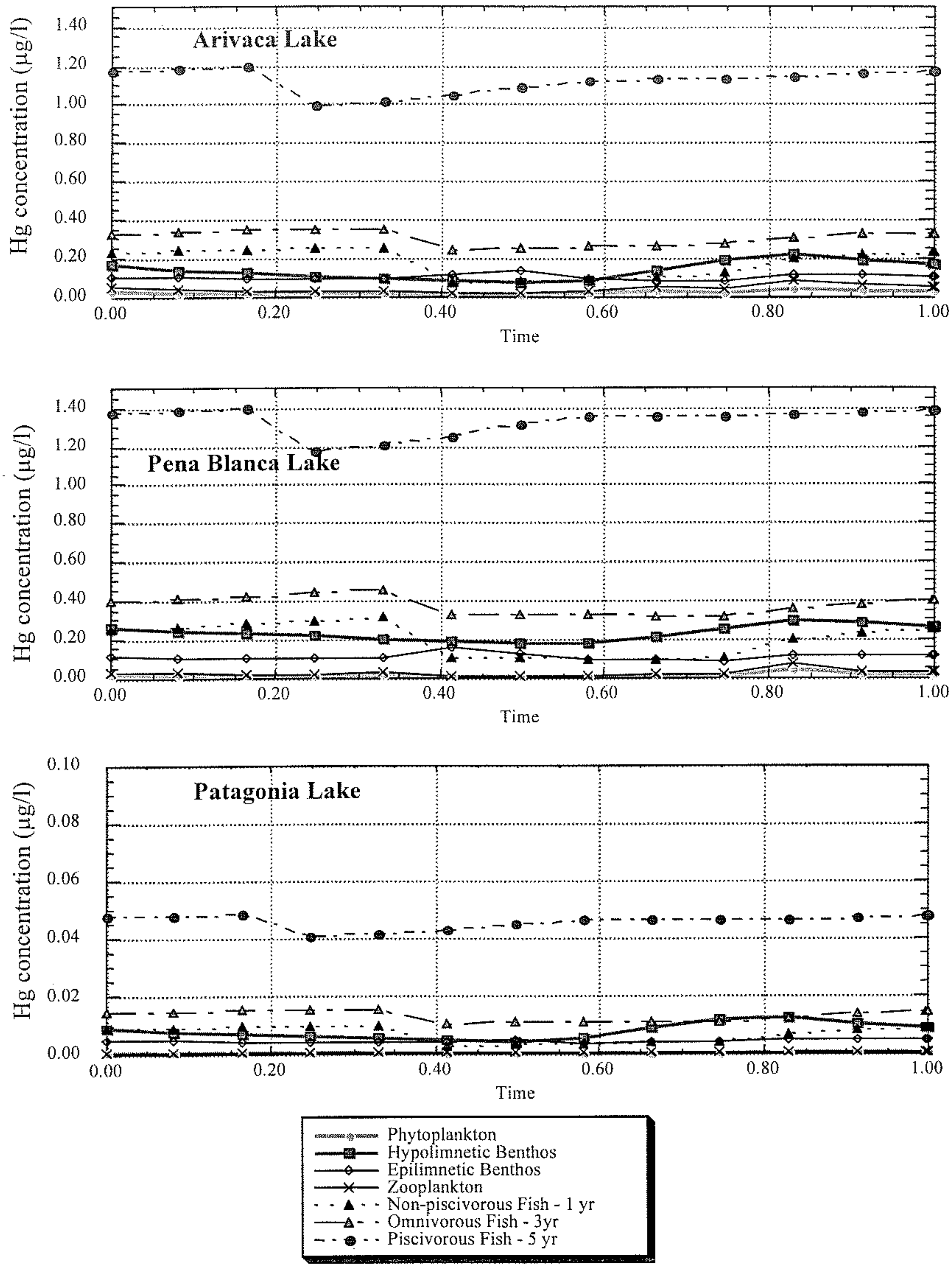


Figure 16. Relationship between Mercury Concentrations in Biotic Compartments Predicted by D-MCM over the Course of a Typical Year

