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Methylmercury and Other Environmental Contaminants in Water and Fish Collected from Four Recreational Fishing Lakes on the Navajo Nation, 2004

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METHYLMERCURY AND OTHER ENVIRONMENTAL CONTAMINANTS IN WATER AND FISH COLLECTED FROM FOUR RECREATIONAL FISHING LAKES ON THE NAVAJO NATION, 2004

by

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CONVERSION FACTORS AND EQUATIONS

Multiply	By	To obtain
inch (in)	25.40	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile	2.590	square kilometer (km^2)
acre	4.047	km^2
ounce (oz)	28.35	gram (g)
pound (lb)	453.59	g
short ton	907.18	kilogram (kg)
acre-feet	1233	cubic meter (m^3)

Celsius (C) and may be converted to degrees Fahrenheit (^oF) using the Equation 1:

$$^oF = (1.8 \times C) + 32 \qquad \text{Equation (1)}$$

Trace element data in fish tissues are reported in either dry weight (DW) or wet weight (WW) concentrations and are so indicated. Dry weight concentrations may be converted into wet weight concentrations using Equation 2:

$$WW = DW \times [1 - (\text{percent sample moisture}/100)] \qquad \text{Equation (2)}$$

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EXECUTIVE SUMMARY

In 2000, the U.S. Environmental Protection Agency (USEPA) stated that the Navajo Nation Water Quality Standards for mercury were likely to adversely affect the bald eagle. In 2002, the USEPA, the Navajo Nation Environmental Protection Agency (Navajo Nation EPA), and the U.S. Fish and Wildlife Service (USFWS) agreed to identify waterbodies on the Navajo Nation where elevated concentrations of mercury in fish could pose a health risk to people or to bald eagles that frequently ate fish from these lakes. In March and April 2004, the USFWS and the Navajo Nation EPA collected fish and water from four recreational fishing lakes on the Navajo Nation. The goal of the Navajo Nation Lake Fish and Water Quality Investigation was to provide data that could be used to evaluate mercury risks to bald eagles and people.

Based on the data collected, people can and should feel comfortable consuming fish on a recreational basis from Asaayi Lake, Wheatfields Lake, and Morgan Lake (that is, no more than 14 meals of fish per year). However, catfish from Red Lake may contain concentrations of methylmercury that may pose health risks to certain people who eat fish frequently (that is, more than two meals of fish per week) – especially women of childbearing age, nursing mothers, infants and young children. Additionally, selenium concentrations in fillets from Morgan Lake may also pose health risks to children who subsist on those fish (that is, eat more than 6 meals of fish per week).

An important technique to manage human health risks is to identify people whose diet contains a large portion of fish and communicate the risks posed by mercury or other contaminants to them while considering the nutritional role fish plays in their diet. The Navajo Nation has the primary responsibility for protecting their residents from the risks of eating contaminated fish. To reduce exposure to these contaminants, people may want to consult the Navajo Nation to help them make choices about which fish to eat and how often in order to reduce any health risks.

Bald eagles that consume catfish from Red Lake on a frequent basis (>30 days per year), also have the potential to experience mercury toxicity. Bald eagles attempting to establish nesting sites on the Navajo Nation may need to be monitored for their long-term mercury exposure and effects. To protect the bald eagle from consumption of mercury in fish, water quality criteria for wildlife were identified. Pollution prevention is also effective means of reducing fish contamination; therefore, it is important to identify the sources of mercury to Red Lake and their magnitude, so that they can be reduced. If necessary, lake oxygenation, increasing pH, riparian shading, excavation, sulfate reduction, flood peak minimization, vegetating uplands, riparian filter strips, increased upland filtration, and recreational fisheries management techniques can alter the forms and bioavailability of mercury and thereby reduce the mercury burden within fish eaten by bald eagles. Selenium contamination was also identified in fish from Morgan Lake at concentrations that may affect the reproductive success of resident fish and wildlife. Sources of selenium contamination should be identified and reduced. With the exception of aluminum, concentrations of contaminants in water samples collected did not exceed applicable Navajo Nation numeric water quality criteria.