After calibration, the model was used to evaluate the load reductions necessary to meet the numeric target. The response of concentrations of mercury in 5-year old largemouth bass to changes in external mercury loads turns out to be nearly linear for these lakes (after a period of several years adjustment), as shown in Figure 17. This is because the sediment burial rates are high, and sediment recycling is low, with the majority of the methylmercury that enters the food chain being created in the anoxic portion of the water column. Figure 17 demonstrates that the numeric target of 1 mg/kg in 5-year old largemouth bass is predicted to be met with a 37 percent reduction in hotspot loads to Peña Blanca Lake, and a 16 percent reduction in total watershed loads to Arivaca Lake (that is, the mercury tissue concentration in 5-year-old largemouth bass is predicted to meet the numeric target of 1 mg/kg when the hot spot load is reduced to 63 percent of current levels for Peña Blanca Lake and the total watershed load is reduced to 84 percent of current levels for Arivaca Lake).

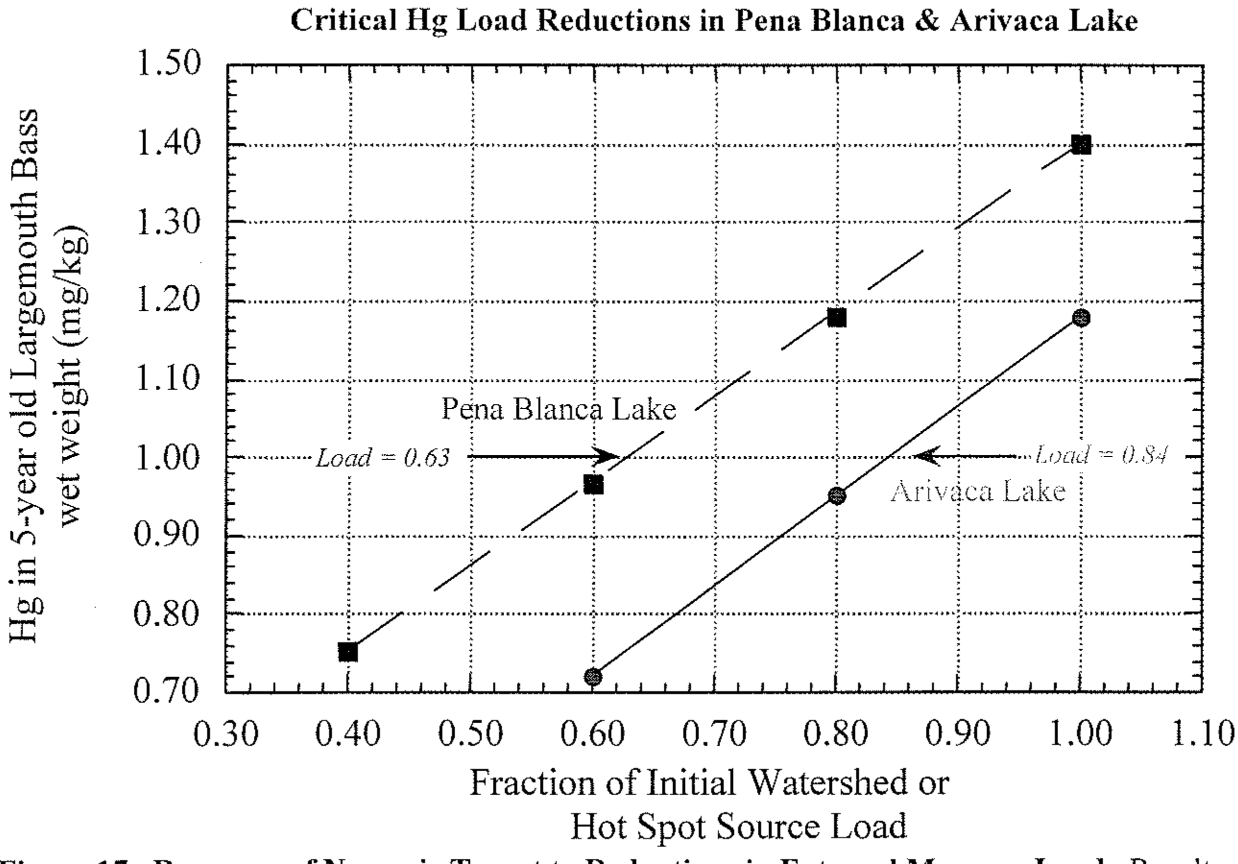


Figure 17. Response of Numeric Target to Reductions in External Mercury Load. Results are shown after approximate stabilization of response. Fractions shown represent fraction of St. Patrick Mine ball mill hot spot load for Peña Blanca Lake, fraction of total watershed load for Arivaca Lake.

Model Uncertainties

The model indicates that methylation is largely driven by release of Hg(II) from particles settling into and through the hypolimnion during the summer stratification period when the hypolimnion is anoxic (see Figure 15). Gross (total) loads to Arivaca and Pena Blanca lakes are very similar (see Table 20) and do not wholly account for predicted differences in cycling of mercury. This becomes particularly evident when comparing the average input concentration of mercury to both lakes derived from the total annual load (hot spot, watershed, and direct atmospheric) and the average total surface water inflow. Critical influent load concentrations (i.e., the maximum allowable load to achieve a target mercury concentration of 1 mg/kg [wet weight] for 5-year-old largemouth bass) for Pena Blanca and Arivaca lakes are 43.2 and 39.8 ng/L respectively. When corrected for the fraction of the load considered non-reactive, the concentrations are 36.5 and 25.1 ng/L, respectively. This difference is largely due to the large differences in DOC, which is approximately two-fold higher in Arivaca (16–24 mg/L compared to 9–10 mg/L), and which helps promote methylation by providing a source of carbon. The high rates of bacterial metabolism supported by the higher concentrations of DOC also are evidenced by the greater degree of depletion of sulfate in Arivaca Lake. Previous studies on apparent rates of sulfate reduction for lakes in the Upper Midwest and Florida showed that the differences in sulfate losses are related to DOC (Pollman, unpublished data). Uncertainties thus include the actual availability of particulate Hg transported to the lakes and whether rates of methylation would decline significantly if the hypolimnia were precluded from going anoxic.

Other uncertainties include model representation of the role of sulfate reduction and the influence of reduced sulfur species. Because of the large amount of sulfate reduction occurring in Arivaca Lake, the effects of reduced sulfur interacting with Hg(II) (the critical substrate for methylation) and the associated effects on methylation are likely important, but not well understood. For example, the formation of neutral Hg(II) – S^{2-} species might facilitate uptake of Hg(II) by methylating bacteria (Benoit and Gilmour, 1999); conversely, as reduced sulfur concentrations increase, Hg(II) can be sequestered as cinnabar and effectively removed from solution, reducing its availability for methylation.

5.9 Determination of Loading Capacity

A waterbody's loading capacity represents the maximum rate of loading of a pollutant that can be assimilated without violating water quality standards (40 CFR 130.2(f)). Application of the D-MCM lake mercury model provides a best estimate of the loading capacity for mercury of Peña Blanca Lake of 144.7 grams total mercury per year. This is the maximum rate of loading consistent with meeting the numeric target of 1 mg/kg mercury in 5-year-old largemouth bass.

This estimate of loading capacity is subject to considerable uncertainty, as described in the preceding sections. Uncertainty in the estimation of the loading capacity, and thus the TMDL, is addressed through the assignment of a Margin of Safety (Section 7).

It should also be noted that the loading capacity is not necessarily a fixed number. The numeric target for the TMDL is expressed as a mercury concentration in fish tissue. This numeric target is linked to external mercury load through a complex series of processes, including methylation/demethylation of mercury and burial of mercury in lake sediments. Any alterations in rates of methylation or in rates of mercury loss to deep sediments will change the relationship between external mercury load and fish tissue concentration and would thus result in a change in the loading capacity for external mercury loads.

6. TMDL, Load Allocations, and Wasteload Allocations

The TMDL and associated allocations are presented in terms of the existing loading capacity of Peña Blanca Lake, as calculated in Section 5.9. The potential for alternative management strategies, which may serve to increase loading capacity, is discussed in Section 6.7.

6.1 Total Maximum Daily Load

The TMDL represents the sum of all individual allocations of portions of the waterbody's loading capacity. Allocations are made to all point sources (wasteload allocations) and non-point sources or natural background (load allocations) The TMDL (sum of allocations) must be less than or equal to the loading capacity; it is equal to the loading capacity only if the entire loading capacity is allocated. In many cases it is appropriate to hold in reserve a portion of the loading capacity to provide a Margin of Safety (MOS), as provided for in the TMDL regulation.