INTRODUCTION

The Navajo Nation

The Navajo Nation is the largest North American Indian Tribe consisting of nearly 200,000 members (U.S. Census Bureau 2001). The Navajo Nation spans over 24,000 square mi (62,160 km^2) of land with its boundaries extending from northwestern New Mexico into northeastern Arizona and southeastern Utah (Figure 1). In 1995, the Navajo Nation Environmental Protection Agency ("Navajo Nation EPA") was established as a regulatory agency within the Navajo Nation government, in order to implement and enforce environmental laws for the protection of human health and the environment. The mission of Navajo Nation EPA is to protect, preserve, and enhance the environment for present and future generations, with respect to Diné values, by developing, implementing, and enforcing environmental laws; and to foster public awareness and cooperation through education.

Recreational fishing lakes are among the ultimate repositories of contaminants released from various natural and anthropogenic activities. Contaminants can come from point source discharges (*e.g.*, industrial and municipal facilities), accidental spills, and nonpoint sources (*e.g.*, atmospheric deposition from various combustion and incineration processes). Once contaminants reach these surface waters, they can undergo processes that affect the aquatic food chain and can bioaccumulate in fish. Thus, fish tissue monitoring can serve as an important indicator of water quality problems, and several Tribes routinely conduct chemical contaminant analyses of fish as part of their comprehensive water quality monitoring programs (Cunningham and Whitaker 1989). Tissue contaminant monitoring can also enable Tribes to detect levels of contamination in fish tissue or the water column that may be harmful to people or wildlife and enable them to take appropriate management actions.

The Navajo Nation has primary responsibility for protecting its members from the health risks of consuming contaminated fish and wildlife. Fish consumption advisories are one method to achieve this goal for the general population, including those who fish for recreation or those whose diet contains a large portion of fish, as well as for sensitive subpopulations (such as pregnant women, nursing mothers, and children). Fish consumption advisories are intended to inform people of concentrations of chemical contaminants found in local fish and can include recommendations to limit or avoid consumption of certain fish.

Sources, Fate and Transformations of Mercury

Mercury (Hg) is a natural element, a silver-colored, shiny metal found in a variety of forms in rocks, soil, water, air, plants, and animals (USEPA 1997; Wiener *et al.* 2003). Sometimes mercury occurs in its elemental liquid form, or gaseous, but more commonly mercury is found combined with other elements in various inorganic (*e.g.*, mercury chlorides, or mercury and sulfur cinnabar deposits) and organic (*e.g.*, methylmercury) compounds (Schierow 2004). Mercury has been used in dental fillings, thermometers, fluorescent lights, thermostats, and it is a constituent of mineral deposits such as coal.