Knowledge of mercury sources and the linkage between mercury sources and fish tissue concentrations in Peña Blanca Lake is subject to many uncertainties at this time. (These uncertainties are discussed in more detail in Section 7). Accordingly, it is appropriate to allocate only a portion of the estimated TMDL at this time. Based on the analysis in Sections 6.3 and 7, an allocation of 55 percent of the loading capacity is proposed in this TMDL study. The Total Maximum Daily Load calculated for Peña Blanca Lake is thus equivalent to a total annual mercury loading rate of 79.5 g-Hg/yr.

6.2 Unallocated Reserve

Forty-five percent of the loading capacity is not being allocated at this time. Therefore, there is an estimated unallocated reserve of 65.2 g-Hg/yr. The best estimate of uncertainty in the loading capacity analysis is that the true loading capacity lies within plus or minus 25 percent or 36.2 g-Hg/yr of the best estimate of 144.7 g-Hg/yr (Section 7.1). The unallocated reserve is thus greater than the estimated Margin of Safety for the TMDL.

6.3 Load Allocations

Load allocations represent assignment of a portion of the TMDL to nonpoint sources. These allocations must be made even where there is considerable uncertainty about nonpoint loading rates. Federal regulations (40 CFR 130.2(g)) define a load allocation as follows:

> *The portion of a receiving water's loading capacity that is attributed either to one of its existing or future nonpoint sources of pollution or to natural background sources. Load allocations are best estimates of the loading, which may range from reasonably accurate estimates to gross allotments, depending on the availability of data and appropriate techniques for predicting loading. Wherever possible, natural and nonpoint source loads should be distinguished.*

The current state of knowledge of mercury sources in the watershed and transport to the lake requires use of a "gross allotment" approach to the watershed as a whole, rather than assigning individual load allocations to specific tracts or land areas within the watershed. Loading from geologic sources has also not been separated from the net impacts of atmospheric deposition onto the watershed. Information is currently available to separate sources for load allocations as follows:

1. Direct atmospheric deposition onto the lake surface.
2. Loading from the St. Patrick Mine ball mill site.
3. Generalized background watershed loading, including mercury derived from parent rock and soil material, small amounts of residual mercury from past mining operations, and the net contribution of atmospheric deposition onto the watershed land surface.

Direct Atmospheric Deposition. Direct deposition to the lake surface is estimated to provide about 2.3 g-Hg per year (Table 20). This amount equals less than 2 percent of the estimated total annual mercury loading to the lake. Atmospheric deposition of mercury to Peña Blanca Lake is believed to derive from long-range transport of global sources. This component is thus of small significance to the total mercury budget in the lake and not readily controllable. Because of these two factors, no reduction in existing loads is proposed, and a load allocation of 2.3 g/year is assigned.

St. Patrick Mine Ball Mill Site. The U.S. Forest Service is in the process of developing a clean up plan for the St. Patrick Mine ball mill site. It is assumed that this remediation effort will need to achieve, at a minimum, the 35 mg/kg Health-Based Guidance Level (HBGL) promulgated by the Arizona Department of Health Services, which is estimated to require removal of about 400 cubic yards of sediment. If the hot spot area was reduced from the current average concentration of 287.4 mg/kg to 35 mg/kg, the associated load to the lake would be reduced to 15.8 g/yr. In addition, loads from the less-contaminated sediments downstream of St. Patrick Mine but outside the hotspot area are estimated to contribute about 2.8 g/yr. The maximum permissible load allocation for the St. Patrick Mine ball mill tailings would thus appear to be about 18.6 g/yr, or a reduction of 114.4 g/yr (86 percent) from current levels.

Background Watershed Loading. Background loading from the watershed is estimated to contribute 58.6 g-Hg/yr to Peña Blanca Lake. No reduction in background loading is required to achieve the loading capacity, after setting off the allocation reserve.

6.4 Wasteload Allocations

Wasteload allocations constitute an assignment of a portion of the TMDL to permitted point sources. There are no permitted point source discharges within the Peña Blanca watershed. Therefore, no wasteload allocations are included in the TMDL and the WLAs are zero.

6.5 Allocation Summary

Proposed allocations for the Peña Blanca mercury TMDL are summarized in Table 24. These allocations, based on best currently available information, are predicted to result in attainment of acceptable fish tissue concentrations within a time horizon of approximately 10 years. A delay in achieving standards is unavoidable because time will be required for mercury to cycle through the lake and food chain after loads are reduced.

Table 24. Summary of TMDL Allocations and Needed Load Reductions (in g-Hg/yr)

Source	Allocation	Existing Load	Needed Reduction
Wasteload Allocations	0.0	0.0	0.0
Load Allocations			
Atmospheric Deposition	2.3	2.3	0.0
St. Patrick Mine Ball Mill Site	18.6	133.0	114.4
Watershed Background	58.6	58.6	0.0
Total	79.5	193.9	114.4
Unallocated Reserve	65.2		
Loading Capacity	144.7		

The current analysis has a high level of uncertainty, as discussed in Section 7. The proposed allocations are believed to be conservative, because an unallocated portion of the TMDL is held in reserve. To provide reasonable assurances that the assigned load allocations will indeed result in compliance with the fish tissue criterion, a commitment to continued monitoring and assessment is warranted. The purposes of such monitoring will be (1) to evaluate the efficacy of control measures instituted to achieve the needed load reductions and (2) to determine if the load reductions required by the TMDL lead to attainment of water quality standards. Although estimates of the assimilative capacity and load allocations are based on best available data and incorporate a Margin of Safety, these estimates may potentially need to be revised as additional data are obtained. Because of the uncertainty inherent in the TMDL, continued monitoring is recommended as part of the implementation plan for this TMDL.

6.6 Feasibility of Achieving Load Allocations

The modeling analysis indicates that a remediation of the St. Patrick Mine ball mill tailings to Arizona Health Based Guidelines (HBGLs) for mercury will result in a sufficient reduction in mercury to achieve the numeric target, along with a significant unallocated reserve. The USFS has scheduled a removal action for the St. Patrick Mine tailings/ball mill site for September, 1999 which is designed to meet the HBGLs. Therefore, it appears highly feasible that the load allocations will be achieved.

6.7 Alternative Management Strategies

As discussed in Section 5.9, an alternative approach to managing the mercury problem in Peña Blanca Lake would be to increase the loading capacity for mercury. This could be accomplished by any management intervention that decreased rates of bacterial methylmercury production within the lake, or increased rates of burial and sequestration of mercury in lake sediment. Selection of such an approach would require considerable further research and feasibility studies; alternative management strategies are mentioned here to indicate that a wider range of options than simply reducing external watershed mercury loads may be available for achieving support of uses. For Peña Blanca Lake, this TMDL study suggests that load reductions associated with removal of tailings from the St. Patrick Mine ball mill site should be sufficient to achieve standards; however, because there is considerable uncertainty in the analysis, this result is not guaranteed. If the tailings removal does not result in achieving standards, it might be desirable to evaluate alternative management strategies that increase loading capacity of the lake.

Alternative management strategies to increase lake loading capacity for mercury should be regarded as experimental. They have not been demonstrated at the field scale to our knowledge. Approaches that may be suitable for further investigation include the following:

- Management that reduces the extent and duration of anoxia in the hypolimnion might be useful to reduce rates of mercury methylation. This approach could potentially be implemented either through mechanical mixing to prevent or reduce the period of stratification or through direct aeration of the hypolimnion. Cost and engineering complexity might significantly limit the feasibility of this approach.
- Altering sulfur chemistry within the lake could potentially increase the rate of precipitation of cinnabar or the activity of demethylating bacteria, thus reducing net rates of methylmercury production. The interactions of sulfur chemistry and lake mercury cycling are incompletely understood at this time, and it is not clear whether practical management options to alter sulfur chemistry exist. Evaluation of this option would require more detailed understanding of chemical and microbial processes within the lake.
- Treating the lake with alum (aluminum sulfate) should result in the formation of an aluminum hydroxide floc, which would scavenge particulate matter from the water column as it settles and form a barrier to solute exchange across the sediment-water interface. This is an approach sometimes used to manage eutrophication due to excessive phosphorus concentrations. Alum treatment could potentially reduce the mercury available for methylation within the system, as well as reducing methylmercury recycling from the sediments. Additional investigations would need to be pursued to determine (1) whether removal of particulate mercury by alum flocculation would indeed result in a sufficient reduction in methylmercury production and recycling to attain standards; (2) the cost and feasibility of alum treatment sufficient to ensure a stable floc in the presence of relatively high dissolved organic carbon levels; and (3) the potential for lowering the pH of the lake and creating a risk of aluminum toxicity.