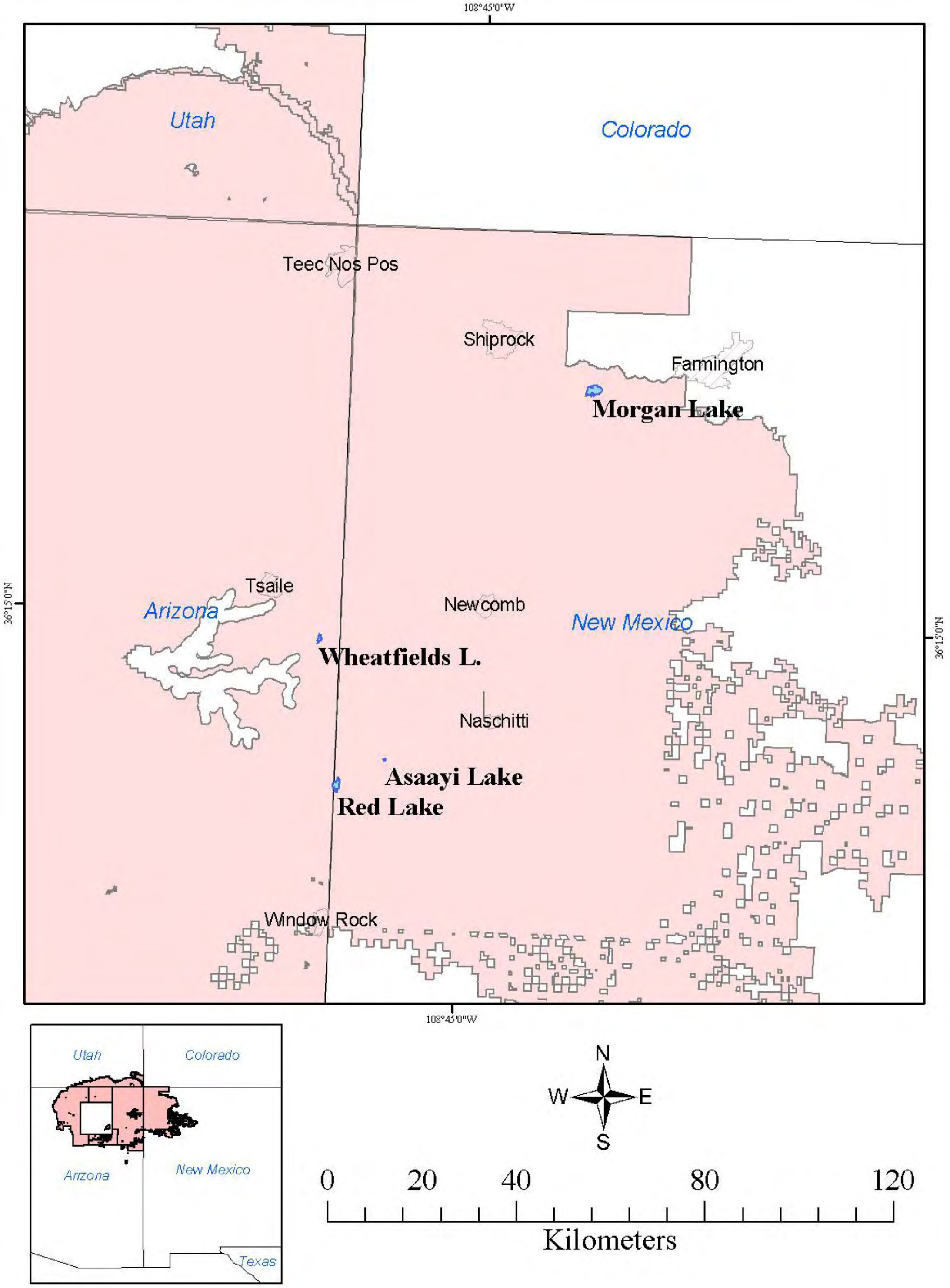

Figure 1. Location of the Lakes Sampled on the Navajo Nation and Nearby Towns. (Inset: Location of the Navajo Nation in the Arizona, New Mexico and Utah).

Mercury is found in the environment because of natural and human activities. Natural forces move mercury through the environment, from air to soil to water, and back again. Industrial activities have increased the portion of mercury in the atmosphere and oceans, and have contaminated some local environments. According to USEPA (1997), coal-fired electric utilities are the largest single unregulated source of mercury emissions in the United States, but other sources such as mines and incinerators are also important. Released mercury may enter the air, persist in the atmosphere and travel great distances or be deposited locally, dissolve in water droplets, settle back onto the land or water, re-enter the air (*i.e.*, be re-emitted), be buried in lake or ocean sediments, or be incorporated into plants and animals (Schierow 2004). These properties make mercury extremely mobile – a "grasshopper" pollutant -- that can enter various components of the environment.

During its movement among the atmosphere, land, and water, mercury undergoes a series of complex chemical transformations. Mercury deposited or delivered to surface water may be re-emitted to air, remain suspended or dissolved in the water column, be deposited in sediments, or absorbed or ingested by living organisms. For the oceans and large or isolated lakes such as the Great Lakes, atmospheric deposition (wet and dry) accounts for the largest portion of mercury contamination (Wiener *et al.* 2003). Rudd (2004) also reported that mercury that is newly deposited seems to be more readily converted into methylmercury than older deposited mercury.

The most biologically significant transformation of mercury occurs in watershed soils or in sediments of lakes or streams, where bacteria (primarily sulfate-reducing bacteria) are capable of converting inorganic mercury to methylmercury (Wiener *et al.* 2003). Methylmercury is easily absorbed by the digestive tract and accumulates in the bodies of fish and other animals, when it is ingested faster than it can be excreted. Because methylmercury tends to be stored in muscle tissue (*i.e.*, the edible meat of fish and other animals), animals higher on the food chain tend to have higher levels of exposure. For example, predatory fish (*e.g.*, walleye, largemouth bass, or tuna), fish-eating birds (*e.g.*, loons, ospreys, bald eagles), and fish-eating mammals (*e.g.*, raccoons, otters, mink) that top the longest food chains accumulate the greatest concentrations of methylmercury. [See Appendix A through F for lists of the common and scientific names of species used in this report]. The degree to which mercury is transformed into methylmercury and transferred up the food chain through bioaccumulation depends on many site-specific factors (such as water chemistry and the complexity of the food web) through processes that are not completely understood (Moore *et al.* 2003).

Generally, the more mercury that is introduced into an ecosystem, either through direct discharge to water, runoff from the surrounding watershed, or deposition from air, the higher the concentrations of methylmercury that will be found in fish (Schierow 2004). However, the rate of methylmercury formation and accumulation is highly variable, even within relatively small geographic areas, because it depends on many factors, in addition to the abundance of inorganic mercury. For example, ecosystems sensitive to mercury contamination are often warmer, oxygen-poor, acidic, contain more sulfate and dissolved humic matter (*i.e.*, characterized by an abundance of dissolved, decomposed, plant or bacterial matter), have more wetland areas or surface water tributaries connected to wetlands, or are subjected to flooding or drying and re-wetting (Moore *et al.* 2003; Wiener *et al.* 2003; Rudd 2004; Schierow 2004). Deposition of flooded vegetation and soils often stimulates methylation of mercury with an accompanying increase of mercury in fish (Rudd 2004).

Human Exposure and Toxicity of Methylmercury

People can be exposed to methylmercury by eating, drinking, inhaling, or absorbing it through their skin (USEPA 2001). The National Research Council (NRC 2000) reported that the nervous system is especially sensitive to methylmercury toxicity, particularly the developing fetus; as even small doses by a pregnant woman can lead to delays and deficits in learning ability in her children. The NRC (2000) reported that the brain is the most sensitive part of nervous system for which suitable data are available to quantify a dose-response relationship for methylmercury toxicity. However, research continues to find evidence of subtle impacts on human health through other types and routes of exposure. For example, Salonen *et al.* (1995) suggested that the adult sensitivity to cardiovascular toxicity due to mercury exposure might be as important as developmental neurotoxicity in children.

The observed effects of toxic levels of methylmercury exposure have generally been similar in laboratory animals, domestic pets, wildlife, and people (NRC 2000). Methylmercury that is absorbed is dispersed by blood throughout the body including the brain, where it may cause structural damage (NRC 2000). After exposure, physical lesions can develop that lead to tingling and numbness in fingers and toes, loss of coordination, difficulty in walking, generalized weakness, impairment of hearing and vision, tremors, as well as loss of consciousness and death (NRC 2000). Quite often, there is a lag time of weeks to months between exposure and the onset of health effects in people (Clarkson 2002). Injury to the brain may exist, however, in the absence of these observable symptoms of toxicity. Lower levels of exposure may have more subtle adverse impacts on coordination, ability to concentrate, and thought processes (Yokoo *et al.* 2003).

Methylmercury readily crosses the placenta of pregnant women to the fetus (USEPA 2001). The fetal brain has been demonstrated to be more sensitive to methylmercury than the adult brain (NRC 2000). Methylmercury exposure to the fetal brain can affect development, as evidenced during childhood by a child’s ability to learn and function normally after birth. At low levels of exposure, the effects may be subtle and detectable only on a population basis— for example, by an increase in the proportion of an exposed population that falls below a level of function defined as impaired (NRC 2000). The NRC (2000) concluded that the sensitivity of the fetus to pre-natal methylmercury exposure, and that the risk to women who eat large amounts of fish and seafood during pregnancy is “likely to be sufficient to result in an increase in the number of children who have to struggle to keep up in school.”