7. Margin of Safety, Seasonal Variations, and Critical Conditions

7.1 Sources of Uncertainty

The analysis for the draft Peña Blanca TMDL contains numerous sources of uncertainty, and load allocations must be proposed as best estimate "gross allotments" in keeping with the TMDL regulation at 40 CFR 130.2(g). Key areas of uncertainty have been highlighted in the Source Assessment and Linkage Analysis sections and are summarized below.

The sources of uncertainty can be divided into two groups. The first group consists of sources of uncertainty that directly affect the ability of the linkage analysis to relate the numeric target fish tissue concentration to external mercury loads. These sources of uncertainty propagate directly to uncertainty in estimation of the loading capacity and TMDL. The second group consists of uncertainty in the estimation of external loads. These have their primary impact on allocations and affect the estimation of loading capacity only indirectly, by causing a potential mis-specification in the data used for lake model calibration. The loading capacity estimate is much more sensitive to uncertainty in the first group and relatively robust to uncertainty in the second group.

The first group includes the following:

- Hydraulic response of the lake, including rate of flushing downstream, is estimated from crude water balance calculations. The reduction in volume of the lake by sedimentation over time since impoundment is unknown and both the current morphometry of the lake and actual rates of outflow are uncertain at this time.
- A key uncertainty of the D-MCM application is the actual availability of particulate mercury transported into the lakes.
- The role of sulfate reduction and the influence of reduced sulfur species on mercury cycling within the lakes is not well understood.
- It is suggested that rates of mercury methylation in the hypolimnion would decline if the hypolimnion was precluded from going anoxic; however, the exact impact is uncertain.

The second group includes the following:

- Watershed background loading of mercury is estimated using a simple water balance/sediment yield model. While the concentrations in tributary sediments are based on measured data, the estimated actual rates of movement of this sediment to the lake are not constrained by field measurements at this time.
- Estimates of atmospheric wet deposition of mercury are based on the MDN station at Caballo, New Mexico, which has only a limited period of record and is several hundred miles removed from the Peña Blanca watershed. Net dry deposition is assumed to be roughly equal to wet deposition, without direct evidence from the watershed. Total mercury deposition to the watershed may well differ from the estimates used by a factor of 3 or more, based on best professional judgement of the authors. Such uncertainty will, however, have only a minor effect on the estimates of total external mercury loads because direct deposition to the lake is a minor component of the total mercury loading

budget and atmospheric loading onto the watershed land surface is combined within the data-based estimated of net mercury loading from the watershed and not estimated from deposition data.

- Estimated loading from the St. Patrick mine ball mill site appears to be highly significant, but is also subject to considerable uncertainty. The estimated rate of contaminated sediment transport from this site to the lake is speculative at best. Because of this high level of uncertainty, rates of loading from the St. Patrick mine ball mill site (after the proposed removal operation), and responses within the lake, should be confirmed with additional monitoring of the system in future.

Quantitative estimates have been made for only some of these sources of uncertainty. It is also not appropriate to assume that all the sources of uncertainty are additive, since some sources will have positive or negative correlations with other sources. A full, quantitative analysis of uncertainty in the TMDL has not yet been feasible, but might be appropriate as additional data are collected. The best professional judgement of the authors is, however, that there is a high probability that the true loading capacity of Peña Blanca Lake lies within plus or minus 25 percent of the best estimate of 144.7 g-Hg/yr.

The uncertainty in the estimation of loading capacity and the TMDL could be reduced directly through collection of additional data to better characterize external loading rates, internal stores of mercury, and year-to-year variability in lake response. Uncertainty in the D-MCM modeling of mercury cycling within the lake could also be reduced through the following efforts:

- Collecting higher-frequency data on thermal stratification and water chemistry within the lake, including mercury species, pH, chlorine, DOC, sulfur species, and particulate concentrations.
- Obtaining better characterization of the particulate matter in the study lakes, including settling velocity and mercury sorption characteristics.
- Developing more information on sulfate reduction and the production of reduced sulfur species in pore water and the hypolimnion. Improved thermodynamic data on sulfur-Hg(II) interactions are also needed.
- Obtaining better understanding as to which Hg(II) species are most readily taken up by methylating bacteria and the rates at which uptake occur.

7.2 Margin of Safety

All TMDLs are required to include a Margin of Safety to account for uncertainty in the understanding of the relationship between pollutant discharges and water quality impacts. The Margin of Safety may be provided explicitly through an unallocated reserve, or implicitly through use of adequately conservative assumptions in the analysis.

This proposed TMDL incorporates an explicit Margin of Safety as an unallocated reserve equal to 45 percent of the estimated loading capacity. As described in Section 7.1, the margin of uncertainty about the estimated loading capacity is believed to be plus or minus 25 percent. Remediation of the St. Patrick Mine ball mill tailings site to Arizona HBGLs is estimated to result in an unallocated reserve of 45 percent of the loading capacity (Section 6.2). Therefore, the unallocated reserve resulting from the cleanup of the St. Patrick Mine ball mill tailings site required by other relevant regulations is believed to be more than sufficient to establish a reasonable Margin of Safety.

In sum, the proposed TMDL incorporates a reasonable Margin of Safety that is believed to account for uncertainty in the understanding of the relationship between pollutant discharges and water quality impacts. It is not, however, possible at this time to precisely estimate the magnitude of uncertainty in the estimation of lake loading capacity. As a result, there is some small, but non-zero potential risk that the proposed allocations will not achieve water quality standards. Continued monitoring and adaptive management should be part of any Management Plan for Peña Blanca Lake.

7.3 Seasonal Variations and Critical Conditions

The TMDL is estimated to address fish tissue concentrations associated with bioaccumulation of mercury within Peña Blanca Lake, and there is no evidence of excursions of water quality standards for mercury. Because methylmercury is a bioaccumulating toxin, concentrations in tissue of game fish integrate exposure over a number of years. As a result, annual mercury loading is more important for the attainment of standards than instantaneous or daily concentrations, and the TMDL is written in terms of annual loads. It is not necessary to address standard wasteload allocation critical conditions, such as concentrations under 7Q10 flow, because it is loading, rather than instantaneous concentration, that is linked to impairment.

The impact of seasonal and other short-term variability in loading is damped out by the biotic response. The numeric target selected is tissue concentration in 5-year-old largemouth bass, which represents an integration over several years of exposure, suggesting that annual rather than seasonal limits are appropriate. Nonetheless, the occurrence of loading which impacts fish does involve seasonal components. First, loading, which is caused by infrequent major washoff events in the watershed, is highly seasonal in nature, with most loading occurring during the July–August wet period. Second, bacterially mediated methylation of mercury is also likely to vary seasonally. The timing of washoff events is not amenable to management intervention. Therefore, it is most important to control average net annual loading, rather than establishing seasonal limits, in calculating the TMDL consistent with the existing loading capacity. There may, however, be a potential for modifying the seasonal cycle of bacterial methylation through management intervention, as discussed in Section 6.7.

8. Implementation Plan

This plan identifies follow-up implementation actions and monitoring activities which are needed to ensure that the TMDL and associated allocations are attained. The implementation plan is explained in Table 25 which identifies actions, time frames for implementation, and potentially responsible parties.

Table 25. Peña Blanca Lake TMDL Implementation Plan

Action	Time Frame For Implementation	Potentially Responsible Party
1. Remove Contaminated Tailings and Sediment from St. Patrick Mine Ball Mill Site – remediate site to Arizona HBGLs	1999	USFS mine owner
2. Fish Tissue Monitoring – develop ongoing fish tissue monitoring plan – collect and test fish for mercury according to plan, beginning in 2003 – evaluate results and consider whether adequate progress toward attainment of TMDL is being made – if adequate progress is being made, continue periodic tissue monitoring – if adequate progress not being made, revise monitoring plan, potentially considering air deposition and sediment monitoring and further characterization of other mine sites in watershed	beginning 1999	ADEQ AZGF
3. TMDL Review and Revision – review TMDL progress consistent with monitoring plan – revised TMDL and implementation plan as necessary	Every 4-5 years	ADEQ EPA

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