In the United States, most people are exposed to mercury primarily through eating the flesh (muscle) of fish (USEPA 1997). People who regularly eat predatory fish, such as largemouth bass, northern pike, tuna, shark, or swordfish, which are often contaminated with mercury, can increase the risk of adverse health effects for themselves or, in the case of women who become pregnant, for any unborn children (Hightower and Moore 2003).

The USEPA (1997) derived a "Reference Dose" (RfD) as a tool to estimate daily intake levels of methylmercury that are expected to be without an appreciable risk of deleterious health effects, even if exposure persists over a person's lifetime. The USEPA (2001) developed an RfD for methylmercury based largely on developmental toxicity to account for sensitive members of the exposed human population, such as pregnant women and infants, though it did not account for individuals with unusual sensitivity due to conditions such as genetic disorders or severe illness. To calculate the RfD, the USEPA generally uses a "no observed adverse effect level" (NOAEL), which is either observed or estimated using a mathematical model. The NOAEL estimates the threshold level of exposure below which adverse effects do not occur. The RfD is then derived by dividing the NOAEL value by uncertainty factors that account for the need to extrapolate from limited data sets to the general population. Therefore, even though the RfD was derived using developmental toxicity as an endpoint of concern, the USEPA (2001) recommends the use of the RfD to protect adults and children in the general population. The RfD for methylmercury is 0.1 micrograms per kilogram bodyweight of consumer per day (µg/kg-bw/day) (USEPA 2001).

Pursuant to section 304(a)(1) of the Clean Water Act, the USEPA (2001) established a water quality criterion for methylmercury of 0.3 milligrams of methylmercury per kilogram of fish tissue on a wet weight basis (mg/kg WW) based on the RfD. This was the first time the USEPA based a water quality criterion on a concentration of a pollutant in fish (and shellfish) rather than dissolved in the water column (Schierow 2004). The USEPA (2001) indicated that to protect consumers of fish and shellfish among the general population, the concentration of methylmercury in tissue should not be exceeded based on an average consumption of 17.5 grams of fish and shellfish consumed per person per day.

Fish Exposure and Mercury Toxicity

Adverse effects of methylmercury on fish, birds and mammals include death, reduced reproductive success, impaired growth and development, and behavioral abnormalities (USEPA 1997). Mercury is persistent and accumulates within the food chain of the environment, successively reaching higher concentrations in predators like eagles, mink, and fish such as tuna or largemouth bass. The USFDA (2003) reported that uncontaminated fish contain less than 0.01 mg/kg methylmercury (on a wet weight [WW] basis) in their muscle tissues, while contaminated shark can contain more than 4.5 mg/kg methylmercury.

The amount of mercury in fish has been found to vary with species, size, and age (Wiener *et al.* 2003). These factors are interrelated. For example, bioaccumulation in bass is greatly influenced by its degree of piscivory, which is a function of size – over time as bass increase in size; they feed almost exclusively on large-bodied fish (Harris *et al.* 2001). A strong relationship between species trophic classification and mercury is often observed at most sites sampled nationwide; however, variations in prey species populations and availability of mercury for bioaccumulation among some sites results in some disconnect between a strict trophic classification and expected mercury bioaccumulation (Brumbaugh *et al.* 2001).

Spatial variation in fish-mercury concentrations is also attributed to differences among surface waters and their watersheds, particularly in their tendency to convert inorganic mercury to methylmercury and in their tendency to accumulate mercury in the aquatic food web (Wiener *et al.* 2003). Verda (2000) reported over 38 water quality factors that may affect the methylmercury concentration in water and therefore, in fish. Generally, fish obtain methylmercury almost entirely through dietary uptake, which is influenced by their size, diet, and trophic structure, while site-specific water quality factors influence the chemistry and methylation potential of the water bodies in which the fish live.

After bioaccumulation, acute toxic effects and death are associated in adult fish ranging from 6 mg/kg WW (*e.g.*, for walleye) to 20 mg/kg WW (*e.g.*, for salmon) in muscle tissue (Wiener *et al.* 2003). Rarely, however, are these elevated concentrations encountered in the wild (Wiener *et al.* 2003). Recent evidence suggests that the reduced reproductive success and reduced survival are chronic toxic effects of dietary exposure of fish to methylmercury (Friedmann *et al.* 1996, 2002). However, the ecological effects of methylmercury exposure to fish populations remains largely unknown and understudied (Wiener *et al.* 2003).

Wildlife Exposure and Mercury Toxicity

Mercury is considered a serious risk to wildlife (Moore *et al.* 2003). Fish consumption is also the dominant pathway for wildlife exposure to methylmercury. Fish-eating predators generally have relatively high concentrations of mercury (Wiener and Spry 1996). Toxic mercury levels have been found in individual mink, otters, loons, and other piscivorous birds and wildlife (Heinz 1979, USEPA 1997, Wolfe *et al.* 1998, Russell 2003).

Methylmercury toxicity in wildlife is primarily manifested as central nervous system damage; including sensory and motor deficits and behavioral impairment (Wolfe *et al.* 1998). Exposed animals may experience weight loss, progressive weakness, liver damage, kidney damage, motor difficulties, reduced food consumption, reduced cardiovascular function, impaired immune response, reduced muscular coordination, impaired growth and development, altered blood and serum chemistry, and reproductive effects (Eisler 1987; Scheuhammer 1987, Scheuhammer and Blancher 1994). Many scientists suspect that the immune system is weakened because of methylmercury exposure. However, the most likely adverse impact on birds of methylmercury exposure is impaired ability to reproduce. For example, reduced egg laying by loons has been associated with concentrations greater than 0.4 mg/kg methylmercury in fish (Scheuhammer and Blancher 1994; Wiener *et al.* 2003).

The USEPA (1995c) also reviewed numerous subchronic and chronic mercury toxicity studies using birds. Data on methylmercury effects in wildlife suitable for dose-response assessment are limited to what are termed "individual effects" (USEPA 1997). The USEPA (1997) ultimately selected a study examining reproductive and behavioral effects in three generations of mallard ducks (Heinz 1979) to determine an appropriate test dose for its avian wildlife criteria calculations. In order to determine the RfD for a given taxonomic group, the test dose selected to represent that group may need to be adjusted by uncertainty factors to incorporate variability in toxicological sensitivity among species and to extrapolate for duration (subchronic-to-chronic) or dose spacing (LOAEL-to-NOAEL) issues. The RfD for wildlife is calculated using the following equation:

$$RfD = \frac{TD}{UF_A \times UF_S \times UF_L} \qquad \text{(Equation 3)}$$

Where:

RfD = Reference Dose (mg/kg-bw/day)
TD = Test Dose (mg/kg-bw/day)
UF_A = Interspecies Uncertainty Factor (unitless) = 1 (USEPA 1997)
UF_S = Subchronic-to-Chronic Uncertainty Factor (unitless) = 1 (USEPA 1997)
UF_L = LOAEL-to-NOAEL Uncertainty Factor (unitless) = 3 (USEPA 1997)

Based on the avian test dose of 0.064 mg/kg-bw/day from the Heinz (1979) mallard duck study, and the uncertainty factor of 3 from USEPA (1997) and Russell (2003), an avian RfD of 0.021 mg/kg-bw/day was calculated and used in the evaluation of bald eagle risks below.

Objectives of the Lake Fish and Water Quality Investigation

The goal of the Navajo Nation Lake Fish and Water Quality Investigation was to provide data that may be used to estimate potential mercury risks to human health and to bald eagles that utilize fish from selected recreational lakes on the Navajo Nation. These data are also to be used to develop site-specific bioaccumulation factors and to evaluate the need for management actions to limit fish consumption, derive wildlife water quality criteria that would protect bald eagle, reduce the process of mercury methylation, or perhaps recommend reductions of local mercury and other contaminant emissions and discharges under various Navajo Nation authorities.

The specific objectives of the Navajo Nation Lake Fish and Water Quality Monitoring Project were:

1. To document the concentrations of mercury, methylmercury, and other trace elements in fish tissues consumed by people and wildlife; and,

2. To document the concentrations of selected trace elements dissolved in the water column and compare these concentrations to ambient Navajo Nation water quality criteria.